Selected Papers on
The Periodic Table by
Eric Scerri

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	Co	Ni	Cu	Zn	Ga	Ge	As	Se
Br	Kr	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
I	Xe	Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
At	Rn	Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh
Uus	Uuo																

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

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I dedicate this book to my mother Ines Scerri and my late father, Edward Scerri.

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Introduction

My interest in the periodic table has at least two aspects. Firstly, like so many people before me, I fell in love with the rational beauty of the periodic chart that appears to systematize all the kinds of elementary substances that a student of chemistry would ever encounter.[1] The extent to which students are exposed to the periodic table and the stage at which this takes place seems to vary a good deal depending on geographical location and on the era in which they learn chemistry. In my own case it was in London in the 1960s where we were not initially taught the periodic table, although it was displayed on the classroom walls.

The first time I recall being clearly directed to the periodic table and some of its features, was on making the transition between Ordinary Level and Advanced Level chemistry at age 16. This delay added to the delight of the discovery, if anything, since I experienced the wonder of seeing how previously covered information suddenly fell into place in a coherent framework.

Unlike some lovers of the periodic table, I am not somebody who played with chemicals or minerals at a young age. My attraction to the periodic table was more in the realm of ideas. It is not too surprising looking back now that I should have ended up with an interest in history and philosophy of chemistry.[2]

My second interest in the periodic table arose much later when I became a PhD student in history and philosophy of science working on the question of the reduction of chemistry to quantum mechanics. First of all, the periodic table serves as an excellent arena in which to pose this question in a more restricted form than asking whether all of chemistry reduces to quantum mechanics. Secondly, the periodic table and the attempts to understand it theoretically were directly responsible for several developments in theoretical physics which contributed to the development of quantum mechanics. For example, Thomson's model of the atom, whereby electrons circulated in rings within the positive charge, provided the earliest forms of the ubiquitous electronic configurations, which these days occur throughout chemistry and physics. Bohr's model of the atom was guided and motivated by trying to understand the periodic table, as was the postulation of a fourth quantum number by Pauli and the subsequent discovery of electron spin.

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[1] Or anyone for that matter, although these days there is a good deal of talk of "dark matter" which is not featured on the periodic table.

[2] E. R. Scerri, *Collected Papers on Philosophy of Chemistry*, Imperial College Press, London, 2008.

The papers in this volume are presented in chronological order in which they were written, rather than being arranged thematically. They begin with material written while I was completing my PhD thesis at King's College, London and they deal primarily with the question of reduction. However, the first two papers are directed at different audiences and so take up different aspects of the question of reduction.

For chemists, and chemical educators especially, there is an area of ongoing debate concerning the periodic table. Some educators regard the periodic table as being primarily about the macroscopic elements and their properties. They typically begin by pointing out the variety among the elements and the striking similarities displayed between some of the elements. This approach tends to be macroscopic, following the historical development of the periodic system and the fact that the system was discovered well before the advent of modern atomic theory and quantum mechanics.[3]

The second approach, and far more common these days, lies in starting with current knowledge and placing the emphasis on a microscopic account. Atomic theory, electronic configurations, electron shells and orbitals are put to the fore with the view that these concepts represent the fundamental basis for chemistry and should therefore come first. The periodic table thereby glides effortlessly from being a table of the elements to being a table of the atoms. What students are deprived of in this approach is the delight that I and many others discovered as students, in seeing the periodic table as a means of unifying a large number of previously encountered chemical facts. Students who encounter the fundamental principles first, simply don't have much information that is in need of unification. Then there is the deeper question of whether the supposedly more fundamental quantum description really does the job that it is claimed to do. But more on this further question a little later. Let me now return to the papers in this volume.

In an article that first appeared in the *Journal of Chemical Education*, I considered the relationship, or perhaps the tension, between the periodic table of the elements arranged according to chemical properties and the periodic table of the atoms coming largely from the field of physics. This is a subject that continues to be at the center of my interests, although I have changed my mind on a number of issues as these papers will show.

For example, in this early paper I considered the Janet or left-step table but quickly dismissed it in spite of its esthetic beauty and apparent coherence with the quantum mechanical account of the periodic table. The left-step periodic table consists of moving the s block elements to the right flank of the periodic table, thereby displaying the blocks in what is perhaps a more logical order of f, d, p and s blocks, reading from left to right, rather than the sequence of s, d, p as one sees in the medium-long form or even s, f, d, p in the long-form table.

This much is quite readily acceptable but proponents of the left-step table make an additional change to the conventional format by moving the element helium from the head of the noble gases to the head of the alkaline earths. Given my initial preference for purely

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[3]Dalton's work, published in the early 1800s, of course precedes the birth of the periodic system which mostly took place in the second half of the 1800s.

chemical arguments over those based primarily on atomic physics and quantum mechanics, I initially sided with the chemists in claiming that helium should not be moved in this manner.[4] After my brief conversion to the left-step table, which took place in the early single digit years, I reverted again to this more traditional, or chemical view, of leaving helium among the noble gases.[5]

Another issue raised in this first paper is that of the elements which should be placed in group 3 of the periodic table. At this time, the paper by William Jensen advocating Sc, Y, Lu, Lr appeared to be quite compelling to me. I believe that I subsequently convinced a number of textbook authors to switch to this grouping rather than the more customary Sc, Y, La, Ac. It came as something of a surprise to me, some years later, to discover that the arrangement advocated by Jensen was being questioned and that some authors were advocating a return to group 3 as Sc, Y, La and Ac. One of these traditionalists is my friend and UCLA colleague Laurence Lavelle, who subsequently published a commentary in the *Journal of Chemical Education* in which he reiterated the traditional grouping for group 3.[6]

Still on the first article in this volume, I also discussed Seaborg's extension of the periodic table and his creation of a completely new series that he termed the actinides. I have long been interested in the genesis of this idea and even had the pleasure of putting this question to Seaborg in the late 1990s.[7] In recent years it has become clearer to me that Seaborg's idea was not quite as original as he implied in his writings and that it is contained in many earlier periodic tables. I believe that more historical work on this question might lead to an interesting story.

One final comment on this first paper is that I recommended the use of many tables and suggested that no one table was better than others. This is something that I no longer believe. According to a realistic interpretation, the periodic system is referring to some objective relationship among the elements that exists in nature and is not the result of mere human construction. I believe that it *does* therefore make perfect sense to be seeking an optimal periodic system in the sense of one that most closely reveals the precise periodic relationship between as many elements as possible.[8]

The second paper first appeared in the *British Journal for the Philosophy of Science*. The emphasis here is naturally more philosophical and considers such questions as the

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[4]As will become clear from later parts of this introduction and from the papers themselves, my views on this issue have gone full-circle and I am currently back supporting the placement of helium among the noble gases after flirting with the possibility of placing helium among the alkaline earths.

[5]I thank my UCLA colleague Herb Kaesz as well as Octavio Novarro for my returning to the view of He among the noble gases. As both of them reminded me, whereas the promotion of 2s electrons into the 2p orbitals can readily take place in beryllium, the promotion of a 1s electron into a 2s orbital in helium is highly improbably, if not completely out of the question, in view of the far larger energetic gap in this case.

[6]I have submitted a response to Lavelle's commentary which contains what I believe to be a conclusive argument in favor of the grouping of Sc, Y, Lu and Lr.

[7]I asked Seaborg this question after a talk that he gave at an ACS meeting in Las Vegas whereupon he asked me and Carmen Giunta to join him for lunch at a local diner. Although he did not really cast any light on my question but it still was a memorable occasion for Carmen and myself.

[8]This theme is resumed in several later papers in this volume.

nature of models and whether the atomic orbital model, in particular, reduces legitimately to quantum mechanics. I also attempted to trace the historical development of this model which serves as one of the central paradigms of modern chemistry.

Starting with Bohr's version of 1913, the evolution of this model was examined in an attempt to highlight the assumptions and approximations that were made at each stage. As in the case of many other papers in this volume, there is an educational motivation for raising these questions, especially in view of the central role of the atomic orbital model at all levels of chemical education. My suspicion is that many chemical educators do not appreciate the extent to which this model is an approximation and the conditions under which it ceases to be applicable.

These days students are presented with the four quantum number description of electrons in many-electron atoms as though these quantum numbers somehow drop out of quantum mechanics in a seamless manner. In fact, they do not and furthermore they emerged, one at a time, beginning with Bohr's use of just one quantum number and culminating with Pauli's introduction of the fourth quantum number and his associated Exclusion Principle.

To return to the philosophical aspects, and with the benefit of hindsight, I would now say that I took a somewhat hard-line approach to the matter in concluding that there was something of a clash between the atomic orbital model and the theory from which it is generally supposed to be derived. This view was softened in subsequent papers[9] but I still believe that it is useful to examine the gulf between the model and the fundamental theory as clearly as possible, especially given the interest in models that has swept through philosophy of science in recent years, and just to repeat myself a little, because of the educational currency of this particular model.

In case the general reader might be wondering about the connection between atomic orbitals and the periodic table, let me address this issue briefly. As mentioned above, in the case of the first paper, the modern explanation for the periodic table is based entirely on the orbital model. It is only by ignoring the approximate nature of the model that the explanation for the periodic system might appear to be full and complete.

The third paper addresses the topic of the periodic table more directly. It appeared in 1997 in the semi-popular magazine, *American Scientist*, during the year celebrating the one hundredth anniversary of the discovery of the electron. Not only did J.J. Thomson discover the first subatomic particle, but he also set about trying to explain the periodic table by means of arrangements of electrons within his plum pudding model of the atom. This was an atomic model in which electrons were regarded as being embedded within the positive charge throughout the atom, like plums in a pudding.

Moreover, Thomson considered that the electrons rotated within the positive charge in the form of concentric rings, an idea which he adopted on reading about Alfred Meyer's

[9]E. R. Scerri, Normative and Descriptive Philosophy of Science and the Role of Chemistry, in *Philosophy of Chemistry, the Synthesis of a New Discipline*, D. Baird, E. R. Scerri, L. McIntyre (eds.), Boston Studies in the Philosophy of Science, Vol. 242, pp. 119–128, 2005; E. R. Scerri, Philosophy of Chemistry — A New Interdisciplinary Field? *Journal of Chemical Education* 77: 522–526, 2000.

experiments with steel needles floating on corks in a basin of water. So it emerges that today's ubiquitous notion of electronic structure originated in a classical mechanical context and did not have to wait for the advent of Niels Bohr or any other quantum mechanicians. In fact, Niels Bohr's even more famous atomic model, with electrons in quantized orbits, arose in direct response to Thomson's model. Bohr was at the time a postdoctoral fellow in the UK, where he divided his time between Thomson in Cambridge and Rutherford, whom he found far more congenial, in Manchester.

In my paper I argue that as atomic orbits morphed into non-deterministic atomic orbitals in the fully quantum mechanical theory of Schrödinger and Heisenberg, so they became regarded instrumentally rather than realistically. Within a quantum mechanical context, orbitals cease to be real in that they cease to exist as referring entities. How ironic then that a mere two years later a team of chemists and physicists should have made front page news in *Nature* magazine by claiming that orbitals had been directly observed for the first time![10]

This was a claim that I and several other authors criticized in a number of journals, but unfortunately not in *Nature* magazine.[11] Although the authors of the "Orbitals Observed" study protested their innocence, it became clear that their claims had been incorrect and exaggerated.[12] In a section of the same paper, I discussed the notion that the 4s atomic orbital is occupied "before" the 3d orbitals. This has subsequently turned out to be incorrect and there is conclusive spectroscopic evidence to the contrary which seemed to have escaped the attention of several authors who have written on this issue, including myself.[13]

Paper four first appeared in the *Journal of Chemical Education* and aimed to highlight one of the important ways in which the periodic table is not fully explained by quantum mechanics. The orbital model and the four quantum number description of electrons, as described earlier, is generally taken as the explanation of the periodic table but there is an important and often neglected limitation in this explanation. This is the fact that the possible combinations of four quantum numbers, which are strictly deduced from the theory, explain the closing of electron shells but not the closing of the periods. That is to say the deductive explanation only shows why successive electron shells can contain 2, 8, 18 and 32 electrons respectively.

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[10] J. M. Zuo, M. Kim, M. O'Keefe, J. H. C. Spence, Direct Observation of d-Orbital Holes and Cu-Cu Bonding, *Nature* 401: 49–52, 1999; C. J. Humphreys, Electrons Seen in Orbit, *Nature* 401: 21–22 1999.

[11] P. Coppens, *International Union of Crystallography Newsletter*, 8: 4, 2000; E. R. Scerri, Have Orbitals Really Been Observed? *Journal of Chemical Education*, 77: 1492–1494, 2000; E. R. Scerri, N. Koertge, ed. The Recently Claimed Observation of Atomic Orbitals and Some Related Philosophical Issues, *Philosophy of Science*, 68: S76–S88, 2001; S. Wang, W. H. E. Schwarz, On Closed-Shell Interactions, Polar Covalences, d Shell Holes, and Direct Images of Orbitals: The Case of Cuprite, *Angewandte Chemie International Edition*, 39: 1757–1762, 2000. Although a number of authors including Coppens, Schwarz and myself wrote to the editor of *Nature* magazine, no letters of dissent were accepted.

[12] If the announcement was designed to attract the notice of the scientific press, it did just that. For example, M., Jacoby, Picture Perfect Orbitals, *Chemical & Engineering News*, 77: 8, 1999.

[13] F. L. Pilar, 4s Is Always Above 3d! Or, How to Tell the Orbitals From the Wavefunctions, *Journal of Chemical Education*, 55: 2–6, 1978; E. R. Scerri, M. Melrose, Why the 4s Orbital Is Occupied Before the 3d, *Journal of Chemical Education*, 73(6): 498–503, 1996; L. G. Vanquickenborne, K. Pierloot, D. Devoghel, Transition Metals and the Aufbau Principle, *Journal of Chemical Education*, 71: 469–471, 1994.

However, this feature alone does not fully explain the form of the periodic table. It is rather the question of the closing of periods which any candidate explanation must provide. But the latter is only available in a semi-empirical form at present. The reason why this additional requirement often seems to go unnoticed lies in something of a coincidence as I try to explain in the article. While the closing of shells occurs after particular numbers of electrons have been added, if one now considers cumulative totals, namely 2, 10, 28, 60 etc., many of these values do not coincide with the atomic numbers representing the closing of periods. In fact the periods close at the atomic numbers of 2, 10, 18, 36, 54 etc., and the discrepancy occurs because electron shells do not fill sequentially. In other words, the filling of electron shells does not proceed according to increasing values of the n quantum number but instead according to increasing $n + \ell$, or according to the Madelung rule as it is sometimes called.

Another aspect of this state of affairs is that all periods repeat once, with the exception of the first period of just two elements, to produce the sequence of 2, 8, 8, 18, 18, 32, etc. The focus of interest thus turns to whether the Madelung rule itself can be strictly deduced from theory, a theme that is taken up in later papers in this collection.

The following paper, the fifth one, marks something of a shift in emphasis. In a long paper co-authored with John Worrall from the London School of Economics (LSE), we set out to examine just how important predictions were in the acceptance of the periodic table by the scientific community of the late 1800s. This question has nothing to do with quantum mechanics which did not exist until 1905, even if one just considers the very early work of Max Planck.

Let me say a little by way of background. I first learned of this issue while writing my PhD thesis at King's College, London from a fellow graduate student who had some connections with the LSE. On reading Worrall's papers I found that there was a long-standing debate over the question of whether successful predictions are more influential than so-called accommodations (explaining already known facts) when scientists come to accept a new theory. The commonplace view is of course that predictions matter more, for the simple reason that in the case of predictions there can be no suspicion that the creator of the new theory might have doctored the theory to explain the facts. The facts were simply not known when the theory was created.

I was also familiar with the work of science historian Stephen Brush who had argued that in most important cases, such as relativity theory and quantum mechanics, and contrary to popular opinion, it was successful accommodations that had swayed scientists of the time rather than any dramatic predictions.

Worrall had made similar claims regarding theories of light developed in the seventeenth century and in particular, the case of Fresnel whose dramatic and subsequently confirmed predictions had not been as influential as his accommodation of already known optical phenomena. Meanwhile, Stephen Brush had turned his attention to chemistry and the periodic table, given that this seemed to be a case for which successful predictions made by Mendeleev are widely held to have been the reason for the acceptance of the periodic

table. Rather surprisingly, to my mind, Brush was claiming that perhaps the periodic table represented one important exception.[14] In this case Brush claimed that successful predictions *had been* the deciding factor in the acceptance of the periodic system.

I published a short paper in a somewhat obscure conference proceedings in which I disagreed with Brush.[15] I then approached Worrall to see if he wanted to team-up with me to take a closer look at the issue. At first he did not seem too interested but this changed after I became a post-doctoral fellow at the LSE and continued to press Worrall to work on this project.

The result of our eventual collaboration is reprinted here. To state our conclusion briefly, we argue that it is not the temporal aspect that is important but rather the question of whether a scientist uses known facts to develop his or her theory (use-novelty). Such use-novelty had been previously discussed by Imre Lakatos and his then graduate students Elie Zahar and none other than John Worrall.[16]

In the paper under discussion, which has subsequently been cited by a number of authors,[17] Worrall and I argue that Mendeleev's ability to literally *accommodate* something like 60 elements into the periodic system, subject to a number of constraints, contributed at least as much, if not more, to the acceptance of the periodic table than did Mendeleev's famous successful predictions.

The sixth article in this collection takes up the story from where paper 4 left off. If the $n + \ell$ (Madelung) rule can be fully reduced, then it might rightly be claimed that the periodic table reduces fully to quantum mechanics. This is a question that has been asked in a much-quoted paper by Per-Olov Löwdin, the influential quantum chemist who for many years led the Quantum Chemistry project at the University of Florida.

The paper resulted from an invitation to contribute to what eventually became a three-volume dedication to the memory of Löwdin. In addition to addressing the question of whether the $n + \ell$ rule has been derived, I used this opportunity to explore the reduction of the periodic table in more general terms.

The term *ab initio* is often used in theoretical chemistry and even in the general chemistry literature. In the paper I try to explore precisely what this term means. Does it really refer to calculations carried out from first principles without any recourse whatsoever to empirical data? Surprisingly, I found that theoretical and computational chemists use this term with

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[14]S. J. Brush, Prediction and Theory Evaluation, *Science*, 246: 1124–1129, 1989.

[15]E. R. Scerri, Stephen Brush, the Periodic Table and the Nature of Chemistry, in *Die Sprache der Chemie*, P. Jannich, N. Psarros (eds.), pp. 169–176, 1996.

[16]It was Zahar who first pointed out to Lakatos the importance of some forms of accommodation, or what was later termed use-novelty. Refer to Lakatos and Zahar, The Methodology of Scientific Research Programmes: Philosophical Papers by Imre Lakatos, John Worrall, Gregory Currie, CUP, 1980.

[17]E. Barnes, On Mendeleev's Predictions: Comment on Scerri and Worrall, *Studies in History and Philosophy of Science*, Part A, 36: 801–812, 2005; S. Schindler, Use-novel predictions and Mendeleev's Periodic Table: Response to Scerri and Worrall, *Studies in History and Philosophy of Science*, Part A, 39: 265–269, 2008; D. Harker, On the Predilections for Predictions, *British Journal for the Philosophy of Science*, 59: 429–453, 2008; E. R. Scerri, Response to Barnes' Critique of Scerri and Worrall, *Studies in History and Philosophy of Science*, 36: 813–816, 2005.

a variety of different meenings. And none of these meanings seem to demand calculations with no experimental input whatsoever.[18]

My article also considers different levels of explanation for the periodic table using increasingly sophisticated approaches. The most elementary explanation of chemical periodicity lies of course in the notion that members of a group of elements share the same number of outer-shell electrons. But this simple model is an approximation. If calculations are carried out on the assumption that atoms possess just their ground state configurations, the predictions obtained are highly inaccurate. Another explanation for the periodic table, already touched on in other papers, lies in the possible combination of quantum numbers. The highest-level explanations abandon the static idea of one arrangement of electrons in a particular set of orbitals, or rather they use the notion as a first level approximation to be augmented by thousands or even millions of contributions from other configurations. But these approaches use basis sets, which are experimentally derived and so not entirely *ab initio* in the pure sense of the term. Finally, the paper discusses more sophisticated approaches such as density functional methods, which offer the promise of a universal solution but which invariably resort to the form of empirical mathematics whereby the Schrödinger equation for every atom must be solved separately.

Paper seven is of a more general nature and again more about the history of chemistry than about the role of quantum mechanics. As in the case of my book on the periodic table, this article was written in commemoration of the one hundredth anniversary of the death of Mendeleev in 1907.[19] The article reviews the many precursors to Mendeleev's discovery including the work of Döbereiner, De Chancourtois, Newlands, Odling, Hinrichs and Lothar Meyer. With the exception of Döbereiner who discovered triads of elements, all the others published coherent periodic tables before Mendeleev's first table of 1869. The article discusses the philosophical distinction between elements as "basic substances" and elements as "simple substances" and the use to which this distinction was put by Paneth at the beginning of the twentieth century following the apparent threat to the periodic system which occurred when so many new isotopes were discovered. The article continues by summarizing the way in which the discovery of the electron provided the key to a deeper understanding of the periodic system through the researches of Thomson, Bohr, Pauli and many others. Finally, alternative forms of the periodic table are discussed including those proposed by Janet, Stewart and Benfey.

Paper eight first appeared in the *Journal of Chemical Education* in 2008. Whereas in my book on the periodic table, I recommended the left-step table as the best possible representation, I subsequently changed my mind and proposed a new table. First of all let me say why I initially supported the left-step table. My attention was first drawn to the left-step table by Henry Bent's unpublished booklets on the subject, although I felt that his

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[18] Of course I exclude the need to derive fundamental constants.

[19] The article began life as an invited talk at the Chemical Heritage Foundation in Philadelphia and was followed by an article in the foundation's magazine, *Chemical Heritage*.

arguments were too partisan, too numerous and that some stretched the reader's credulity a little too far.

What actually converted me to the left-step table, at least for a period of a few years, was a rather concise paper by the periodic table designer Gary Katz, which appeared in *The Chemical Educator*.[20] My own support for this form of the table centered on my interest in the dual sense of the term "element" and in particular the more fundamental sense, called element as a "basic substance" by Paneth.

But I am getting ahead of myself. Let me first say what I see as the advantages of this representation. Instead of confining the s-block of elements to the left side of the table where it looks a little out of place, the left-step table moves the s-block to the right hand edge of the table. This produces a pleasing and seemingly more natural sequence in the main blocks of the periodic table. Whereas in the convention of medium-long form table these blocks appear in the order s, d, p with the f block as a kind of footnote, in the left-step table one has the order of f, d, p and s reading from left to right. Moreover, the element helium is removed from its usual place at the head of the noble gases and placed instead at the head of the alkaline earth elements on the basis of its s^2 electronic configuration that is shared by these metals.

As a result of these two changes, the left-step table removes a rather annoying blemish from the conventional periodic table. It has been a source of puzzlement to many authors as to why the first short period of two elements does not repeat in the same way that the other period lengths repeat (8,8,18,18,32, and presumably 32). In the left-step table, the first very short period consisting of two elements *does* repeat. In addition, the order of orbital filling appears to be better reflected in the left-step table as mentioned earlier in this introduction. In the conventional or medium-long table or even the long-form table, there is an important sense in which these tables are predicated on the false notion that orbital filling takes place according to increasing values of the main quantum number n. The order of filling does not follow this order but to a good approximation obeys a rule on increasing $n + \ell$, the Madelung rule. In the left-step table, each distinct period reflects a particular value of $n + \ell$ and not n. Finally, although this may be somewhat of a cosmetic feature, there are no gaps such as between Be and B or Mg and Al in the left-step table as one finds in the conventional table format.

With all these advantages one might well wonder why the left-step table has not attracted more attention and indeed why it has not been widely adopted. The answer to this question lies in the placement of one crucial element, helium. In the left-step table, helium is placed among the alkaline earth metals as mentioned above. To most chemists this is completely abhorrent since helium is regarded as the noble gas *par excellence*. Meanwhile, to a physicist or somebody who emphasizes electronic properties, helium falls rather naturally into the alkaline earths since it has two outer-shell electrons.

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[20]G. Katz, The Periodic Table: An Eight Period Table for the 21st Century, *The Chemical Educator*, 6: 324–332, 2001.

Here then is an interesting case of the clash between chemistry and physics, an example, which highlights the importance of the question of the reduction of chemistry. Should one follow chemical intuition in resisting the evidence from electronic configurations and the suggestive nature of the left-step table? Or should one follow the reductionist approach in insisting that helium is an alkaline earth in the belief that it might eventually even show chemical similarities to the alkaline earths? These are the standard arguments for and against the left-step table.

What I hope to have added to the discussion has been a philosophical reflection on the nature of the concept of "element" and in particular an emphasis on elements in the sense of basic substances rather than just simple substances. The view of elements as basic substances, is one with a long history. The term is due to Fritz Paneth, the prominent twentieth century radio-chemist. This sense of the term element refers to the underlying reality that supports element-hood or is prior to the more familiar sense of an element as a simple substance. Elements as basic substances are said to have no properties as such although they act as the bearers of properties. I suppose one can think of it as a substratum for the elements. Moreover, as Paneth and before him Mendeleev among others stressed, it is elements as basic substances rather than as simple substances that are summarized by the periodic table of the elements. This notion can easily be appreciated when it is realized that carbon, for example, occurs in three main allotropes of diamond, graphite and buckminsterfullenes. But the element carbon, which takes its place in the periodic system, is none of these three simple substances but the more abstract concept of carbon as a basic substance.

It occurred to me that if one concentrated on this more fundamental sense of the concept of element, then the fact that helium does not seem to have properties in common with the alkaline earths would not be sufficient reason for not placing it among these elements in the periodic table. As I have later described this position, it was a form of "why not argument" rather than a positive reason for why helium *should* be placed among the alkaline earths.

Then came my change of mind. Rather than relying on such a convoluted justification for the placement of helium among the alkaline earths, and having failed to convince a large number of colleagues of the view that helium belongs with the alkaline earths, I decided to return to my original anti-reductionist point of view and to insist, like most chemists, that helium must remain among the noble gases despite its s^2 configuration. However, I also suggested the repositioning of another element for reasons which I believe have not been previously considered.

I became increasingly interested in triads of elements, partly because of their historical importance. As I claimed in my book, the discovery of atomic weight triads represents the first major hint that there exists some regularity that underlies the elements.[21] Triads represent the first hint of a systematic and quantitative foundation between the numerical properties of the elements. Now since atomic weight was replaced by atomic number, it is

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[21]E. R. Scerri, *The Periodic System, Its Story and Its Significance*, Oxford University Press, New York, p. 179, 2007.

natural to consider atomic number triads. With the exception of a single obscure paper published in the 1930s, nobody had paid much attention to atomic number triads.[22] Unlike atomic weight triads, these modern versions are exact in about 50% of all possible triads among the elements in the periodic system. For example, Li, Na and K form a perfect atomic number triad, $[(3 + 19)/2 = 11]$, whereas Na, K and Rb do not even do so approximately $[(11 + 37)/2 = 24 \neq 19]$.

I wondered whether there might be some means of maximizing the number of atomic number triads that appear on the periodic table. One thing was immediately clear, namely that the relocation of helium, as proponents of the left-step favor, would lead to the *loss* rather than the gain of an atomic number triad. This was therefore one more argument against the relocation of helium.

On the other hand, the relocation of hydrogen, helium's traditional partner in the first very short period, would produce a new atomic number triad if hydrogen were moved to the halogen group. $[H(1) + Cl(17)/2 = F(9)]$. So rather than moving helium from right to left in the periodic table, I proposed moving hydrogen from left to right.

Paper nine is another one that appeared in *American Scientist*. In it I took a philosophical look at two important ideas that contributed to the evolution of the periodic system. These two ideas are Prout's hypothesis and the notion of triads, which was the subject of paper eight. Both hypotheses are interesting because they were extremely productive even though they both turned out to be refuted some time later. The fact that this should happen lends some support to the views of Karl Popper who always claimed that refutability was the all important aspect of good hypotheses and theories and not whether they turn out to be correct or not.[23] For Popper, all that we really have is tentative theories and not theories that last forever.

The final paper in this collection is very recent and appeared in the *International Journal of Quantum Chemistry* where articles on Madelung's rule have previously been published. It was in this journal that its founder Per Olov Löwdin first drew attention to the fact that the rule had not yet been derived from quantum mechanics.[24] More recently Allen and Knight published what they claimed provided just such a long-awaited derivation.[25]

My own paper addresses various attempts to derive the Madelung rule, including that of Allen and Knight as well as a more recent attempt by Bent and Weinhold.[26] But I believe my paper also breaks new ground by discussing whether there is any need at all to derive the Madelung rule, a notion which I thank Eugen Schwarz for first drawing my attention to. In addition to Madelung's rule, the paper examines all the recent themes that I think are

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[23] This is actually the pessimistic meta-induction associated with Larry Laudan among other philosophers. L. Laudan, A Confutation of Convergent Realism, *Philosophy of Science*, 48: 1–49, 1981.

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important in the study of the foundations of the periodic table, including the dual nature of the concept of an element and whether or not an optimal form of the periodic system might exist. I carry out an analysis of the recent work of Schwarz who has been one of the few chemists to take seriously the distinction between an element as a basic substance and as a simple substance.[27]

Schwarz also makes the interesting identification between neutral atoms and elements as simple substances on one hand, and between bonded atoms and elements as basic substances on the other hand. As a frequent participant at conferences on the philosophy of chemistry, Schwarz seems to have fully grasped the importance of this distinction between the two senses of the macroscopic element. Whether or not his one-to-one identification of the dual sense of an "element" with microscopic atoms is meaningful remains to be seen, but here I argue that he is mistaken.

Schwarz uses his understanding of the situation to suggest that all the recent attention on the Madelung rule is misplaced. He argues that if the periodic system is fundamentally a classification of the elements as basic substances, then it should also be regarded as a classification of bonded atoms rather than of neutral isolated atoms. Consequently he believes that one should concentrate on an orbital filling rule that applies to bonded atoms or ions. Such a rule is that orbitals are filled in order of increasing main quantum number n and not the more complicated Madelung rule of increasing $n + \ell$.

To take this idea seriously would require that we abandon the familiar table of isolated atoms and begin to think about how to set up a table of bonded atoms of the elements. Schwarz does not actually carry out this further step in his own writing. In my own paper, which is reproduced in this collection, I try to build such a table and quickly arrive at the conclusion that the idea is un-workable since it cannot be carried out categorically.

Instead I propose a more radical solution, namely that of *not* identifying bonded atoms with elements as basic substances, a view for which I claim support from the work of Mendeleev and Paneth. This does not solve the problem of redesigning a periodic table to reflect the behavior of bonded atoms. But if we are to retain the traditional periodic table of neutral atoms, we may still forge a connection with elements as "basic substances" by arranging the elements so as to maximize atomic number triads, where atomic number may now be interpreted to also mean "element number".

Chemistry, Spectroscopy, and the Question of Reduction

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Modern Chemical Education. Too Much So-Called Theory?

The modern approach to chemical education appears to be strongly biased toward theories, particularly quantum mechanics. Many authors have remarked that classical chemistry and its invaluable predictive rules have been downgraded since chemistry was put into orbit around physics. School and undergraduate courses as well as textbooks show an increasing tendency to begin with the establishment of theoretical concepts such as orbitals and hybridization. There is a continuing debate in the chemical literature on the relative merits of theory as opposed to qualitative or descriptive chemistry (1–6). To quote the late J. J. Zuckerman who supported the latter approach (3).

> Inorganic chemistry is facing an identity crisis. The old jumble of facts has given way to the new jumble of theories. Worse still the distinction between fact and theory itself has been allowed to blur. Inorganic chemists have been coaxed away from their formerly strong, central position based on a monopoly of information on syntheses, reactions, and properties of the elements and their compounds by the more ephemeral allure and false sophistication of spectroscopy and theory.

The supporters of this view appear to be fighting a losing battle if one considers the pervasiveness of the current orbitals paradigm in chemistry (2). Atomic and molecular orbitals are freely used at all levels of chemistry in an attempt to explain chemical structure, bonding, and reactivity. This is a very unfortunate situation since the concept of orbitals cannot be strictly maintained in the light of quantum theory from which it supposedly derives.

The notion of electrons in orbitals consists essentially of ascribing four distinct quantum numbers to each electron in a many-electron atom. It can be shown that this notion is strictly inconsistent with quantum mechanics (7). Definite quantum numbers for individual electrons do not have any meaning in the framework of quantum mechanics. The erroneous view stems from the original formulation of the Pauli principle in 1925, which stated that no two electrons could share the same four quantum numbers (8). This version of the principle was superseded by a new formulation that avoids any reference to individual quantum numbers for separate electrons. The new version due to the independent work of Heisenberg and Dirac in 1926 states that the wave function of a many-electron atom must be antisymmetrical with respect to the interchange of any two particles (9, 10).

The use of the older restricted version of the Pauli principle has persisted, however, and is routinely employed to develop the electronic version of the periodic table. Modern chemistry appears to be committing two mistakes. Firstly, there is a rejection of the classical chemical heritage whereby the classification of elements is based on the accumulation of data on the properties and reactions of elements. Secondly, modern chemistry looks to physics with reverence and the false assumption that therein lies the underlying explanation to all of chemistry. Chemistry in common with all other branches of science appears to have succumbed to the prevailing tendency that attempts to reduce everything to physics (11). In the case of the Pauli principle, chemists frequently fall short of a full understanding of the subject matter, and

advocate its use without realizing that their version of the principle is strictly inconsistent with current physics.

The Periodic Table According to Chemistry or According to Spectroscopy

There are two ways to develop the periodic table of elements. The first is based on chemical evidence and is the version originally proposed by Mendeleef and others. The second method is based on the electronic configurations of atoms, as first suggested by Bohr, and based on atomic spectroscopy (12). The second scheme is the more recent, of course, and, since it was first proposed, numerous examples have been found where the two approaches show disagreement as to how the elements should be arranged in the periodic table. Some of these differences persist up to the present time. The periodicity in the chemical properties of the elements is a complicated matter and is only approximately reflected in the electronic configurations of atoms. This need not be cause for concern, however, since electronic configurations themselves represent an approximation. The simple notion that elements in the same group of the periodic table share the same outer electron configuration shows a number of exceptions. The elements helium and beryllium for example have the configurations of $1s^2$ and $2s^2$, respectively, but are certainly not in the same group of the periodic table. On the other hand, nickel, palladium, and platinum are in the same group (10 according to the new 18 group scheme) and yet have very different outer shell configurations. Jorgensen (13) has concluded that,

> no simple relation exists between the electron configuration of the ground state of the atom and the chemistry of the element under consideration.

The inability to reduce chemistry to electronic configurations does not in itself rule out the reduction of chemistry to physics, and quantum mechanics in particular, as some authors seem wrongly to conclude. Those who favor the spectroscopic or electronic version of the periodic table have explored whether there may be some underlying symmetry that governs the building-up of electronic orbitals (14, 15). This work has led to the proposal of a new form of the periodic table in which the alkaline earth elements, instead of the noble gases are placed at the right-hand edge (16, 17).

Empirically, the electron shells are not filled in a strict sequential order according to their average distance from the nucleus (18). In the element scandium, for example, the 4s orbital is thought to be filled before the 3d orbital begins to fill. This effect may be explained in terms of the relative stabilities of the two orbitals and interelectronic repulsive effects. It emerges that, although the 3d orbital has a lower energy, it is less stable when electron repulsion effects are taken into account correctly (19). The greater overall stability of the 4s orbital occurs due to a greater degree of electron penetration in s orbitals. Similar effects occur at other positions in the periodic table, and the correct sequence of electron filling is given by the following order, although there are about 20 exceptions for neutral atoms:

$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f$

$$< 5d < 6p < 7s < 5f, \text{etc.}$$

This sequence is not theoretically derivable but based on spectroscopic data. This fact is seldom stressed in textbook accounts, which imply that it refers to the energies of the various orbitals as calculated from the theory. As was mentioned above, the stated sequence refers strictly to the order of filling of orbitals, which may be rationalized by the correct inclusion of electronic repulsion effects.

Confusion is created by the often-quoted results of calculations by Latter that did predict some of the above ordering on the basis of the rather crude Thomas–Fermi method of approximation (20). More recent Hartree–Fock calculations on atoms show, for example, that the 3d level is definitely of lower energy than that of 4s (21).

Various mnemonic diagrams has been suggested for remembering the sequence of filling of orbitals (22–25), and they have been generally adopted in chemical education. Most chemistry texts include a form of the diagram shown in Figure 1.

If we consider the angular momentum quantum number of each of these orbitals, s = 0, p = 1, d = 2, f = 3, etc., we obtain the following sequence of numbers for the order of filling. Each sequence shown on consecutive lines, is repeated just once.

<div align="center">

0,

0,

1, 0,

1, 0,

2, 1, 0,

2, 1, 0,

3, 2, 1, 0,

3, 2, 1, 0,

. . . .

. . . .

</div>

The periodic table may be seen to take on a more symmetrical or systematic form with respect to these numbers if the elements are arranged so that the alkaline earths occur at the right-hand edge of the table as shown below. It is claimed that in the conventional form of the periodic table the inherent symmetry in electronic configurations is not emphasized and that the order of filling of electronic orbitals takes on a puzzling form (16). The proposed new fdps version shown in
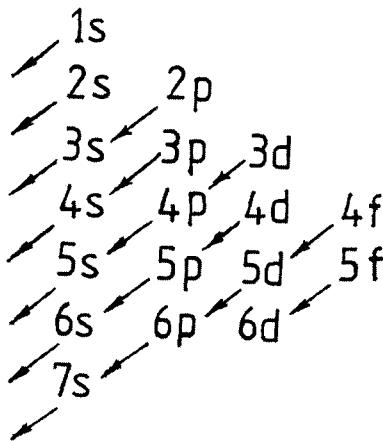

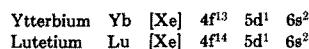Figure 1. Mnemonic to obtain the order of filling of orbitals.

Figure 2 does not yield any new predictions as to chemical or physical behavior of the elements, and this in itself argues against its adoption. Moreover, the proposed version leads to the grouping together of the element helium with the alkaline earth metals, which is a little difficult to accept in chemical terms. The conventional periodic table places helium in group 8 of the periodic table in keeping with its close similarities with the other noble gases. This form of adjustment should not be possible in a table that is strictly committed to regularities based on particular sequences of quantum numbers, but precisely such an adjustment was made for helium by the originators of the scheme (17). Not surprisingly this proposed electronic form of the periodic table has not been generally adopted by chemists, although the quantum mechanical development of the subject through electronic orbitals is now very widespread. It should be mentioned, however, that some authors feel that a good case does exist for putting helium above beryllium in the same group. They claim that first members are frequently anomalous and that the ionization energy of helium can be predicted quite well from those of other elements to its left and below it, in the fdps form of the periodic table (26).

Figure 2. New proposed form of the periodic table based on symmetry of electronic configurations and quantum numbers.

A Recent Modification to the Form of the Periodic Table

It is interesting to note that the adoption of electronic configurations as a means of developing the periodic table has led to some regressions in our understanding of atomic chemistry. A good example is provided by the question of which element to place under scandium and yttrium in the first column of the transition metals. Prior to the introduction of electronic configurations, the choice was invariably in favor of the element lutetium, which shows a number of chemical similarities with the two above-named elements. Until relatively recently the use of electronic configurations dictated that the element lanthanum should appear in this position instead of lutetium. In order to appreciate this situation, we need to consider the electronic configurations that were supposed to occur in the atoms of ytterbium (atomic number 70) as well as lutetium (atomic number 71).

<div align="center">

Ytterbium   Yb   [Xe] $4f^{13}$ $5d^1$ $6s^2$

Lutetium   Lu   [Xe] $4f^{14}$ $5d^1$ $6s^2$

</div>

According to this assignment the differentiating electron, that is, the final electron to enter the atom of lutetium, was seen as an f electron. This suggested that lutetium should be the final element in the first row of the rare earth elements, in which f electrons are progressively filled, and not a transition element as had been believed by the chemists. As a result of more recent spectroscopic experiments the configuration of ytterbium has been altered to (27)

Ytterbium Yb [Xe] $4f^{14}$ $5d^0$ $6s^2$

while that of lutetium remains unchanged. Ytterbium therefore now appears to mark the end of the rare earths, and the subsequent element lutetium shows a d differentiating electron and thus makes it an equally good candidate as lanthanum, of configuration [Xe] $5d^1$ $6s^2$, for the role of the first element in the first transition. Renewed chemical and physical measurements then showed conclusively that lutetium rather than lanthanum bears a close similarity with scandium and yttrium (28–30). Electronic configurations have reestablished what was already known from old-fashioned chemical evidence. Precisely analogous arguments have been used to show that the fourth transition series should begin with the element lawrencium and not actinium as had been generally supposed on the basis of earlier electronic configurations. The older as well as the revised forms of the periodic table are shown in Figure 3.

Other Changes in Electronic Configurations Including the Rare Earths

The approximate nature of orbitals and configurations is reflected in the changes that have occurred in the supposed ground state configurations of 20 or so elements, even following the introduction of electron spin. If we were to consider earlier changes in electronic configurations, they would be far more numerous. The configurations ascribed to various elements by Bohr and Stoner underwent several important changes following the introduction of the fourth quantum number and the Pauli exclusion principle. Alterations that have occurred since Pauli's principle was first used to

Idealized and Observed (36) Outer Shell Configurations for the Rare Earths

Element	Atomic number	Idealized configuration	Observed configuration	
La	57	$5d^1 6s^2$		$5d^1 6s^2$
Ce	58	$4f^1 5d^1 6s^2$	$4f^2$	$6s^2$
Pr	59	$4f^2 5d^1 6s^2$	$4f^3$	$6s^2$
Nd	60	$4f^3 5d^1 6s^2$	$4f^4$	$6s^2$
Pm	61	$4f^4 5d^1 6s^2$	$4f^5$	$6s^2$
Sm	62	$4f^5 5d^1 6s^2$	$4f^6$	$6s^2$
Eu	63	$4f^6 5d^1 6s^2$	$4f^7$	$6s^2$
Gd	64	$4f^7 5d^1 6s^2$	$4f^7$	$5d^1 6s^2$
Tb	65	$4f^8 5d^1 6s^2$	$4f^9$	$6s^2$
Dy	66	$4f^9 5d^1 6s^2$	$4f^{10}$	$6s^2$
Ho	67	$4f^{10} 5d^1 6s^2$	$4f^{11}$	$6s^2$
Er	68	$4f^{11} 5d^1 6s^2$	$4f^{12}$	$6s^2$
Tm	69	$4f^{12} 5d^1 6s^2$	$4f^{13}$	$6s^2$
Yb	70	$4f^{13} 5d^1 6s^2$	$4f^{14}$	$6s^2$

order the elements do not involve any major conceptual changes but depend on detailed spectroscopic experiments. Several theoretical studies have also been conducted aimed at finding which element marks the true beginning of the rare earths (31, 32). The section above mentioned a change in the configuration of ytterbium. Indeed most rare earth elements have undergone recent changes with regard to their supposed ground state configurations. To judge by the variations in inorganic texts, the precise configuration of the cerium atom appears to be particularly troublesome (33–35).

The table shows the most definitive and currently available outer shell configurations for the rare earths (36).

The idealized configurations refer to those expected on the basis of Hund's rule, that is configurations in which spin multiplicity is maximized. The only elements where the idealized configurations are found to occur are Ce, Gd, and Lu. Many early assignments of rare earth configurations had assumed the above-given idealized versions, due to the predominant trivalency of the rare earths. This provides another example of a difference between the chemical and spectroscopic periodic tables.

The identification of the ground state configuration is obtained from measurements of the splitting of spectral lines in an external magnetic field (Zeeman effect). The degree of splitting depends on the Landé splitting factor, g, which is related to the quantum numbers of the atom, L, S, and J, where L represents the orbital angular momentum, S the spin angular momentum, and J the overall angular momentum.

$$g = 1 + J(J + 1) - L(L + 1) - S(S + 1)/2J(J + 1)$$

The same g value may often arise for different spectroscopic terms, having differing values of L, S, and J, such as to render the deduction of the configuration ambiguous. For example, Moore's tables list as many as 30 terms corresponding to $g = 1.500$ (37). As a result, it is not always possible to obtain an unambiguous assignment of configurations from spectral measurements.

Furthermore, Landé's theory only represents a first-order approximation, and the L and S quantum numbers only behave as good quantum numbers when spin–orbit coupling is neglected. It is interesting to note that the most modern method for establishing the atomic ground state and its configuration is neither chemical nor spectroscopic in the usual sense of the word but makes use of atomic beam techniques (38).

The Actinides. A Case Where Spectroscopy Triumphs over Chemistry?

Up to this point we have argued in favor of chemical evidence over physical evidence with regard to the form of the periodic table. We now turn briefly to the controversy
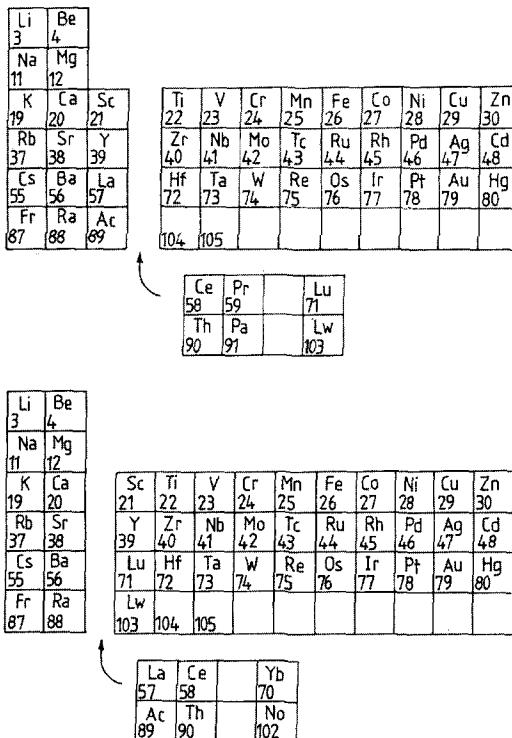
Figure 3. The old (a), and revised version (b) of the periodic table showing changes with regard to the first elements in the third and fourth transition series.

regarding the elements from numbers 89 to 102 where spectroscopic evidence appears to have settled the question as to where these elements should be placed. It would seem that in this case the chemical evidence available confused the issue. In the 1950's several authors including F. Paneth argued that these elements should be regarded as transitional in view of chemical similarities (39).

> Seaborg and those who follow him like to break off the last row of the periodic table at actinium and to write the elements 89–96 (and now 98) as the group of "actinides" under the group of "lanthanides" 57–72. They can point out in favour of this arrangement that in this way the probable similarities in the electronic structure of the respective members of the two groups are clearly indicated. However, those similarities, even if present, do not manifest themselves in the chemical behaviour of the first members, and those chemists who want to show above all in the periodic table the a grouping according to chemical relationships, hold that the discovery of the transuranium elements does not justify the neglect of the old-established and obvious correspondence between thorium and hafnium, protactinium and tantalum, and uranium and tungsten. They prefer to leave the periodic system up to uranium unchanged, and to put the group of transuranic elements, or "uranides" as they are sometimes called, at the end of the table.

Two years later H. R. Paneth reassessed this question and took a more impartial view (40). He considered the possible analogies of the element plutonium (93) with osmium (76), treating the elements in question as transition elements, or with the rare earth samarium (62), treating the elements as rare earths. If the analogy holds with osmium we would expect higher valencies up to 8 to be displayed by the elements, whereas, if it behaves more like samarium, its valency should typically be 3. Chemical evidence shows that plutonium shows its most stable valency as 4, while 3 and 6 also occur. This finding suggests that plutonium be regarded as one of the rare earth metals, which generally show low valencies. Transition metals, however, show higher valencies by promoting available d electrons to the outer valency shell, according to the electronic configuration model. This form of electron promotion does not readily take place in rare earths due to the deeper lying nature of its supposedly occupied f electrons. However, the author points out that, if we consider the elements preceding plutonium, the analogy with the rare earths is far from perfect particularly in the case of thorium and uranium. The latter is most stable in the 6 state, thus suggesting an analogy with the transition elements instead of the rare earths.

Earlier, in 1945, Seaborg had proposed that the elements starting at number 89 should be considered as a rare earth series. This resulted from attempts to synthesise elements 95 and 96. Seaborg suggested that the new series of rare earth elements should not begin after uranium as had been supposed but instead earlier, with the element actinium (41). He found that his proposed version of the periodic table suggested an analogy between elements 95 and 96 with europium and gadolinium, respectively. On the basis of this analogy he was able to identify the two new elements. The concept also led to the discovery of the remainder of the actinide elements and their eventual acceptance by the scientific community. The general opinion is now that the gradual increase in the oxidation states of thorium, protactinium, and uranium misled chemists into believing that these elements were members of a transition series in which the 6d levels were being built up. Following the discovery of the transuranium elements, it was found that successive elements ceased to show an increase in oxidation states and behaved like a second series of rare earth elements. More recently obtained spectral evidence has also been interpreted to mean that these elements add successive electrons to orbitals of the f type. Figure 4 shows the periodic tables given by F. Paneth and Seaborg, respectively.

Conclusion

The greatest success of quantum mechanics has been in the field of spectroscopy, and there are some striking analogies between chemical periodicity and the periodicity shown by atomic spectra. However, an analogy does not imply an identity (42) between the two forms of the periodic table.

There are also a number of differences between chemistry and spectroscopy with regard to the properties of atoms. For example, according to spectroscopic measurements, it should be more energetically favorable for the element aluminium to form Al^{1+} or Al^{2+} ions, whereas in chemical compounds only Al^{3+} is formed. This chemical fact may be explained by recourse to the Born–Haber cycle, which shows that, when all relevant energetic terms are considered, the Al^{3+} ion represents the most favorable possibility. On the other hand, spectroscopy knows nothing of these chemical arguments involving energetic terms such as the lattice enthalpy. The attempt to reduce chemistry to quantum mechanics through electronic configurations was prompted by the analogies with optical and X-ray spectra (43). The failure to reduce chemistry to electronic configurations is hardly surprising since configurations represent an approximation that is strictly inconsistent with quantum mechanics. At the same time, this failure to reduce chemistry to electronic configurations does not rule out the possibility of reducing chemistry to quantum mechanics.

Most of the arguments presented in the present paper may be resolved if one accepts the coexistence of many forms of the periodic table that are similar but far from identical, rather than trying to reach one single compromise version. The electronic forms of the periodic table should not be considered as being more fundamental in some way.

Group

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
I																	H	He
II	Li	Be											B	C	N	O	F	Ne
III	Na	Mg											Al	Si	P	S	Cl	Ar
IV	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
V	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
VI	Cs	Ba	57-71	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
VII	Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf						

Rare Earths

VI
57-71

La	Ce	Pr	Nd	Pu	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

H																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	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	57-71	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	89-															

Lanthanides

La	Ce	Pr	Nd	Pu	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

57

Actinides

Ac	Th	Pa	U	Np	Pu									

89

Figure 4. Comparison of periodic tables given by Paneth (42) and Seaborg (44).

The more general question of whether chemistry is reducible to quantum mechanics is more subtle and requires a consideration of the nature of ab initio calculations. According to some authors, the question even depends on the problems in the foundations of quantum mechanics (44).

The use of atomic orbitals in ab initio calculations has yielded some very accurate results, but this should not be taken to indicate the truth of the orbital model. The zero-order orbital model consists in assuming the electrons of a many-electron atom to be independent and that they possess definite quantum numbers. The wavefunction for a many-electron atom is expanded by taking an infinite series whose terms consist of a complete set of orthogonal functions. More precisely the expansion consists of a series of terms that are members of a set of normalized orthogonal functions each multiplied by a constant coefficient or weighting factor. Provided that sufficient terms are considered and that the series converges, it is possible to approach progressively closer to the experimentally observed energy of the atom in question. This feature is quite general and applies to the mathematical modelling of any arbitrary function. The mistake is to attribute some significance to the zero-order approximation, that is, to take the zero order approximation out of its mathematical context.

It should also be acknowledged that in recent years computational quantum chemistry has achieved a number of predictions that have since been experimentally confirmed (45–47). On the other hand, since numerous anomalies remain even within attempts to explain the properties of atoms in terms of quantum mechanics, the field of molecular quantum mechanics can hardly be regarded as resting on a firm foundation (48). Also, as many authors have pointed out, the vast majority of ab initio research judges its methods merely by comparison with experimental data and does not seek to establish internal criteria to predict error bounds theoretically (49–51). The message to chemical education must, therefore, be not to emphasize the power of quantum mechanics in chemistry and not to imply that it necessarily holds the final answers to difficult chemical questions (52).

As to the general issue of reduction, chemists would do well to consider the work of philosophers of science, who have for some time renounced the notion that any particular branch of science may be strictly reduced to a more basic science. The classic work giving conditions for strict reduction is by Nagel (53), and several detailed criticisms of his views have been published (54, 55). More recently there appears to be a partial return to reductionism under the guise of "supervenience". Chemistry is said to supervene over physics even though it cannot be shown to be strictly reducible in the sense of Nagel. Whether supervenience represents merely a hope and whether it holds any explanatory power is the focus of much current work in philosophy (56–58).

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The Electronic Configuration Model, Quantum Mechanics and Reduction

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ABSTRACT

The historical development of the electronic configuration model is traced and the status of the model with respect to quantum mechanics is examined. The successes and problems raised by the model are explored, particularly in chemical *ab initio* calculations. The relevance of these issues to whether chemistry has been reduced to quantum mechanics is discussed, as are some general notions on reduction.

1 *Introduction*
2 *Historical*
3 *Present Status and Applications*
4 *Conclusions*

I INTRODUCTION

This paper deals with some questions in the foundations of chemistry. The atomic orbital (or electronic configuration) model is examined, with regards to both its origins and current usage. I explore the question of whether the commonly-used electronic configuration of atoms have any basis in quantum mechanics as is often claimed particularly in chemical education.

I restrict my attention to non-relativistic pioneer quantum mechanics of 1925–6, and even further to the time independent formulation. Numerous other developments have taken place in quantum theory, such as Dirac's relativistic treatment of the hydrogen atom (Dirac [1928]) and various modern quantum field theories have been constructed (Redhead [1986]). Also, much work has been done in the philosophy of quantum theory such as the question of E.P.R. correlations (Bell [1966]). However, it seems fair to say that no fundamental change has occurred in quantum mechanics since the pioneer version was established. The version of quantum mechanics used on a day-to-day basis by most chemists and physicists remains as the 1925–6 version (Heisenberg [1925], Schrodinger [1926]).

First I consider the origin of tables of electronic configuration which are learned in school chemistry and which appear in all chemistry texts. The aim is

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to see if these tables can be derived from quantum theory as is often claimed or implied. Electronic configurations of atoms form the basis for the teaching of chemistry at all levels, and serve to shape the thoughts of even professional chemists.

As Harré [1961] has said concerning models:

> they carry the picture with which everyone, schoolboy, student, engineer and research worker, operates in dealing with problems in his field. You may deny that you have a model and be as positivistic as you like, but while the standard expressions continue to be used you cannot but have a picture.

In chemical education, the main motivation for basing chemistry on electronic configurations seems to be that if one knows the number of outer shell electrons in any particular atom, one can predict its chemical properties (Cotton and Wilkinson [1966], Kotz and Purcell [1987]).

2 HISTORICAL

One of the first attempts to explain chemical periodicity in terms of electronic structure was by Niels Bohr [1923]. His method called the 'aufbau principle' consists in building-up successive atoms by the addition of an extra electron to the previous atom. Bohr developed his account of the periodic table according to two quantum numbers, n the main quantum number and k the azimuthal quantum number. These numbers emerge from the quantum conditions and serve to identify the stationary states of the system, that is states which do not vary with time. Electrons in these stationary states do not radiate energy unless they undergo a transition between stationary states. The introduction of stationary states to atomic physics was Bohr's main contribution to the quanatum theory of atoms. The problem in classical physics had been to explain why the orbiting electrons did not lose energy and spiral into the nucleus (Jammer [1966]). Bohr postulated that electrons exist in stationary, non-radiating states and only emit radiation on undergoing a transition between stationary states (Bohr [1913]) (Table 1).

According to this scheme an atom of sulphur, for example, with sixteen electrons, would have an electronic configuration of 2, 4, 4, 6 (Bohr [1923]). The main feature of the building-up procedure was Bohr's assumption that the stationary states would also exist in the next atom, obtained by the addition of a further electron. He also assumed that the number of stationary states would remain unchanged apart from any additional states of the newly introduced electron. In other words the assumption was one of the existence of sharp stationary states, and their retention on adding both an electron and a proton to an atom. To quote Bohr:

> The demand for the presence of sharp, stable stationary states can be referred to in the language of quantum theory as a general principle of the existence and permanence of quantum numbers.

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TABLE 1. Assignment of
electrons to shells accord-
ing to Bohr's scheme.

n	k	Maximum number of electrons
1	1	2
2	1	4
2	2	4
3	1	6
3	2	6
3	3	6
.	.	.
.	.	.

It should be added that the stationary states in the newly obtained atom are not identical, since the accompanying addition of a proton causes a contraction in the size of the electron orbits.

At the basis of the building up procedure used by Bohr there lies the adiabatic principle introduced by Ehrenfest [1917].

> If a system be affected in a reversible adiabatic way, the allowed motions are transformed into allowed motions.

Elsewhere Ehrenfest states:

> Suppose that for some class of motions we for the first time, introduce the quanta. In some cases the hypothesis fixes completely which special motions are to be considered as allowed. This occurs if the new class of motions are derived by means of an adiabatic transformation from some class of motions already known (Ehrenfest [1917]).

This adiabatic principle was one of the corner-stones of the old quantum theory. It allowed one to find the quantum conditions when an adiabatic change was imposed on a system. It was used successfully to account for the Stark and Zeeman effects in the spectrum of atomic hydrogen, resulting from the application of an electric and magnetic field respectively (Schwartzchild [1916]; Epstein [1916]).

There are however some stringent restrictions on the applicability of the adiabatic principle (Mehra and Rechenberg [1982]). Ehrenfest himself [1917] showed that it was applicable to simply periodic systems. These are systems having two or more frequencies which are rational fractions of each other. In such systems the motion will necessarily repeat itself after a fixed interval of time. Burgers [1917], a student of Ehrenfest, showed that it was also applicable

to multiply periodic systems. In these more general systems of motion the various frequencies are not rational fractions of each other, and so the motion does not necessarily repeat itself (Goldstein [1980]). The hydrogen atom provides an example of a multiply periodic system, with two degrees of freedom being the orbital frequency of the electron, and the precession of the orbital frequency.

An even more general class of systems is termed aperiodic, and as far as we know the adiabatic principle does not apply here. At least nobody has found a proof of its applicability to this day. Unfortunately for the field of atomic physics all atoms larger than that of hydrogen constitute aperiodic systems for which the adiabatic principle does not apply. In the helium atom, for example, the motion of each of the two orbiting electrons varies due to the varying interaction with the other electron as their distance apart changes, in terms of the early Bohr theory. We may no longer speak of a constant period for either of the electrons. Bohr was well aware of this limitation of the adiabatic principle but he continued to use it even for many electron atoms, in the hope that it might still remain valid for these aperiodic systems. He repeatedly acknowledged this point in his writings:

> For the purposes of fixing the stationary states we have up to this point only considered simply or multiply periodic systems. However the general solution of the equations frequently yield motions of a more complicated character. In such a case the considerations previously discussed are not consistent with the existence and stability of stationary states whose energy is fixed with the same exactness as in multiply periodic systems. But now in order to give an account of the properties of the elements, we are forced to assume that the atoms, in the absence of external forces at any rate always possess sharp stationary states, although the general solution of the equations of motion for the atoms with several electrons exhibits no simple periodic properties of the type mentioned (Bohr [1923]).

Returning to the historical sequence of events, the hypothesis of the permanence of quantum numbers came under attack from the spectroscopic analysis of the splitting of the lines under the influence of a magnetic field (Lande [1923]). An atomic core consisting of the nucleus and inner shell electrons, showed a total of N spectroscopic terms in a magnetic field. If an additional electron were added, having an azimuthal quantum number k, the new composite system would be expected to show $N(2k-1)$ terms since the additional electron was associated with $2k-1$ terms. However, experiments revealed more terms. In general the terms split into two types, one consisting of $(N+1)(2k-1)$ components and the second consisting of $(N-1)(2k-1)$ components, giving a total number of $2N(2k-1)$ components.

This represents a violation of the number of quantum states, since a two-fold increase in terms of the atomic core seems to occur on the introduction of an additional electron. Bohr's response was to maintain adherence to the

permanence of quantum numbers even in the face of this evidence. He merely alluded to a mystical device which he called a non-mechanical constraint or 'Zwang' to save the quantum numbers (Hendry [1984]).

Bohr's account of the periodic table also came under attack from chemical evidence. The element sulphur, for example, was attributed an electronic configuration of 2, 4, 4, 6 as noted previously. This grouping of electrons suggested that 6 electrons were more loosely bound than the others and successfully accounted for the formation of compounds such as sulphur hexafluoride SF_6. However, this element is also capable of forming a tetrachloride or SCl_4, and a dichloride SCl_2 (Purcell and Kotz [1977]). The formation of these compounds suggests that two or four electrons may be more loosely bound than the remaining electrons, but this notion cannot be accommodated by the configuration given by Bohr.

The next major advance in tables of electronic configurations was provided by the little known English physicist, Stoner [1924]. His approach was based on using not merely two quantum numbers, but also the recently introduced third quantum number of Sommerfeld. The third or inner quantum number j refers to the precession of the orbital motion in the presence of a magnetic field. The occurrence of this third quantum number suggested additional stationary states in the atom, and yet Bohr did not extend his electronic configuration scheme accordingly. The reason for this is not clear, but perhaps Bohr was becoming increasingly concerned with the question of the existence of stationary states for individual electrons in many electron atoms. Stoner, undaunted by these theoretical problems, suggested that the number of electrons in each completed level should equal twice the inner quantum number of that particular shell. This produced the scheme for ascribing electrons to shells (Table 2).

TABLE 2. Stoner's scheme for assignment of electronic configurations.

n	k	j	Maximum number of electrons
1	1	1	2
2	1	1	2
2	2	1	2
2	2	2	4
3	1	1	2
3	2	1	2
3	2	2	4
.	.	.	.

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According to the Stoner scheme the electronic configuration for the element sulphur, for example, is 2, 2, 2, 4, 2, 2, 2. This configuration could account successfully for the various valency states shown by the element, that is 2, 4, 6 as mentioned before. However, this new scheme did nothing to resolve the problem of the violation of quantum numbers as seen in the splitting of spectral lines in a magnetic field.

In 1923 Bohr wrote to Pauli asking him to try to bring order to the increasingly complicated situation in atomic physics which included the occurrence of half quantum numbers, the problems of the anomalous Zeeman effect and the doublet riddle (the origin of doublets in the X-ray and optical spectra of alkali atoms) (Hendry [1984]). Bohr specifically asked Pauli to attempt to save the quantum numbers. The latter soon responded with two papers which did indeed seem to restore order to atomic physics. Pauli's first main contribution was to challenge the view held at the time, that the core of an atom possesses an angular momentum. This theory had been proposed by Landé in order to explain the origin of the complex structure of atomic spectra. The basic assumption consisted in the interaction of the angular momentum due to the outermost electrons of the atom with that of the inner electrons, or atomic core (Landé [1923]). Pauli began by assuming that the core did indeed have an angular momentum, due to the contribution from the innermost or K shell. He then went on to examine the relativistic consequences of this assumption and was able to show that it was false (Pauli [1925a, b]). The classical expression for the ratio of the magnetic moment M, to the angular momentum J of the innermost shell of the atom is

$$M/J = e/2m_e c$$

where e is the electronic charge, m_e the mass of the electron and c the velocity of light. Pauli's relativistic calculation of this ratio yielded

$$M/J = \gamma e/2m_e c$$

where $\gamma = [1 - \alpha(Z-1)]^{1/2}$, $\alpha = e^2/hc$ is the fine structure constant, and Z is the nuclear charge.

The element barium, to take an example, has a value of $\gamma = \cdot 924$ which should result in an easily detectable variation in the ratio M/J, as compared with an element with low nuclear charge. This charge dependence of the ratio had not been observed, and Pauli took this to mean that the initial assumption of an angular momentum for the K shell was in error. He concluded that closed electron shells or the core of an atom contributes nothing to the magnetic moment of an atom. He suggested that the spectral lines and their shifts in the presence of magnetic fields were due entirely to the presence of outer electrons. He went on to suggest the assignment of a fourth quantum number m, to each electron. This fourth number is due in Pauli's words to,

TABLE 3. Allocation of electron shells based on Pauli's scheme. (Modern labels for the quantum numbers have been used instead of k's and j's. This does not alter any of the arguments presented here.)

n	l	m_l	m_s	Maximum number of electrons
1	0	0	$\left\{\begin{array}{c}+1/2\\-1/2\end{array}\right\}$	2
2	0	0	$\left\{\begin{array}{c}+1/2\\-1/2\end{array}\right\}$	2
2	1	+1	$\left\{\begin{array}{c}+1/2\\-1/2\end{array}\right\}$	2
2	1	0	$\left\{\begin{array}{c}+1/2\\-1/2\end{array}\right\}$	2
2	1	−1	$\left\{\begin{array}{c}+1/2\\-1/2\end{array}\right\}$	2
3	0	0	$\left\{\begin{array}{c}+1/2\\-1/2\end{array}\right\}$	2
3	1	+1	$\left\{\begin{array}{c}+1/2\\-1/2\end{array}\right\}$	2
.	.	.	.	.
.	.	.	.	.

a classically non-describeable duplicity in the quantum theoretical properties of the series electron (Pauli [1925a]).

This is the property we now call spin angular momentum. Pauli found that he could obtain Stoner's classification of electronic configurations from the following simple assumption which constitutes the famous exclusion principle in its original form.

It should be forbidden for more than one electron with the same value of the main quantum number n to have the same value for the other three quantum numbers k, j and m (Pauli [1925a]).

This is often stated as, 'no two electrons can have the same set of four quantum numbers' (Table 3).

Pauli justified the identification of four quantum numbers with each electron with the following apparently clever argument. He supposed that if a strong magnetic field is applied, the electrons are decoupled and so do not interact, and can be said to be in individual stationary states. Of course, the periodic table arrangement must also apply in the absence of a magnetic field.

In order to maintain the validity of the four quantum numbers for each electron even in the absence of a field Pauli appealed to what he called a 'thermodynamic argument'. He proposed to consider an adiabatic transformation in which the strength of the magnetic field is gradually reduced so that even in the absence of the field the characterization of stationary states for individual electrons remains valid. This argument seems to ensure the existence of sharp stationary states for individual electrons, but how does it fare with regards to the experimental evidence showing a violation in the number of quantum states? This problem was mentioned earlier where we saw that a system expected to show $N(2k-1)$ states on the addition of a single electron to the atomic core was in fact transformed into two sets of states numbering

$(N+1)(2k-1)$ and $(N-1)(2k-1)$ states, or a total of $2N(2k-1)$.

According to Pauli the additional electron possesses $2(2k-1)$ states in contrast to the former view of only $(2k-1)$. The two-fold increase in the number of observed states arises from the proposed duplicity of states of the new electron. The number of states of the atomic core remains as N. The arguments appear very persuasive and were received enthusiastically by the atomic physics community. Not suprisingly Bohr was pleased with Pauli's contribution and congratulated him warmly, although in all fairness both men seemed to view this step as a temporary measure. What they and everybody else failed to notice was that Pauli had committed a fallacy concerning the applicability of the adiabatic principle. A many electron atom constitutes an aperiodic system to which the adiabatic principle does not apply as emphasized by Bohr. Pauli merely changed the argument from the addition of an extra electron as in the aufbau principle, to a single atom in which the strength of a magnetic field is gradually diminished. This does not alter the issue, however, since the system remains aperiodic, and so the adiabatic principle does not apply. Perhaps the reason why such theoretical considerations were suspended was that Pauli's new scheme resolved some major problems. Firstly the existence and permanence of the quantum numbers could be retained as Bohr had hoped. Secondly, the long-standing problem of the closing of electron shells in atoms was resolved. The question had been one of how to explain the series of whole numbers 2, 8, 18, 32 ... which characterizes the lengths of the periods in the periodic system of chemical elements. These numbers corresponding to the maximum number of electrons in each shell were found to be a consequence of Pauli's principle which forbids any two electrons from sharing the same four quantum numbers and the supposition that the fourth quantum number itself can only adopt two possible values (Pauli [1946]). Pauli was later awarded the Nobel prize for these contributions.

3 PRESENT STATUS AND APPLICATIONS

It is now known that the view of electrons in individual well-defined quantum states represents an approximation. The new quantum mechanics formulated in 1926 shows unambiguously that this model is strictly incorrect. The field of chemistry continues to adhere to the model, however. Pauli's scheme and the view that each electron is in a stationary state are the basis of the current approach to chemistry teaching and the electronic account of the periodic table. The fact that Pauli unwittingly contributed to the retention of the orbital model, albeit in modified form, is somewhat paradoxical in view of his frequent criticism of the older Bohr orbits model. For example Pauli writes,

> . . . We must not put the atoms in the shackles of our prejudices (of which the assumption of electron orbits in the sense of ordinary kinematics is an example); on the contrary we must adapt our concepts to experience (Pauli [1924]).

The new quantum mechanics contradicts this independent electron model as it is often called. In Heisenberg's formulation of quantum mechanics the fundamental equation is,

$$dF/dt = i[\hat{H}, \hat{F}]/\hbar$$

where $[\hat{H}, \hat{F}]$ denotes $\hat{H}\hat{F} - \hat{F}\hat{H}$, $\hat{F}$ is any operator, $\hat{H}$ is the Hamiltonian operator of the system and $\hbar$ is $h/2\pi$. If the operators $\hat{F}$ and $\hat{H}$ commute, then the right hand side is equal to zero and any observable corresponding to the operator $\hat{F}$ does not vary with time, *i.e.* is a stationary state. Now it can be shown that the quantum numbers corresponding to individual electrons in a many electron atom do not commute with the Hamiltonian (Pilar [1968]). Only the overall angular momentum quantum number J is found to commute with the Hamiltonian. This number is calculated by the coupling together of individual angular momenta of different electrons. Standard quantum mechanics thus shows that giving electrons individual quantum numbers, or putting them into boxes or orbitals is incorrect.

Pauli's original version of the exclusion principle was found lacking precisely because it ascribes stationary states to individual electrons. According to the new quantum mechanics, only the atomic system as a whole possesses stationary states. The original version of the exclusion principle was replaced by the statement that the wavefunction for a system of fermions must be antisymmetrical with respect to the interchange of any two particles (Heisenberg [1925], Dirac [1928]).

There are two possible cases for the wavefunction of a system of identical fundamental particles such as electrons and photons. These are the symmetric and the antisymmetric cases. Experimental evidence shows that for fermions such as electrons and other particles of half integer spin the wavefunction must be anti-symmetric with respect to the interchange of particle labels. This

represents an additional postulate for quantum mechanics. Further, the anti-symmetry requirement can be shown to arise theoretically from relativistic quantum mechanics. On the other hand it can be shown that bosons or spin zero particles require a symmetric wavefunction (Pauli [1946]). Most of the formulations of quantum mechanics introduce the non-individuality of elementary particles right at the start and do not refer at all to individual particles.

> Only the so called first quantisation in particular Schrodinger's formulation, starts off heavily on the wrong foot, by assuming an index, label or name to each particle. But this individualisation is immediately wiped out by systematically permuting the labels of all like particles: Any one labelled particle occurs simultaneously in all positions occupied by like particles (Post [1963]).

Although Pauli's principle was rescued by the new quantum theory, the notion of individual quantum numbers for each electron was lost. The concept of electronic configurations cannot be derived from quantum mechanics. It represents an approximation and a book-keeping scheme for finding the number of outer electrons in an atom, but does not necessarily provide information as to the inner electron shells. The limitations of the model are seldom stated. In the words of Post, it represents a 'floating model' which is neither theoretically justifiable nor experimentally verified (Post [1974], Redhead [1980]). In trying to explain the spectra of atoms we are forced to abandon configurations and to consider coupling schemes between the various electrons. Configurations themselves are not directly observable.

In spite of the insecure basis which the orbital model possesses, it has proved fruitful in the field of atomic chemistry and physics. Firstly the use of electronic configurations serve as a basis for the classification of the lines shown by atomic spectra (Condon and Shortley [1935], Slater [1949]).

The first 100 to 400 J levels in all atoms can be classified on the basis of terms arising from assumed electronic configurations for the ground and excited states. These J levels are characterized by the value of the overall angular momentum of the atom. The various J levels arise from the removal of degeneracy from states corresponding to any particular presumed electronic configuration. This process may be thought of as occurring in two stages. First the Coulombic repulsion between electrons produces a number of spectro-scopic terms with differing values for the quantum numbers L and S or orbital and spin angular momentum respectively. Secondly the inclusion of coupling between the orbital and spin angular momenta causes further splitting of lines into levels characterized by the overall angular momentum quantum number or J. These J values alone represent spectroscopic observables, while the L and S quantum numbers for the whole atom as well as the quantum numbers for each of the individual electrons are not observed.

A mark of the success of this theory lies in the fact that no low lying superfluous J levels have been found which defy classification according to a plausible electronic configuration for the atom in question. On the other hand, there are sometimes predicted levels which have not yet been observed as in the case of three of the six terms for the s^1p^3 configuration in carbon (Moore [1949]).

There are some rather impressive cases of the resolution of almost complete configurations in atoms known to have very complex spectra. For example 38 of the predicted 41 J levels have been found in the lowest configuration of $[Xe]$ $4f^3$ (Sugar [1963]), and 101 out of a predicted 107 J levels of the next lowest configuration $[Xe]\,4f^2\,5d^1$ in the Pr^{+2} ion (Trees [1964]). Very recently 33 out of 34 predicted J levels have been detected in the Mn^{+3} ion with a configuration of $3d^4$ (Tchang-Brillet *et al.* [1986]), and 32 out of a predicted 34 J levels in the Ni^{+6} ion having the same electronic configuration (Van het Hof *et al* [1989]).

However, the taxonomic effectiveness of electronic configurations is not a basis for thinking that quantum mechanics can successfully account even for the restricted field of atomic chemistry. Clearly, molecular quantum chemistry is even less secure due to the additional assumptions which must be made apart from the validity of atomic orbitals.

Moreover the conventional theory of atomic spectra itself is forced to admit the element of configurational mixing in order to account for some of the discrepencies encountered between predictions and the observed ordering and spacing of spectral lines. Configurational mixing simply denies the assumption of a single fixed configuration for an atom. This feature has been known since the original development of the theory of atomic spectra through the work of Ufford and Shortley [1932] and Condon [1929], among others.

One contemporary author has described the situation regarding atomic spectroscopy in the following manner:

> Taxonomic classification invariantly have been first (and frequently the only until now) constructive influence of quantum theory on a given area in chemistry, and numerical approximations to wavefunctions have been remarkably unproductive compared with the enormous amount of mathematical quantities handled by modern computers (Jorgensen [1986]).

Overall, the effectiveness of electronic configurations in the classification of spectral lines is surprising as expressed by Jorgensen [1971].

> Nature plays a masquerade and behaves as if electron configurations most frequently are meaningful. They are traxologically valid. We do not know why.

The second main application of the orbital model lies with *ab initio* calculations in chemistry (Szabo and Ostlund [1982]). The basic problem is to calculate the energy of an atom, for example, from first principles, without recourse to any experimental facts. The procedure consists in solving the time independent Schrodinger for the atom in question, but unfortunately only

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hydrogenic systems such as H, He^+ and Li^{+2} which have a single electron posses exact solutions.

In the case of many electron atoms, the Hamiltonian operator includes terms due to inter-electronic repulsions. Nobody has yet discovered any means of solving such equations exactly, and a variety of approximation methods have been devised. In the vast majority of these schemes it is assumed as a zero order approximation, that the atomic wavefunction may be expressed as a product of wavefunctions of independent electrons, or in other words the orbital approximation is used. All efforts are then directed towards accounting for the interaction between electrons which is denied by the zero order theory. The most commonly used Hartree–Fock method consists of an iterative procedure which calculates the average configuration of all the electrons in the atom. The method is described as a self-consistent calculation since the energy of each electron is minimized with respect to every single other electron in the atom (Hartree [1957]). It fails to capture instantaneous changes in configurations, however, and the latter may be modelled by several approaches including configuration interaction (Shavitt [1984]), cluster methods (Sinanoglu [1961]), many body perturbation theory (Wilson [1984]) and several other more recent methods (Wilson [1987]).

Alternative methods are based on the pioneering work of Hylleraas ([1928], [1964]). In these cases orbitals do not form the starting point, not even in zero order. Instead, the troublesome inter-electronic terms appear explicitly in the expression for the atomic wavefunction. However the Hylleraas methods become mathematically very cumbersome as the number of electrons in the atom increases, and they have not been very successfully applied in atoms beyond beryllium, which has only four electrons. Interestingly, one recent survey of *ab initio* calculations on the beryllium atom showed that the Hylleraas method in fact produced the closest agreement with the experimentally determined ground state atomic energy (Froese-Fischer [1977]).

Another problem associated with most orbital based calculations concerns the convergence of the atomic and molecular wavefunction. This is a notoriously difficult problem which has not been solved generally (Klahn and Bingel [1977]). Although it is perfectly legitimate to represent an atomic or molecular wavefunction as an infinite series of terms due to independent electron functions, in practice the series must be truncated in order to carry out a calculation. In many cases the point at which truncation is carried out appears to be arbitrary. Indeed many theoretical chemists pride themselves on the artistry involved in knowing at what point an expansion should be truncated in order to obtain good agreement with experimental data. As some authors have pointed out, a truly *ab initio* calculation should provide an unambiguous and systematic theoretical criterion for truncation, which is independent of comparison with experimental data, as well as an estimate of the expected error for the calculation (Weinhold [1972], Schwartz [1963]).

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Furthermore, the reliance on experimental data to check the validity of calculations presents a certain dilemma, since it is precisely in cases where little or no experimental data are available that calculations would be of the greatest benefit.

4 CONCLUSIONS

I conclude that in many *ab initio* calculations the orbital approximation represents the only practical approach, but its proponents might benefit by moderating their claims to success. As an example of a recent exaggerated claim we find.

> In the future we expect to find an increasing number of situations in which the theory will be the preferred source of information for aspects of complex chemical systems (Wasserman and Schaefer [1986]).

Since in most cases convergence has not been proved, these authors are merely playing the game of the wise gambler who quits while he is still winning. There is no guarantee that a series which seems to be converging, will not start to diverge after a certain point. Convergence must ideally be proved analytically independently of experimental data. Even if the orbital approach could be shown to be entirely successful in these terms it would still be wrong to conclude that atomic chemistry had been reduced by quantum mechanics since the use of orbitals is strictly denied by this theory.

Similarly the apparent success shown by orbital model as a zero order basis for the classification of spectral lines should not be taken to suggest a reduction of the chemical phenomena to quantum mechanics.

The problems which the orbital approximation raises in chemical education have been discussed elsewhere by the author (Scerri [1989], [1991]). Briefly, chemistry textbooks often fail to stress the approximate nature of atomic orbitals and imply that the solution to all difficult chemical problems ultimately lies in quantum mechanics. There has been an increasing tendency for chemical education to be biased towards theories, particularly quantum mechanics. Textbooks show a growing tendency to begin with the establishment of theoretical concepts such as atomic orbitals. Only recently has a reaction begun to take place, with a call for more qualitatively based courses and texts (Zuckermann [1986]). A careful consideration of the orbital model would therefore have consequences for chemical education and would clarify the status of various approximate theories purporting to be based on quantum mechanics.

The claim that even atomic chemistry has been reduced to quantum mechanics would appear to be highly exaggerated according to the arguments we have presented. To those interested in theory reduction in general this conclusion may not be so surprising. It appears to be increasingly acknow-

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ledged that strict theory reduction as envisaged by Nagel [1961] among others is not tenable. Nagel's views have been criticized by many authors, and the overall conclusion seems to be that we may only speak of approximate reduction (Nickles [1973], Sklar [1967], Vollmer [1984]). There are even those who deny that reduction of any form cannot be achieved (Feyerabend [1962], Kuhn [1962]). These views are not shared by the present author and will not be discussed further. The majority of scientists still hold that the special sciences are in some sense reducible to physics. Similarly a number of philosophers are not prepared to abandon the notion of reduction altogether, but try to refine the views of Nagel on the subject. Following our examination of the orbital model, we wish to point out that it represents an even weaker form of reduction than the frequently discussed approximate reductions. For example the reduction of the laws describing ideal gases by classical kinetic theory provides a good example of approximate reduction.

In this model the gas particles are assumed to show no interactions between each other. This model can be realized or at least approached closely in a physical sense, since under conditions of low pressure and high temperatures interaction between particles becomes progressively weaker. Another example consists in the relationship between relativistic and classifical mechanics. The relativistic expression for momentum.

$$p = m_o v / (1 - v^2/c^2)^{\frac{1}{2}}$$

reduces to the classical expression

$$P = m_o v$$

as the velocity tends to zero. Once again this reduction can be achieved physically by reducing the velocity.

However, in the case of the electronic orbital model there is no way in which the inter-electronic repulsions can be physically reduced. This form of distinction has not been sufficiently emphasized by philosophers. I believe that the nature of the orbital model shows that not all theoretical models can be lumped together as in the work of Achinstein [1968].

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The Periodic Table and the Electron

Although electronic configurations are traditionally invoked to explain the periodic system, their explanatory power remains only approximate

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J. J. Thomson's momentous discovery of the electron 100 years ago this year is a story familiar to anyone who has enrolled in an undergraduate chemistry course. His experiments with cathode-ray tubes allowed him to determine the charge-to-mass ratio of the electron—with a mass some 1,000 times less than the smallest particle previously found—and to establish that it was a component of all matter. Thus Thomson earned a place in the annals of physics—and the honor of a centenary. We might also, however, take note of another contribution Thomson made, one that is not so widely known.

Thomson also had a deep interest in chemistry, which motivated him, among other things, to put forward the first explanation in terms of electrons of the periodic table of the elements—that enduring icon adorning the walls of chemistry lecture halls and laboratories throughout the world. Ninety years later, most chemists and physicists continue to believe that the electron holds the key to understanding the periodic table. Yet over the years, numerous versions of such explanations have come and gone, been adapted and adjusted, and generally subjected to subtle manipulation to match experimental evidence. Despite such "evolution," however, I shall argue that the modern explanation as it is generally portrayed remains far from satisfactory.

The Genesis of the Table

To understand how the electron has been applied to explanations of the periodic table we must start with the discovery of the periodic system itself. The Russian chemist Dimitri Mendeleev announced in 1869 that the properties of elements arranged in order of increasing atomic weight appeared to repeat after certain definite intervals. Yet even as this discovery became increasingly well established, Mendeleev remained strongly opposed to any attempt to reduce or explain the periodicity in terms of atomic structure. He resisted the notion of any form of primary matter, which was actively discussed by his contemporaries, and opposed Prout's hypothesis that the atoms of all elements were composites of hydrogen. Further, Mendeleev was particularly fond of emphasizing that smooth curves should not be drawn through the points representing numerical data on the elements, since such curves would imply continuity instead of strict individuality.

Mendeleev's reluctance toward reduction was not widely shared. One of the codiscoverers of the periodic system, the German Lothar Meyer, accepted the possibility of primary matter and supported Prout's hypothesis. He was also happy to draw curves through numerical data, including his famous plot of atomic volumes that showed such remarkable periodicity that it helped in the acceptance of the periodic system. Nonetheless, prior to Thomson's discovery of the electron, no accepted model of atomic substructure existed to explain the periodic system, and the matter was still very much in dispute.

Magnets and Electrons

It took little time, however, for the newly discovered electron to begin featuring in several postulated models of the atom. In 1901 the Frenchman Jean Perrin suggested the first planetary conception of the atom, proposing that each atom consisted of one or more highly charged positive bodies, much like a positive sun, around which small negative planets (electrons) were in orbit. He also thought that the total negative charge in the atom would be exactly equal to the total positive charge. These views are in remarkable anticipation of present views on the structure of the atom.

In 1904 the Japanese physicist Hantaro Nagaoka discussed what he called the Saturnian atom, in which electrons orbited the atom in a series of rings. That same year, J. J. Thomson himself began to think about how the electrons might be arranged in the atom, suggesting that they were embedded in the positive charge of the nucleus. This conception became known as the "plum pudding" model of the atom. He also envisaged the electrons as circulating

Figure 1. Since J. J. Thomson's discovery of the electron in 1897, the particle has been considered fundamental and has been used in various combinations to explain the periodic system of the elements, following a precedent set by Thomson himself. The history of the electron reveals, however, that electron configurations and quantum mechanics can provide only approximate (though useful) explanations of the periodic system. A hundred years after Thomson's work, long-established notions about the electron are coming into question. Recent models of the electron developed in Germany and the U.S. suggest that the particle may have an underlying structure. The model depicted here, in an image developed by physicist Dennis Harp of Purdue University, is based on work by David Koltick and his experimental group at Purdue.

within this positive charge and went on to produce the first set of electronic arrangements—what today would be called electronic configurations. In taking this step Thomson went beyond Perrin and Nagaoka in conceiving of the electrons as not just moving around the atom but doing so in a structured manner.

Thomson based his configurations on the work of an American physicist, Alfred Mayer, who had experimented with magnets attached to corks and floated in a circular basin of water. When five magnets were placed in the water, for example, they formed a single ring. The ad-

dition of a sixth magnet, however, led to the formation of a second ring. Thomson thought that the same principle might operate in the case of electrons and was motivated to develop these views by a desire to explain the periodic table in terms of the particle that he had discovered. Thus, in many respects J. J. Thomson can be regarded as the grandfather of electronic configurations.

In keeping with the arrangements of Mayer's magnets, Thomson's configuration shifted to a second ring at six electrons, waited until 10 electrons to add a first electron to the sec-

Figure 2. Dimitri Mendeleev's discovery of the periodic system in 1869 was quickly followed by controversy over how it should be used. Mendeleev resisted reduction or explanation of the system in terms of atomic structure, and was specifically opposed to attempts to draw curves through points representing numerical data. Lothar Meyer, who contributed to the discovery of the periodic system, was not so averse to reduction, however. One of his graphs, shown here in an 1870 publication, plotted atomic volume and was instrumental in the acceptance of the periodic system.

ond ring, formed a third ring at element 17 (configured with 11 in the outer ring and 5 in the middle), and so on. It is interesting to note that some crucial, or differentiating, electrons are being added to an inner ring. Such an electronic arrangement suggests an analogy between boron (element 5) and sulfur (element 16), both of which have a ring with 5 electrons.
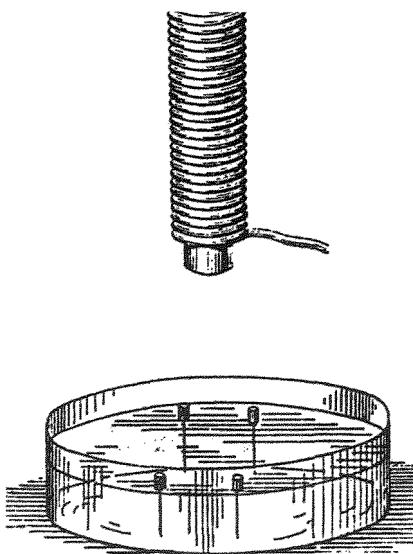
Figure 3. Alfred Mayer's experiments with magnets floating in water (illustrated in one of his publications with this sketch) were the template J. J. Thomson used to develop his first electron configurations (see Figure 4). Mayer found that the magnets adopted different patterns depending on the number introduced, leading Thomson to suspect that similar principles would pertain to electron configurations.

Of course, that is not in fact the case. It would be a mistake, however, to dismiss Thomson's work. He and his contemporaries did not know th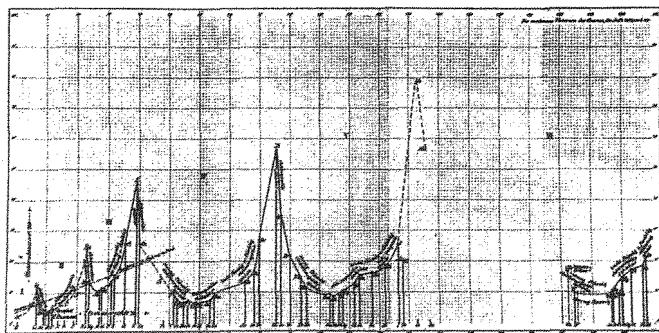e number of electrons in any particular atom. Thomson believed, for example, that an oxygen atom had as many as 56 electrons, whereas the current value stands at just eight. Rather, his scheme should be considered an attempt to explain periodicity according to similarities in electronic structures between different elements.

Counting on Quanta

In the course of investigating the stability of Thomson's electron rings during a postdoctoral fellowship spent at Cambridge and Manchester, the Danish physicist Niels Bohr hit upon the idea that the energy of the orbiting electrons manifested itself in discrete amounts, or *quanta*. This approach allowed Bohr to construct a highly successful theory of the hydrogen atom. It is rather interesting that the popular account of this episode is that Bohr developed his theory in order to explain the spectrum of the hydrogen atom. In fact, however, the historians John Heilbron and Thomas S. Kuhn have shown conclusively that the initial motivation for Bohr's theory was, instead, an attempt to gain an understanding of the periodic table through electronic configurations.

Bohr began by devising electronic configurations in terms of just one quantum number, the principal quantum number that could be used to characterize the stationary or nonradiating states of the atom. It is clear from the configurations he chose that he used essentially chemical considerations. For example, in moving from element 6 (carbon) to element 7 (nitrogen), he suddenly rearranges the inner shell, which in carbon had two electrons, to four electrons in order to have the outer shell of nitrogen contain three electrons—a nod to the well-known trivalency of nitrogen, that is, its tendency to form three bonds. Bohr clearly tinkered with his configurations to make things come out right and gave no theoretical arguments for such a rearrangement. Instead of rigorous derivation from quantum theory, his approach consisted of a mix of intuition with spectroscopic and chemical considerations.

What Bohr accomplished in this work was to introduce the important idea that the differentiating electron should, in most cases, occupy the outer shell of the atom. Also, however arbitrary this scheme may have been, there was at least some correlation between electronic configurations and chemical periodicity. The configuration of lithium, for example, is 2,1, whereas that of sodium, which lies in the same group chemically, is 8,2,1. Similarly, beryllium and magnesium, which are found together in group two of the periodic table, share the same property of having two outer-

shell electrons. Here then emerged the now well-known concept that atoms fall into the same group of the periodic table if they possess the same number of outer-shell electrons.

Soon after Bohr developed his initial configuration, Arnold Sommerfeld in Munich realized the need to characterize the stationary states of the electron in the hydrogen atom by means of a second quantum number—the so-called angular-momentum quantum number. Bohr immediately applied this discovery to many-electron atoms and in 1922 produced a set of more detailed electronic configurations. In turn, Sommerfeld went on to discover the third, or inner, quantum number, thus enabling the British physicist Edmund Stoner to come up with an even more refined set of electronic configurations in 1924.

Bohr himself had been aware of the discovery of the third quantum number, but by that time he had begun to be concerned about the use of quantum numbers in many-electron atoms. It had become clear that such numbers could not be rigorously defined, and a problem called "retention of quantum numbers" began to exert an increasing influence on Bohr. According to Ehrenfest's adiabatic principle, calculations of quantum states of one system could be made from another one provided they could be connected by an adiabatic—a gradual transformation whereby a system's energy, but not its state, changes. Such procedures, however, can only be strictly applied to simply or multiply periodic systems. Many-electron atoms are aperiodic systems and thus remain beyond this procedure.

This problem clearly did not worry Stoner, who just went ahead and assumed that three quantum numbers could be specified in many-electron atoms. In any case, Stoner's scheme solved certain problems present in Bohr's configurations. For example, Bohr had assigned phosphorus the configuration 2,4,4,4,1, but this failed to explain the fact that phosphorus shows valencies of three and five. Stoner's configuration for phosphorus was 2,2,2,4,2,2,1, which easily explains the valencies, since it becomes plausible that either the two or the three outermost subshells of electrons form bonds.

Bohr continued to be concerned about the deeper theoretical aspects of the problem and appealed to his young colleague, Wolfgang Pauli, to try to clarify the situation within the principles of quantum theory. Pauli began by introducing a fourth quantum number to characterize the stationary state of each electron and produced his celebrated *exclusion principle*. Unlike the previously introduced quantum numbers, this one could take values of only +1/2 or –1/2. The biggest advantage of this new approach was that it became possible to explain the closing of the electron shells in the periodic table—that is, it ex-

segment of J. J. Thomson's electron rings	
number of electrons	rings
5	5
6	1+5
7	1+6
8	1+7
9	1+8
10	2+8
...	...
16	5+11
17	1+5+11
18	1+6+11
19	1+7+11
20	1+7+12
21	1+8+12

Figure 4. Thomson's system of rings of electrons embedded in the positive charge of the nucleus developed a second, inner ring when six electrons were present and a third ring, inside the second, at 17 electrons. Unfortunately, this arrangement suggests an analogy between boron (element 5) and sulfur (element 16), which is not the case. Thomson and his colleagues were impeded by a lack of knowledge of the number of electrons in various atoms.

plained why each successive shell can occupy 2, 8, 18 ... $2n^2$ electrons, where n denotes the shell number.

When the first quantum number takes the value one, the second quantum number can only be zero and likewise the third quantum number. Now according to Pauli's exclusion principle it is forbidden for more than one electron in a shell, therefore having the same n value, to have the same values for the remaining three quantum numbers. This gives the prediction that a maximum of two electrons occupy the first shell and that these share the same first three quantum numbers but differ in the value of the fourth, adopting one of two values. For the $n = 2$ shell the situation is more complicated, since there are two possible values for the second quantum number, namely one and zero (as shown in *Figure 6*). When the second quan-

segment of Bohr's electron configurations				
atomic number	element	rings		
5	B	2,	3	
6	C	2,	4	
7	N	4,	3	
8	O	4,	2,	2

Figure 5. Niels Bohr came up with the idea that the energy of orbiting electrons would be in discrete amounts, or *quanta*. This enabled him to successfully describe the hydrogen atom, with its single electron. In developing the remainder of his first table of electron configurations, however, Bohr clearly relied on chemical properties, rather than quantum theory, to assign electrons to shells. In this segment of his configuration table, one can see that Bohr adjusted the number of electrons in nitrogen's inner shell in order to make the outer shell, or the reactive shell, reflect the element's known trivalency.

segment of Pauli's electron configurations					
n	l	m_l	m_s	number of electrons	running total
1	0	0	+1/2		
			-1/2	2	2
2	0	0	+1/2		
			-1/2	2	
2	1	-1	+1/2		
			-1/2	2	
2	1	0	+1/2		
			-1/2	2	8
2	1	1	+1/2		
			-1/2	2	
3	0	0	+1/2		
			-1/2	2	

Figure 6. Wolfgang Pauli's discovery of the *exclusion principle* led to his development of a fourth quantum number to describe the electron. At the time, it was known that each successive electron shell in an atom could contain 2, 8, 18 ... $2n^2$ electrons (where n is the shell number), and Pauli's fourth number made it possible to explain this. When an electron's first quantum number is one, the second and third must be zero, leaving two possibilities for the fourth number. Thus the first shell can contain only two electrons. At $n = 2$, there are four possible combinations of the second and third numbers, each of which has two possible fourth numbers. Thus the second shell closes when it contains eight electrons.

tum number is zero, the third quantum number also adopts a zero value, and since the fourth quantum number can be one of two values, two electrons are accounted for. When the second quantum number in the second shell takes the value of one, however, the third quantum number may be –1, 0 or +1, each of which can show two values for the fourth quantum number, accounting for a further six electrons. Similar considerations for the third and fourth shells predict 18 and 32 electrons respectively. Thus Pauli's fourth quantum number, along with his exclusion principle, allowed the various shells to be closed while retaining the rules for assigning the previously established quantum numbers.

Figure 7. In the conventional medium-long form of the periodic table, the elements are shown with the *d*-block *(pink)* between the *s*-block *(blue)* and the *p*-block *(lavender)*, to reflect the order of subshell filling shown in figure 10 and contrary to the order expected from figure 6.

The popularly used, medium-long form of the periodic table *(see Figure 7)* does not display the regular and symmetrical increase in the size of the periods to quite the extent that it could. This is because the elements in groups I and II (*s*-block) of the table are conventionally depicted on the left of the table, which is then interrupted by a block consisting of the transition elements (*d*-block) and followed by the elements in the *p*-block. (The names for each of the blocks are derived from the labels for the orbitals occupied by the differentiating electrons, s, p, d, and f). From time to time, alternative representations of the periodic system have been proposed in an attempt to emphasize its underlying symmetry, including a three-dimensional design by Fernando Dufour *(see Figure 9)* and two-dimensional versions independently proposed by Thomas Bayley, Jørgen Thomsen and Bohr. Unfortunately, these tables have not been widely adopted.

Quantum Numbers in Question
To return to the historical sequence, although Pauli had upheld the use of quantum numbers in specifying stationary states of the atom, he began to share Bohr's worries and soon became the leading advocate against the use of mechanical models—in particular, electron orbits and electronic configurations—of atoms. He claimed that thinking in terms of electron orbits amounted to putting atoms in the "shackles of our prejudices," and that people who needed the "crutch of the conception of uniquely defined electron orbits and mechanical models [were] weak." He thought that atomic theories should be based not on visualizable models but rather on observable quantities. Although Pauli regarded his treatment of electron orbits using four quantum numbers as a temporary stage in
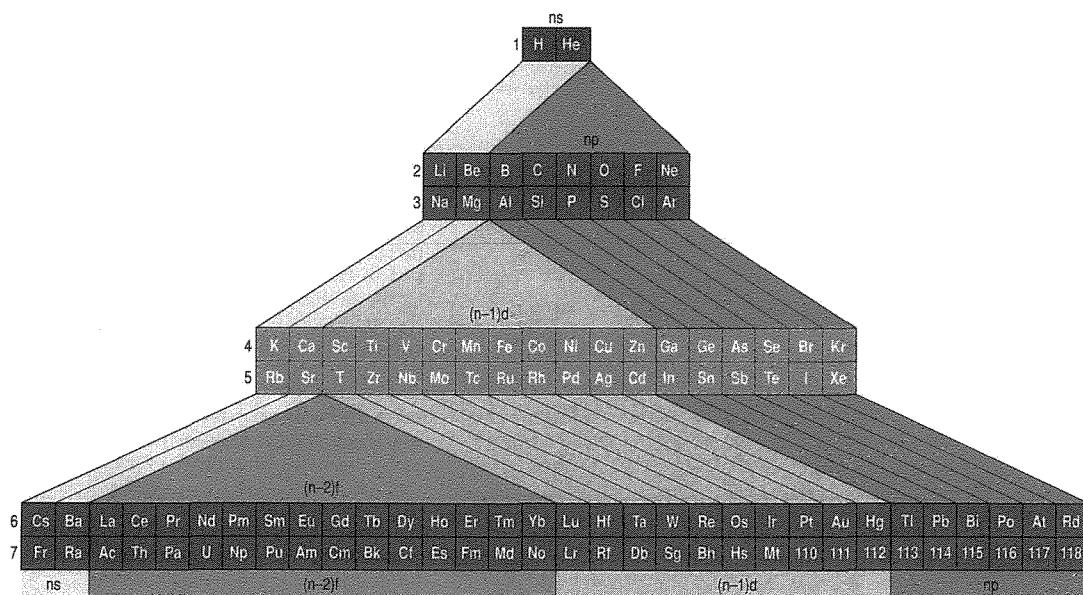
Figure 8. Alternative and updated periodic table, adapted from tables developed by Thomas Bayley, Jørgen Thomsen and Niels Bohr. These tables all depict the symmetrical nature of the periodic law regarding the increase in intervals before periodicity occurs in every other period with the exception of the first one. Tie lines denote chemical analogies.

the evolution of physics, the success of his discovery in apparently explaining the structure of the periodic table unwittingly legitimized and carried forward its use.

Very soon thereafter Werner Heisenberg did what Pauli had been advocating and developed a form of mechanics that had nothing to do with electron orbits and was concerned only with what could be observed. At approximately the same time Erwin Schrödinger developed his wave-mechanical version of quantum mechanics. For a while it seemed as though there were two different theories of quantum mechanics, until they were shown to be mathematically equivalent. According to the new quantum mechanics, the very notion of individual electrons in stationary states was shown to be invalid, as Pauli had earlier speculated. The quantum mechanics of Heisenberg and Schrödinger shows that orbitals simply do not exist. There is a clear-cut mathematical proof of this; it is not just a question of interpretation.

This is a crucial and frequently overlooked point about electronic configurations. They are far from being based in quantum mechanics; it is precisely this theory that shows them to be an inadequate concept. The notion that electron orbits and configurations really exist or "refer" is a relic of the old quantum theory and of Pauli's introduction of the exclusion principle in its original and now strictly incorrect

form. In quantum mechanics the principle is restated: The wavefunction for a system of fermions such as electrons is antisymmetrical on the interchange of any two particles.

Of course, nowadays, as every student of chemistry and physics knows, electron orbits have been replaced by orbitals that are supposed to be smeared out in space. But this view misses the point somewhat and is not the whole lesson from quantum mechanics. The more radical lesson is that even these probability-based orbitals simply do not exist. The notion of assigning four quantum numbers to each electron is just an approximation, albeit a powerful one.

The Periodic Table Explained?

So what are we to make of the claim that the periodic table has now been explained in terms of electronic configurations and the number of outer-shell electrons possessed by atoms of the elements? Perhaps the best way to answer this question is to admit that the explanation is approximate and that a number of objections can be raised to it.

For example, whichever form of the table is used, an interesting feature emerges: The sequence 2, 10, 18, 36, 54, 86 of atomic numbers, in which each period is closed in the sense of reaching a noble-gas structure, does not appear to have a strictly quantum-mechanical explanation. Although Pauli's brilliant discovery

Figure 9. Fernando Dufour's symmetrical and three-dimensional periodic table. (Photograph courtesy of the author.)

succeeded in explaining the total number of electrons that are required for the closing of each shell, his principle does not explain the point at which each period is closed unless the observed order of shell filling is assumed. Even

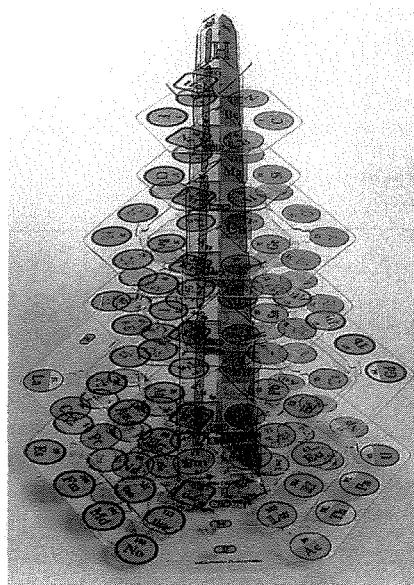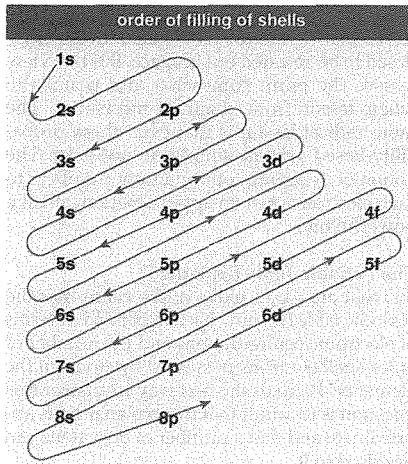Figure 10. Electron shell closure fails to coincide with the closing of periods in the periodic table because the shells do not fill in strictly sequential order. As shown here, the fourth shell begins to fill before the third shell has been completed. The resumption of third-shell filling accounts for the appearance of the first transition-metal series, beginning with scandium and ending with zinc.

more remarkable, as the leading theoretical chemist Per-Olav Löwdin has pointed out, the sequence of atomic numbers denoting the closing of the periods has never been derived from the principles of quantum mechanics.

The reason why the closing of the shells does not coincide with the closing of the periods is that the shells are not filled in strictly sequential order. For example, the fourth shell begins to fill at the element potassium, even though the third shell has not yet been completed. The resumption of third-shell filling after the 4s subshell has been filled accounts for the appearance of the first transition-metal series beginning with scandium and ending with zinc. Even more perversely, the order in which shells are filled, contrary to the accounts in many textbooks of chemistry and physics, does not reflect the order of increasing energy of atomic orbitals. As a result of such features, electronic configurations must be assigned by reference to spectroscopic evidence on each of the elements and not by relying entirely on the putative explanation of the periodic system in terms of quantum-mechanical theory.

But matters get worse. Even the experimentally obtained filling scheme shown in Figure 10 does not lead to the observed electronic configurations of all the elements. In fact there are about 20 genuine exceptions to this procedure, starting with chromium. According to the standard filling order, chromium should adopt the configuration [Ar] $4s^2 3d^4$, where the notation [Ar] is shorthand for the argon core, the labels 4s and 3d refer to particular orbitals, and the superscripts denote how many electrons each orbital contains. Instead, however, chromium adopts the configuration [Ar] $4s^1 3d^5$. Also, the simple electron filling order fails to indicate that the three final electrons to enter an atom such as nitrogen do so in such a way as to occupy three separate atomic orbitals. This too is an experimental finding embodied in *Hund's rule*, which states that when multiple electrons occupy a set of orbitals having equal energies, they occupy as many different orbitals as possible. Seen in light of the need for these somewhat *ad hoc* maneuvers, the purely quantum-mechanical explanation for the periodic table in terms of electrons seems illusory.

In order to appreciate another problem with electronic configurations, suppose we consider the element scandium, which has atomic number 21. This atom could conceivably have one of the following configurations: Sc [Ar] $4s^2 3d^1$, Sc [Ar] $4s^1 3d^2$ or Sc [Ar] $4s^0 3d^3$. Can the experimentally observed first configuration be predicted from first principles by quantum-mechanics? No. In fact, all that quantum mechanical calculations can do is compute which of these three configurations has the minimum energy. That is not the same as deriving the correct configuration from first principles.

The basic idea underlying the view that the periodic table has been reduced to electronic configurations is that elements sharing the same number of outer-shell electrons are in the same group of the periodic table. But this is simply not the case, since the possession of a particular configuration is neither a necessary nor a sufficient condition for elements to fall within the same group of the periodic system. If it were a necessary condition, elements falling into the same group would be bound to possess the same outer-shell configuration. But counterexamples are easily found, including nickel (Ni, $4s^2$), palladium (Pd, $5s^0$) and platinum (Pt, $6s^1$). Each shows a different outer-shell configuration, yet they are grouped together because of their marked chemical similarities. If it were the case that possession of a particular configuration is a sufficient condition for membership to a particular group, possession of a certain configuration would ensure that the atoms of those elements would fall into a particular group. Yet the elements helium, beryllium and magnesium—all of which share the property of having two outer-shell electrons—do not fall within the same group. Helium is a highly inert gas invariably placed at the head of the noble gases, whereas beryllium and magnesium are reactive metals belonging in group II of the periodic table.

Pragmatic Approximation

Although the preceding paragraphs have raised doubts about the traditional explanation for the periodic system in terms of numbers of outer-shell electrons, there is an important sense in which the quantum-mechanical theory of electron motion can provide a much better, though still approximate, explanation. This alternative explanation does not lend itself to visualizable models involving electrons in shells. Instead, it is the notion that the properties of atoms that show periodicity—such as the total energy of any atom—can be calculated from the Schrödinger equation to a high degree of accuracy for any particular atom. These calculations typically involve a description of the atom in terms of sums of contributions from numerous, literally billions of, electronic configurations. Yet the atom itself cannot be said to possess any of the particular configurations that are used as aids to calculation. The configurations that contribute to the atom's energy are not thought to be "real," but merely function as useful instruments in carrying out the calculations. This approach has the character of what philosophers of science call *instrumentalism* or *antirealism*.

Taking a telescopic view of all these developments, we see an interesting turnabout regarding the periodic table. Over 125 years ago Mendeleev, probably the leading discoverer of the periodic system, refused to adopt a realis-

tic view of the system and emphasized only its classifying aspects. Exactly 100 years ago, the electron, the first subatomic component, was discovered and pointed the way for a swing back toward a realistic account of atomic physics. In due course, this led to the equally realistic electron-shell approach to the periodic system. About 30 years later, the reality of electron shells and orbitals had evaporated into the formalism of quantum mechanics, leaving behind just the mathematical utility of superimposed expressions of electronic configurations. Thus, although the reality and utility of electrons are now taken for granted, electron orbitals have been discovered not to exist and their explanatory power proves to be only approximate.

Other aspects of the traditional view of the electron continue to come into question. Experiments carried out in Germany this year suggest that the electron may not be fundamental after all. Instead, it may possess a substructure consisting of lepto quarks. One cannot help but speculate whether there may come a point when the electron itself, which has been the cause of so many celebrations this year, might also turn out to be not so real.

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Commentary ——

How Good Is the Quantum Mechanical Explanation
of the Periodic System?

by Eric R. Scerri

The use of quantum mechanics, or more specifically, orbitals and electronic configurations in teaching general chemistry is now such a widespread trend that it would be utterly futile to try to reverse it. Moreover, orbitals and configurations have been extremely useful in providing a theoretical framework for the unification of a multitude of chemical facts.

However, in the course of this brief commentary, I would like to issue a caution regarding the extent to which the periodic table, for example, is truly explained by quantum mechanics so that chemical educators might refrain from overstating the success of this approach. I would also like to raise an issue which, to the best of my knowledge, has only recently been explicitly pointed out in the literature (*1*).

Pauli's explanation for the closing of electron shells is rightly regarded as the high point in the old quantum theory. Many chemistry textbooks take Pauli's introduction of the fourth quantum number, later associated with spin angular momentum, as the foundation of the modern periodic table. Combining this two-valued quantum number with the earlier three quantum numbers and the numerical relationships between them allow one to infer that successive electron shells should contain 2, 8, 18, or $2n^2$ electrons in general, where n denotes the shell number. This explanation may rightly be regarded as being deductive in the sense that it flows directly from the old quantum theory's view of quantum numbers, Pauli's additional postulate of a fourth quantum number, and the fact that no two electrons may share the same four quantum numbers (Pauli's exclusion principle).

However, Pauli's Nobel Prize-winning work did not provide a solution to the question which I shall call the "closing of the periods"—that is why the periods end, in the sense of achieving a full-shell configuration, at atomic numbers 2, 10, 18, 36, 54, and so forth. This is a separate question from the closing of the shells. For example, if the shells were to fill sequentially, Pauli's scheme would predict that the second period should end with element number 28 or nickel, which of course it does not. Now, this feature is important in chemical education since it implies that quantum mechanics cannot strictly predict where chemical properties recur in the periodic table. It would seem that quantum mechanics does not fully explain the single most important aspect of the periodic table as far as general chemistry is concerned.

The discrepancy between the two sequences of numbers representing the closing of shells and the closing of periods occurs, as is well known, due to the fact that the shells are not sequentially filled. Instead, the sequence of filling follows the so-called Madelung rule, whereby the lowest sum of the first two quantum numbers, n + 1, is preferentially occupied. As the eminent quantum chemist Löwdin (among others) has pointed out, this filling order has never been derived from quantum mechanics (*2*).

Pauli's contribution can only be said to explain the closing of the periods if the correct order of filling is assumed, as indeed it was, in the early electronic versions of the periodic table compiled by Bohr and others. But this order of filling was obtained by reference to experimental facts, especially the spectroscopic characteristics of each of the elements (*3*).

To make matters worse, the Madelung rule shows as many as twenty exceptions, starting with the elements chromium and copper where, although the order of orbital filling is adhered to, the implicit notion that a subshell should be completely filled before proceeding to the next one is violated. As is well known, chromium and copper have electronic configurations involving $4s^1$ configurations rather than the expected $4s^2$. Once again, the "correct" configuration is arrived at not from theory but by reference to the experimental facts. In some of these, the anomalous configuration can be rationalized, again after the facts, by appeal to relativistic effects (*4*), but there is no general explanation for why anomalous configurations occur in the places they do. Yet another blemish in the theoretical aufbau scheme consists of the configurations of elements such as nitrogen and phosphorus where Hund's first rule must be invoked in order to obtain the experimentally correct configurations involving three unpaired p electrons. While acknowledging the work carried out to rationalize Hund's rules in terms of quantum mechanical principles (*5*), this is not the same as strictly deducing the rules from these principles.

Of course, most of what I have said so far is well known. Nevertheless, I hope to have given these issues a new perspective by adopting an almost perversely rigorous approach in demanding that every aspect of electronic configurations should be strictly deducible from quantum mechanics. Although I am not in a position to propose a better explanation, I do not think that we should be complacent about what the present explanation achieves. As I have tried to argue, in terms of deduction from theoretical principles, the present semi-empirical explanation is not fully adequate.

Finally, given that quantum mechanics is here to stay, I would also like to make a plea for presenting chemistry from relativistic quantum mechanics rather than the usually invoked non-relativistic version. Over the past twenty or so years, an increasing number of fairly commonplace chemical phenomena have been explained (admittedly, also after the facts) by detailed calculations that take account of relativistic effects (*6–10*) due to fast-moving, usually inner, electrons. These phenomena include the color of gold (*8*), the saw-toothed patterns seen in the properties of elements in some groups of the periodic table (*6*), the inert-pair effect such as in group IV (*8*), the liquid nature of mercury (*8*), and the anomalous electronic configurations of some elements of the sixth row of the periodic table (*7*).

If we are to take a reductionist approach, then let it be one that is consistent with both of the fundamental theories of physics, the science that chemistry approximately reduces to (11).

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Prediction and the Periodic Table

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The debate about the relative epistemic weights carried in favour of a theory by predictions of new phenomena as opposed to accommodations of already known phenomena has a long history. We readdress the issue through a detailed re-examination of a particular historical case that has often been discussed in connection with it—that of Mendeleev and the prediction by his periodic law of the three 'new' elements, gallium, scandium and germanium. We find little support for the standard story that these predictive successes were outstandingly important in the success of Mendeleev's scheme. Accommodations played an equal role—notably that of argon, the first of the 'noble gases' to be discovered; and the methodological situation in this chemical example turns out to be in interesting ways different from that in other cases—invariably from physics—that have been discussed in this connection. The historical episode when accurately analysed provides support for a different account of the relative weight of prediction and accommodation—one that is further articulated here. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Mendeleev; Prediction; Periodic Table; Weight of Evidence.

1. Introduction

A scientific theory T (in conjunction with accepted auxiliary assumptions) deductively entails some empirical sentence e; e is, moreover, true (or, rather, accepted as true on the basis of experiment or observation). Does the extent to which this success lends confirmation or support to T depend on whether e describes some state of affairs that was unknown at the time of T's articulation or instead on whether it describes some already well known state of affairs? The methodological issue of whether, roughly speaking, successful prediction 'counts more' for a theory than successful accommodation formed a celebrated part of the debate between William Whewell and John Stuart Mill. The latter, while allowing that successful predictions were 'well calculated' to impress the 'ignorant vulgar', expressed utter

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amazement that 'persons of scientific attainments' (such as Whewell) should
believe that such predictions carry extra evidential weight. The issue has sub-
sequently been raised time and again in the philosophy of science literature and
remains live and controversial. Not only is there disagreement over whether predic-
tions 'count more', there is great disagreement (on both sides) over why they do
(or do not).[1]

The direct focus of the present paper, however, is not this general issue, but
rather a famous particular case from the history of science that has become embro-
iled in it. The episode involves Mendeleev and the 'prediction' of the existence of
hitherto unknown elements on the basis of his celebrated periodic table. According
to an account that has widespread currency, Mendeleev's table was given little or
no general credit by his contemporary scientists in virtue of its 'accommodation'
of the already known elements. What really told with Mendeleev's peers, according
to this account, was the fact that 'gaps' in the table were used as the basis of
predictions of the existence of hitherto unrecognised elements, that turned out really
to exist. So, for example, Isaac Asimov writes:

> ... in the January 7, 1871, issue of the *Journal of the Russian Chemical Society*,
> [Mendeleev] advanced the crucial notion for which he truly deserves all the credit
> he gets for the discovery of the periodic table, to the exclusion of his contemporaries
> and predecessors who also contributed to it. He left gaps in the table in order to make
> the elements fit into proper columns, and announced that the gaps represented
> elements not yet discovered ... This prediction ... was met with considerable scepti-
> cism ... However, in 1875 Lecoq de Boisbaudran ... discovered an element which
> matched, to the last property, Mendeleev's prediction for one of the gaps. In 1879,
> Nilson and Cleve produced another ... and in 1885 Winkler produced still another
> ... Mendeleev and his periodic table were vindicated in the most dramatic manner
> possible ... Mendeleev was suddenly the most famous chemist in the world. (Asimov,
> 1975, p. 410)

This popular account has been endorsed in the recent philosophical literature by
Patrick Maher, and, following him, Peter Lipton. Maher writes:

> By the middle of the nineteenth century more than 60 elements were known with
> new ones continuing to be discovered. For each of these elements, chemists attempted
> to determine its atomic weight, density, specific heat, and other properties. The result
> was a collection of facts, which lacked rational order. Mendeleev noticed that if the
> elements were arranged by their atomic weights, then valencies and other properties
> tended to recur periodically. However, there were gaps in the pattern and in a paper
> of 1871 Mendeleev asserted that these corresponded to elements that existed but had
> not yet been discovered. He named three of these elements eka-aluminium, eka-boron
> and eka-silicon and gave detailed descriptions of their properties. The reaction of the
> scientific world was sceptical. But then in 1874 Lecoq de Boisbaudran found an

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[1]Mill's remark is from Mill (1843). For the more recent controversy see, for example, Campbell and
Vinci (1983), Howson (1984), Giere (1984), Redhead (1986) and Mayo (1996). Bayesians in particular
have been divided on the issue—the debate within the Bayesian camp revolving round the so-called
'Problem of Old Evidence' (see Earman and Glymour, 1980).

element which corresponded to Mendeleev's description of eka-aluminium which he called gallium. This was regarded as a remarkable event; it was the first time in history that a person had correctly foreseen the existence and properties of an undiscovered element. Confidence that Mendeleev's other predictions would be confirmed increased markedly. Four years later, Nilsson discovered an element which corresponded to Mendeleev's description of eka-boron, and which he named scandium. Now chemists were expecting to find Mendeleev's third element, though the Royal Society did not wait for that discovery, awarding Mendeleev its Davy Medal in 1882. Mendeleev's eka-silicon was discovered by Winkler in 1886 and named germanium (Maher, 1988, p. 274).

And Maher goes on explicitly to underline the conclusions about confirmatory weight that he sees as illustrated by this episode. He claims that Mendeleev's prediction of the existence of the third of the new elements, eka-silicon (aka germanium), was initially regarded as quite unlikely to be true; but then later, with the discovery of the first two new elements (gallium and scandium), confidence in the prediction of the existence of the third new element became so high that its eventual empirical confirmation was widely regarded as a matter of course. Maher writes:

> If scientists accord no special confirmatory value to predictions, then it is quite inexplicable why their confidence in Mendeleev's predictions should have increased substantially after one or two of these predictions had been verified. There were 62 elements in Mendeleev's periodic table of 1871, so we could say that Mendeleev's prediction of [germanium] was initially made on the basis of evidence concerning 62 elements. After the discovery of gallium, the prediction concerning [germanium] was now backed by evidence concerning 63 elements and after the discovery of scandium, it was backed by evidence concerning 64 elements. But the difference between these bodies of evidence is much too small by itself to account for the dramatically altered attitude to Mendeleev's prediction of [germanium]. The only plausible explanation is that scientists were impressed by the fact that these latter pieces of evidence [the 63rd and 64th] were verified predictions rather than accommodated evidence. (Maher, 1988, p. 275)

In similar vein, and citing Maher, Peter Lipton asserts:

> Successful theories typically both accommodate and predict. Most people, however, are more impressed by predictions than by accommodations. When Mendeleev produced a theory of the periodic table that accounted for all sixty [really sixty-two] known elements, the scientific community was only mildly impressed. When he went on to use his theory to predict the existence of two unknown elements that were then independently detected, the Royal Society awarded him its Davy Medal ... Sixty accommodations paled next to two predictions. (Lipton, 1991, p. 134)

This particular passage from Lipton is ambiguous. It might simply be making the descriptive claim that, *rightly or wrongly*, 'most people' are, as a matter of psychological fact, more impressed by predictions. But Lipton goes on to endorse a version of the *normative* pro-predictivist thesis, in other words, to assert that what

was allegedly most people's reaction was in fact the methodologically correct one.[2] Maher too uses the episode as support for his preferred version of predictivism—claiming that the episode shows that sometimes *temporal* novelty (the mere fact that the evidence was unknown at the time the theory predicted it) is of special methodological significance.

However, any philosophical conclusions from this case must be based on a fuller and more accurate understanding of the history than anything cited by Maher or Lipton. We seek to supply this here. We argue that there are features of the history which, to say the least, do not sit well with the Maher–Lipton view. Of course, no one could sensibly deny that the successful prediction of the new elements played *an* important role in the reception of Mendeleev's work; nor can it be denied, perhaps, that successful (temporal) predictions have a special psychological effect and that their impact can easily be felt by a wider audience than just specialists in the field.[3] We shall argue however that the real evidential situation, so far as the experts were concerned, was altogether more cumulative and multi-faceted. There is no real sign of a 'dramatically altered attitude' towards Mendeleev's table and its underpinnings between, say, 1871 and 1874; there seems instead to have been a gradual process of diffusion and 'acceptance' (though this term too hides important complexities)—a process in which certain 'corrections' of previously accepted 'data' (about atomic weights of known elements) and certain 'accommodations' of already known evidence played equally significant roles alongside the predictive successes. Moreover there are, we shall argue, special features of this case that make it materially different from others—such as the general theory of relativity and the star-shift observations,[4] or Fresnel's wave theory and the 'white spot'[5]—that have previously been analysed in the attempt to shed light on the general issue of prediction and theory-confirmation.

Some of the material we shall use in arguing against the Maher–Lipton claim

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[2]Lipton does not connect his specific remarks about the Mendeleev case in any detailed way with his general normative account about prediction and accommodation (Lipton, 1991). This general account seems to us a mixture of insight and error. Despite the impression given in his remarks about Mendeleev, his considered view seems to be that the important difference is not in fact that between prediction and accommodation *per se* but that between prediction and 'fudged' accommodation. Although it is not clear exactly what he has in mind by 'fudging', it may well be that much of his view is in the end broadly consistent with our own general view as explained *below* in Section 2.5. But then, in order to link this general view with the particular example of Mendeleev, it is not enough to remark that Mendeleev 'accommodated' the known elements; Lipton needs to consider whether or not this was a case of 'fudged' accommodation. This is precisely the issue that we shall treat—based, of course, on our own preferred version of the general account. (One source of divergence is that Lipton, in our view, confuses matters by bringing *suspicions* into the account: scientists cannot suspect predictive successes of having been produced by 'fudging', but accommodations *may* have been fudged; hence predictions are *prima facie* more telling than *any* accommodation, fudged or not. But suspicions can, surely, play no role in objective accounts of evidential support; and nor, we suggest, would they play any role in the thoughts at least of expert scientists, who would be able to resolve any suspicion one way or the other by recognising whether or not the accommodations were indeed 'fudged'.)

[3]See particularly the quote from Ne'eman in note 18, below.

[4]See, for example, Earman and Glymour (1980).

[5]See, for example, Worrall (1989).

has also been analysed in a recent paper by Stephen Brush (1996). Brush gives an altogether more detailed and scholarly treatment, but arrives at a view that, while much more measured, is none the less similarly pro-predictivist. Indeed he states that this Mendeleev episode is:

> the first case [he has] found in which scientists give substantial weight to evidence predicted in advance rather than treating such evidence as being no more important than similar evidence already known and deduced from or accommodated by the new theory. (Brush, 1996, p. 596)

As this indicates, Brush's view of *other* historical cases (see for example Brush, 1989) has been that, whatever philosophers of science may claim about the relative merits of prediction and accommodation, there is no historical evidence that the scientists concerned in these cases gave any special weight to predictive success. But he feels forced by the evidence in the case of Mendeleev to conclude that there—perhaps uniquely—special weight was indeed given to predictions. We will argue that the historical evidence that Brush himself alludes to in fact, on careful analysis, fails to support this conclusion.

We begin with some detailed worries about Lipton's and Maher's accounts and a brief account of our basic methodological thesis about the value of prediction (Section 2). Next (in Section 3) comes our detailed analysis of Brush's treatment of the episode. Then we draw attention to a difference between the Mendeleev case and others that have been analysed from the point of view of the relative weight of prediction and accommodation that has not previously been highlighted and yet which is of fundamental significance (Section 4). These all form necessary preliminaries for our own positive account (in Section 5) of this historical episode and the relative weights accorded to various predictions and various accommodations in it. We argue in particular that certain 'accommodations' within Mendeleev's table were at least as significant as any predictive success—notably the accommodation of argon, the first of the 'noble gases' to be identified.

2. Some Preliminary Clarifications and Counterarguments

2.1. Publication and Prediction

Any claim of the kind endorsed by Maher and Lipton (and, as we already pointed out, the claim has, in one form or another, widespread currency) seems implicitly committed to the existence of two stages in the reception of Mendeleev's ideas. At stage one the scientific community was, as Peter Lipton puts it, 'only mildly impressed', whereas at stage two there was a 'dramatic alteration' (Maher) and Mendeleev became a bemedalled scientific star. According to Lipton, the first stage occurred when Mendeleev produced 'a theory of the periodic table that accounted for all [sixty-two] known elements'. One interpretation of this (though we do not suggest that this is what Lipton really meant) would be that, at stage one, Mendeleev's 'theory' made (or was perceived as making) no predictions, while stage two

then consisted of the recognition that the theory (or some further development of it) did indeed make predictions—ones that proved successful on experimental test.

But this characterisation is difficult to reconcile with the historical record. Ihde, the only historian of chemistry quoted by either Maher or Lipton, identifies Mendeleev's famous paper of 1871 as the major turning-point:

> Mendeleev's real insight was revealed in his 1871 paper in connection with vacant spaces in the periodic table. He gave the provisional names eka-aluminium, eka-boron and eka-silicon [to the elements he expected to fill these gaps]. (Ihde, 1964, p. 283)

Assuming, then, that 1871 marks stage two, where, in the historical record, lies stage one? It is true that Mendeleev published an account of the periodic table before the one contained in his 1871 paper—in fact in 1869. However, if the claim were that his 1869 paper attracted scarcely any attention at the time because it contained no predictions of hitherto unknown elements, whereas the tide began to turn with the 1871 paper which did predict 'new' elements, then the claim is unsustainable. Mendeleev's first paper of 1869 is just as celebrated as the 1871 piece (and seems to have attracted no less attention at the time). Moreover, the 1869 paper already contained predictions of the unknown elements. Mendeleev there concluded, 'We must expect many yet unknown elements e.g. elements analogous to aluminium and silicon with atomic weights 65–75' (Mendeleev, 1958, p. 31). The periodic tables published in that 1869 paper contain entries for unknown elements in the form of '?=68' and '?=70' in the rows containing Al and Si respectively. (The atomic weights of these new elements turned out to be gallium=69.2 and germanium=72 respectively.) Moreover, Mendeleev's 'attempt at a system' of 1869 contains an entry '?=45'. This turned out to correspond to scandium with an atomic weight of 44.6.

Not only did Mendeleev predict the atomic weights of the famous three new elements already in 1869, he also made predictions of some of their other properties. In a talk to a Moscow Congress in that same year he suggested that two elements missing from the system, which show resemblances to aluminium and silicon, would have atomic volumes of 10 or 15 and specific gravities of about 6 (Mendeleev, 1959, p. 42). In the following year, 1870, he listed the expected atomic volumes of the elements that would become known as scandium, gallium and germanium as 15, 11.5 and 13 respectively.[6]

Nor, finally, can it plausibly be argued that what distinguishes the 1871 paper was that there were no details about the predictions in 1869 and these details were published only in 1871. Certainly there are *more* details about some predicted elements in the 1871 paper—as one would expect given that Mendeleev had done two more years' work—but this was very much a gradual process, with nothing of a qualitatively new kind being provided in 1871 that was not already there in

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[6]Mendeleev, Manuscript Table 19 (M13), dating from summer/early autumn of 1870 (the numbering denotes the 13th manuscript table and the 19th table in the overall sequence of 65 tables of all forms).

1869. Surely no one could believe that the 1871 predictions were more definitive than those of 1869 just on the basis that Mendeleev was prepared to give the elements names (eka-silicon, *etc.*) in the 1871 paper, while he had been content with question marks in the relevant positions in 1869! But aside from this, it is difficult to discern any qualitative difference between the two papers that might count as significant in this regard.[7]

Of course, a defender of this account might react to these points by simply repositioning stage two at 1869. After all, Lipton himself makes no particular claim about Mendeleev's 1871 paper being the one that turned the tide. But then it is difficult to identify a stage one: Mendeleev's paper of 1869 contains his first ever published periodic table and hence the first candidate for 'mild scepticism'.

Another possibility for the 'two-stage theorist' is to identify stage one as the stage at which predictions—then of course unverified—were made, and stage two as that at which some of those predictions began to be experimentally verified. It would not, then, matter much whether stage one is taken as starting in 1869 or in 1871, since stage two then begins in 1874, with the discovery of the first new element, gallium. Maher seems to have been unaware of the 1869 paper (or at least he never mentions it), so he seems clearly committed to this version of the view with stage one in 1871 and stage two in 1874. And it seems likely that Lipton too was implicitly assuming that the change in attitude arose from the *verification* of the predictions beginning in 1874 rather than their simply being made on the basis of Mendeleev's table—whether in 1871 or 1869.

No one could deny, of course, that it is one thing for a theory to make predictions of the existence of hitherto unknown elements and quite another for it to make *successful*, empirically verified predictions. But neither Maher nor Lipton—nor, so far as we can see, anyone else—cites any substantial evidence for the 'sceptical' attitude of Mendeleev's fellow scientists in 1869 or 1871; and the only evidence they cite for the 'increased confidence' in the theory as a result of the successful predictions is the award to Mendeleev of the Davy Medal in 1882—and this, as we show in the next sub-section, turns out to be (worse than) unconvincing.

Of course there were *some* scientists who were sceptical of the value of Mendeleev's classification in 1869/1871 (and indeed some who remained sceptical *after* the new elements began to be discovered). However, at least two historical facts seem to us to speak unambiguously against any general scepticism about the value

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[7]Certainly Mendeleev himself consistently described 1869 as the starting point of the crucial part of his investigations—the time at which he 'saw the periodic law', began to 'regard it as a new, strictly-established law of nature' and hence 'deduced such logical consequences from it as could show whether it were true or not' (see Mendeleev, 1891, p. 24, n. 13). Mendeleev insisted several times that what principally distinguished him from others who claimed priority over the table was his treatment of the 'periodic law' as a definite theory rather than a mere working hypothesis and hence his expectation right from the start that predictions from it would be borne out. Since he quite explicitly states that 'from the start' means 'from 1869', this also scotches any possible suggestion that the question marks in Mendeleev's 1869 account compared with the names in the 1871 account betoken an increased confidence and increased definiteness about the predictions.

of Mendeleev's work even when it was first published. *First*, his 1869 paper—quite unlike other Russian scientific publications of the time—was immediately translated into German and thereby made readily available to the scholarly world. *Second*, very similar ideas were being developed independently by others in 1869 and indeed earlier—Lothar Meyer, for example, had essentially the same table; and other periodic tables with some differences to Mendeleev's but with much overlap, were, as is well known, developed by Hinrich, Odling, de Chancourtois and Newlands. These facts surely show that Mendeleev's ideas were, right from 1869, accorded enough credibility to at least not be dismissed out of hand.

But this in turn adds to the implausibility of Maher's story about the impact of the predictive success. So long as Mendeleev's scheme was not regarded as beyond the pale of credibility in the period around 1869 to 1871, then *if* the success of the predictions it made was going to prove the crucial evidence that greatly increased its rational believability and gave the scientific community high confidence in further predictions from it, what would be the expected attitude amongst that community towards the scheme in 1869/71? Surely it would be one not of scepticism but rather of 'everything (or at any rate an awful lot) is going to depend on whether or not these bold predictions are verified'. One would have expected the opinion-making scientists interested in the issue to encourage immediate work to see if these bold predictions could be verified experimentally.[8]

Quite aside, then, from the cogency of the cited historical evidence, Patrick Maher's story does not seem to us to stand up in terms of internal coherence. But what of the historical evidence?

2.2.   Why was the Davy Medal Awarded to Mendeleev?

The Royal Society awarded its Davy Medal to Mendeleev in 1882—three years after the discovery of scandium, the second 'new' element, and three years before the discovery of germanium. Both Maher and Lipton see this award as an important marker of the change from the initial 'mild scepticism' concerning Mendeleev's scheme to much greater enthusiasm.[9] Indeed this is the only evidence that either of them cites for a marked change in attitude within the scientific community. But then if, as each alleges, Mendeleev's predictive success was the principal cause of this changed attitude, one would surely expect the citation accompanying the award

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[8]This was certainly the attitude of William Crookes writing in 1877, after the discovery of gallium but *before* those of scandium and germanium. Crookes commented on these latter predictions as follows: 'M. Mendeleeff has also announced the probable existence of another metal, to which he gives the name of "eka-silicium", ES=72, forming an oxide EsO_2. Its properties ought to be intermediate between those of of silicium and tin, and it is to be especially sought for among arseniferous and titaniferous minerals or residues. To the discovery of this metal . . . *we must look forward with anxious interest, not so much for its own sake as for the light which it must throw upon the theory in question*' (Crookes, 1877, p. 298; emphasis added).

[9]This again follows several popular accounts. For example, Asimov (1975) immediately follows his remark that 'Mendeleev was suddenly the most famous chemist in the world' with (what we are presumably to take as evidence for this) 'The Royal Society awarded him the Davy medal in 1882 and other honors were showered on him.'

of the Davy medal to at least lay some substantial emphasis on the successful predictions. Let us see if this meta-level prediction is verified.

In order to obviate any suggestion of 'fudging' the historical data to fit our favoured interpretation, it seems best to quote the citation in full:

> The Davy Medal has been awarded to Dimitri Ivanovich Mendeleeff and Lothar Meyer.
>
> The attention of the chemists had for many years been directed to the relations between the atomic weights of the elements and their respective physical and chemical properties; and a considerable number of remarkable facts had been established by previous workers in this field of enquiry.
>
> The labours of Mendeleeff and Lothar Meyer have generalised and extended our knowledge of those relations, and have laid the foundation of a general system of classification of the elements. They arrange the elements in the empirical order of their atomic weights, beginning with the lightest and proceeding step by step to the heaviest known elementary atom. After hydrogen the first fifteen terms of this series are the following, viz:—

Lithium	7	Sodium	23
Beryllium	9.4	Magnesium	24
Boron	11	Aluminium	27.4
Carbon	12	Silicon	28
Nitrogen	14	Phosphorous	31
Oxygen	16	Sulphur	31
Fluorine	19	Chlorine	35.5
		Potassium	39

> No one who is acquainted with the most fundamental properties of these elements can fail to recognise the marvellous regularity with which the differences of property, distinguishing each of the first seven terms in the series from the next term, are reproduced in the next seven terms.
>
> Such periodic re-appearance of analogous properties in the series of elements has been graphically illustrated in a very striking manner with respect to their physical properties, such as the melting points and atomic volumes. In the curve which represents the relations of atomic volumes and atomic weights analogous elements occupy very similar positions, and the same thing holds good in a striking manner with respect to the curve representing the relations of melting-points and atomic weights.
>
> Like every great step in our knowledge of the order of nature, this periodic series not only enables us to see clearly much that we could not see before; it also raises new difficulties, and points to many problems which need investigation. It is certainly a most important extension to the science of chemistry.[10]

[10]Spottiswode (1883), p. 392.

The first striking fact here is that medal was awarded *not* to Mendeleev alone, but rather jointly to him and the German chemist Lothar Meyer. This already poses a problem for the predictivist thesis. Although Lothar Meyer's scheme was, as he himself pointed out, 'essentially identical' to Mendeleev's, Meyer failed to draw attention to the existence of 'gaps' in the periodicities displayed by the table and hence failed to predict new elements. Only Mendeleev explicitly derived the consequence that the scheme must be regarded as containing 'gaps' and therefore only Mendeleev explicitly predicted the 'new' elements.[11]

It might, of course, be argued that the true locus of scientific achievement lies not in which aspects of a theory the inventor of a theory highlights, but rather in the objective logical characteristics of the theory itself (in Frege and Popper's logical 'world 3' rather than the psychological 'world 2'); and that therefore it was reasonable to honour the two jointly in so far as their schemes (as opposed to the features of the schemes they happened to emphasise and draw logical consequences from) were 'essentially identical'.

The issue is somewhat clouded in this case by a feature that we shall eventually need to comment on at some length—that 'the' periodic table is not itself a theory and therefore directly underwrites no prediction. It is the 'periodic law' lurking in the background, underpinning the table, that makes the predictions if anything does. We shall shortly show that there are important problems here. But certainly Mendeleev himself was quite insistent that the periodic law was 'a new, strictly-established law of nature'. Indeed, he repeatedly insisted that it was precisely the fact that only he viewed the 'periodic law' in this way, and hence that only he was ready, for example, to overturn previously accepted values of atomic weights of certain already known elements so that they fitted the table better, that gave him priority over others, like Meyer, who had considered similar classifications of the elements to his own. Mendeleev explicitly contrasted his own attitude of standing ready to 'correct' atomic weight assignments in view of the law, with that of Meyer, whom he quotes as cautioning that 'it would be rash to change the accepted atomic weights on the basis of so uncertain a starting-point'.[12] It seems that Mendeleev was ready to *assert* 'the' periodic law and therefore to assert what he saw as its consequences concerning both revised atomic weights and hitherto undiscovered

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[11]On the other hand, predictions of new elements were made by other periodic table constructors. For example, in his system of 1864 (and hence 5 years before Mendeleev) William Odling left spaces and used the symbol '""' to indicate elements still to be discovered. These spaces included ones that would eventually be filled by gallium and germanium; though Odling did not leave a space for scandium (see Odling, 1864). Also Newlands made several predictions of atomic weights of then unknown elements. One especially successful prediction was that of an element of atomic weight 73—lying very close to Mendeleev's prediction of an atomic weight of 72 for eka-silicon (germanium). See Newlands (1865). The fact that others made predictions, and successful ones too, surely makes still more implausible the story that the acceptance of Mendeleev's scheme and the recognition he received were crucially dependent on his predictive successes.

[12]See Mendeleev (1891), p. 24, n. 13. Brush (1996) used the apt term 'contraprediction' for these corrections of hitherto accepted values of atomic weights of known elements. For more on these contrapredictions and their role see below.

elements, while Meyer treated the law more as a working hypothesis or perhaps a codification scheme and drew no predictions from it.

This makes it all the more mysterious why, if those making the award had been specially impressed by predictive success, they made no reference whatsoever in the citation to the fact that only Mendeleev pointed out, and explicitly stood ready to be judged by, the success or failure of these predictive 'consequences'.

Indeed, and more embarrassingly still for those defending the story about the crucial role of the new elements, not only does the Davy citation fail to mention Mendeleev's exclusive role in articulating the predictions of further elements, it makes no explicit mention of any new elements whatsoever. Its emphasis is very much on the 'marvellous regularity' revealed in the recurrence of the properties in two series each consisting of seven already known elements. There is a reference to 'seeing clearly much that we could not see before', but this too seems, in the context, to refer to hitherto unthought—of relations between known elements (at any rate no explicit mention is made of new elements). The only remark that unmistakably refers to hitherto unconsidered matters talks not about successful predictions but about 'new *difficulties,* and ... *problems* which need investigation' (emphases added).

2.3. Mendeleev and the Discovery of Gallium

Maher draws attention to the 1874 paper of Lecoq de Boisbaudran in which he announced the discovery of gallium, the first of Mendeleev's predictions to be confirmed. And this is, indeed, an important paper. One possible misconception should, however, be quashed immediately. De Boisbaudran did *not* discover gallium as a result of testing Mendeleev's prediction. Instead he operated quite independently by empirical means in ignorance of Mendeleev's prediction and he proceeded to characterise the new element spectroscopically. De Boisbaudran's findings were published in the *Comptes Rendus*.

Mendeleev later read a Russian translation of this paper, and sent a note to *Comptes Rendus* claiming that this was the element which he had predicted and provisionally named eka-aluminium. De Boisbaudran at first reacted suspiciously to this claim—seeming to believe that Mendeleev was asserting priority over the discovery of the element. Indeed he initially maintained that his own element had significantly different properties from those of the element predicted by Mendeleev (perhaps motivated by a desire to support his priority claims), although he did later change his mind on this score.[13] He did, however, continue to insist that his discovery of gallium involved empirical techniques quite separate from anything related to Mendeleev's work and that prior knowledge of that work would, if anything, have hindered the discovery of the new element.

This raises an important point. Since no one disputes that de Boisbaudran disco-

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[13]As reported in Brock (1992), p. 324.

vered gallium by pursuing considerations quite independent of Mendeleev's periodic table, it is, relative to Mendeleev's work, surely nothing more than a historical accident that gallium had not been discovered, say, six years earlier—in which case this would have been, historically speaking, a question of accommodation within the table rather than prediction. Can it seriously be held that gallium gives significantly greater support to Mendeleev's table because of having only been discovered in 1874 than it would have done had it been discovered in 1868? It certainly appears that, so far as any consideration connected with Mendeleev goes, it perfectly well might have been discovered at the earlier date.

Admittedly, some question might arise concerning de Boisbaudran's eventual 'concession' over the properties of gallium—might he perhaps have 'fudged' his results here to agree with Mendeleev's predictions in view of the Russian's growing authority?[14] Given de Boisbaudran's independent nature, evinced by his continuing insistence that Mendeleev's prediction had played no role, this seems to us extremely unlikely. But in any event, it is simply a question of independent testability: were there independent reasons (coming from the independent confirmation of the theoretical assumptions underlying the experimental techniques) for accepting the values of the atomic weight, atomic volume, valency and so on at issue? We believe that there were, but shall not argue this here. It is enough for us that no one disputes that the actual identification of the new element was quite independent of any consideration associated with Mendeleev's views, from which it follows that, so far as those views are concerned, the new element might just have well have been identified in 1868. Given that, as a matter of fact, Mendeleev's views were developed in ignorance of the existence of gallium (necessary ignorance since it had not yet been discovered), and hence that there was a heuristic path to those views that did not presuppose its existence, it follows that no detail of those views could have been 'read off' the facts about gallium had they been known and that no detail of those views *needed* to be read off such facts. Given these circumstances, the counterfactual claim that *had* gallium been discovered in 1868 it would have counted significantly less strongly in favour of Mendeleev's claims strikes us as frankly bizarre.

2.4. Grounded Confidence about Germanium?

Lipton talks of the predictive successes with gallium and scandium as giving greater credence to Mendeleev's 'theory' (a troublesome notion as already noted and as we shall see later in more detail) and only thence to the further prediction of germanium from that general theory. But Maher talks more directly of the impact of the successes with the first two new elements on the confidence that chemists

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[14]Similar questions have been raised, for example, about Eddington's confirmation of Einstein's star shift predictions. See Earman and Glymour (1980).

of the time had concerning the prediction of the existence of the third new element, later found and called germanium. Maher's claim is, in effect, that while the chemical community had been quite sceptical about Mendeleev's predictions of the existence of gallium and scandium, once those two elements had been identified, the community was *very* confident that the prediction of (what turned out to be) germanium would pan out. We are given the impression that his fellow chemists regarded the success with germanium as being more or less a matter of course: their degree of confidence had been 'dramatically altered' and 'now chemists were expecting to find Mendeleev's third element, though the Royal Society did not wait for that discovery, awarding Mendeleev its Davy Medal in 1882' (Maher, 1988, p. 274).

We have already pointed out that Maher cites no historical evidence for this dramatically increased confidence beyond the award of the Davy Medal; and we have shown that the citation for that award tells against his claim rather than for it. But what if—for all the lack of evidence—chemists at the time *did* regard the eventual discovery of germanium as a matter of course? Would they have been wise to do so?

The answer is patently 'no'—not because of any general sceptical-philosophical scruples about induction, but because of the particular fact that the impression of consistent predictive success for Mendeleev's scheme is a complete misrepresentation of history: a classic example of an 'effect' (Mendeleev's 'predictive success') created by selection-bias. Mendeleev made any number of predictions on the basis of his scheme (or rather schemes—there are at least 65 versions of Mendeleev's table, published and unpublished). Many of these predictions (depending on how exactly they are individuated)—perhaps a majority—were *unsuccessful*.

For example, if we consider the list of what Brock (1992) calls Mendeleev's 'later predictions', then alongside the five successes—eka-manganese (technetium, discovered in 1939), tri-manganese (rhenium, 1925), dvi-tellurium (polonium, 1898), dvi-caesium (francium, 1939), eka-tantalum (protactinium, 1917)—there were four failures—'coronium' (which turned out to be ionised iron), ether, eka-niobium and eka-caesium. (Since many of these predictions were made in the 1871 paper, Brock's reason for calling them the '*later* predictions' was presumably that they were the ones whose empirical fate was *settled* only later.)

Ether constitutes an especially interesting case. Several of Mendeleev's published tables, postdating the discovery and subsequent accommodation of the noble gases, contain predictions of elements lighter than hydrogen, including the constituent of the optical ether, which Mendeleev named 'newtonium'. Mendeleev (initially at least quite reasonably) took the existence of the ether to have been established by the current success of theories of light based on it. The fact that newtonium, if it existed at all, must permeate all transparent bodies without chemically interacting with any of their constituents had initially been perceived as a problem. But this was made unproblematic by the discovery of the nonreactive noble gases. After

this discovery, Mendeleev became fully confident that newtonium and at least one other element lighter than hydrogen existed. Indeed, in 1904 Mendeleev claimed:

> At the present time, when there remains not the slightest doubt that group I, which contains hydrogen, is preceded by a zero group containing elements of lesser atomic weights than the elements of group I, it seems to me impossible to deny the existence of elements lighter than hydrogen. (Mendeleev, 1958, p. 316)

And, in that same paper (p. 27):

> As a consequence of this [satisfactory placing of the inert gases in a zero group preceding group I] . . . we can . . . expect elements of a zero series with atomic weights much smaller than that of hydrogen.

Needless to say, these predictions were entirely unsuccessful. There can be no doubt that Mendeleev took them very seriously however—just as seriously as the successful ones concerning gallium and the rest. There *are* admittedly various predictions scattered round Mendeleev's published and, especially, unpublished versions of his tables that might be thought of as rather half-hearted: for example, alongside those for the three famous successful predictions, question marks are also associated with the atomic weights 8 and 22 in an unpublished precursor of the 1869 paper. No such elements exist, of course, but then these predictive question marks did not make it to the published 1869 or later 1871 papers, and so Mendeleev may have been, for some never-divulged reason, relatively uncommitted to them. But in the case of elements lighter than hydrogen, Mendeleev not only claimed that it was 'impossible to deny' their existence, he put a good deal of effort into detailed prediction of their properties—just as much effort as in the cases of gallium, scandium and germanium.

Calling two such elements x and y—both lighter than hydrogen and x being the element that consituted the optical ether—Mendeleev based his predictions of their properties on numerical relations between atomic weight ratios in the following periodic table which he devised in 1904:

x

y	H = 1.008
He = 4.0	Li = 7.03
Ne = 19.9	Na = 23.05
Ar = 38	K = 39.1
	Cu = 63.3
Kr = 81.8	Rb = 85.4

Fig. 1.   Fragment of Mendeleev's periodic table of 1904 showing the positions of predicted elements x and y which were not found.

In order to predict the atomic weight of element x—'newtonium'—he considered the atomic mass ratios of the known noble gas elements:

$$Xe/Kr=1.56, \ Kr/Ar=2.15, \ Ar/He=9.5$$

From these figures he extrapolated the ratio

$$He/Newt=23.6$$

thus giving an atomic mass of 0.17 for newtonium.[15]

In order to estimate the atomic weight for the element which he designated as y Mendeleev considered the ratios of atomic weights for the first two members of adjacent groups in the periodic tables. He noted that the value for this ratio decreased smoothly from left to right:

He/Ne	Na/Li	Mg/Be	Al/B	Si/C	P/N	S/O	Cl/F
4.98	3.28	2.67	2.45	2.37	2.21	2.00	1.86

Extrapolating from this atomic weight and the additional ratio of *Li/H=6.97* Mendeleev estimated that the ratio of He/y should be at least 10, from which he deduced a value of at least 0.4 for element y.

The discovery of the noble gases also suggested to Mendeleev the possible presence of six new elements *between* the elements hydrogen and lithium. These six empty spaces were indicated in Mendeleev's periodic table of 1904. In one of these cases Mendeleev was more specific, namely in predicting a possible homologue of the halogen fluorine. This alleged new element would serve to restore symmetry to the table by making the number of halogens five thus coinciding with the five known alkali metals. Again these predictions were entirely unsuccessful.

Finally, Mendeleev's failures were not restricted to predicting non-existent new elements; he was, quite contrary to the frequently given impression, often wrong—sometimes quite badly wrong—about the properties of the elements whose existence he *did* successfully predict. For example,

1. Mendeleev predicted that the melting point of gallium would fall between those of aluminium (660°C) and indium (115°C). In fact gallium has an anomalously low melting point of 30°C.

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[15]The interest of the case of the ether, or newtonium, is given a further twist by the fact that it resists straightforward categorisation in terms of prediction or accommodation. So far as Mendeleev was concerned this was an element whose existence was already known. So in that sense its existence was not predicted but rather accommodated within Mendeleev's tables from 1904 onward. But in fact Maxwell's electromagnetic theory and persistent failures to reduce the electromagnetic field to a material ether had, in the minds of experts in these areas, made the existence of the material ether at least highly problematic—and, for many, in fact unlikely. Mendeleev's post-1904 schemes are left, therefore, logically speaking now *predicting* the existence (and indeed some of the properties such as atomic weight) of the material ether. From this point of view, this now is indeed a bold prediction—since it is certainly not (any longer) already known to be true. And of course it became bolder still in the light of Einstein's 1905 Special Theory of Relativity, which definitely expelled the material ether from 'already accepted background knowledge'.

2. Mendeleev predicted that salts of germanium are less stable than those of aluminium. In fact aluminium salts are the more readily hydrolysed.
3. Mendeleev predicted that scandium would be precipitated by hydrogen sulphide. This is not the case.
4. Mendeleev predicted that eka-boron sulphate is less soluble than aluminium sulphate. This is not the case.
5. Mendeleev predicted that eka-silicon is a refractory substance as predicted by Mendeleev. In fact it melts at the relatively low temperature of 950°C.[16]

If, in line with Maher's account, Mendeleev's fellow chemists were very confident about germanium ahead of its actual discovery on account of his previous successes (and we have seen no evidence that they were), then they were right only by serendipity. But there was surely enough clearsightedness—at any rate amongst experts—about the total picture regarding Mendeleev and prediction to make it very doubtful that his fellow chemists would in fact have had the unconstrained confidence attributed to them by Maher.

Since many of these unsuccessful predictions were indeed settled only after— in some cases long after—1871, their fate is not *directly* relevant to the dispute between ourselves and Maher, Lipton and others. However, Maher—following the popular account—gives the impression that once the first two predictions had proved successful, the success of the 'remaining' third prediction was regarded by the scientific community as something of a foregone conclusion—this in turn indicating just how major an evidential impact those two successful predictions had. But there was not one remaining prediction, there were many—and of these several were eventually empirically refuted. There is no historical evidence, so far as we can tell, that the prediction of the existence of germanium was regarded in 1871 as in any way outstandingly important compared to the many other predictions. It is, of course, *possible* that chemists at the time were highly confident both about the germanium prediction and about the others—in which case they happened (by pure serendipity) to be right about the first such prediction that turned out to be empirically checkable. However the existence of these other predictions and their decidedly mixed empirical fates, together with the complete lack of historical evidence for it, makes the claim about the high confidence concerning the 'third' prediction in our view highly dubious.

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[16]Notice that we do *not* claim that all of these predictive failures stand on a par. The whole business of assessing the relative success rate of Mendeleev's predictions is itself a complex and tricky one. This is why we have avoided any straightforward count of successes *vs* failures. It is, for instance, clear that there were reasons to be more confident about predictions made about elements in certain areas of the tables than in others. And perhaps there are reasons to be more confident of interpolation as compared with extrapolation regarding trends in the periodic table. Nonetheless Mendeleev was entirely successful in no area and this seems enough to undermine Maher's claim.

2.5. A Methodological Preliminary: Prediction and Pre*diction*

Having clarified, and attempted to counter misunderstandings of, some particular aspects of the history, we need also to clarify the general methodological view of the evidential impact of prediction that we endorse—a view that, again, could easily be misunderstood. We shall be brief and rather dogmatic—arguments are developed in more detail elsewhere (see Worrall, 1985b, and, especially, Worrall, 2001).

Our view is that *of course* the time-order of theory and evidence is of no significance *in itself*. The phenomena of planetary stations and retrogressions, for example, provide strong support for Copernicus's heliocentric theory of the solar system irrespective of the fact that those phenomena had been known for centuries before Copernicus articulated his theory. Newton's account of the (already known) precession of the equinoxes provides at least as much support for his theory as the theory's prediction of the (of course, at the time Newton first formulated his theory, unobserved) return of Halley's comet in 1758. On the other hand, the planetary stations and retrogressions provide little or no support for the Ptolemaic geocentric theory. And, similarly, the details of the fossil record provide no support for 'scientific' creationism, as supplemented by 'the Gosse dodge'—according to which pretty pictures in the rocks and bone-*like* structures in desert sands just happened to be parts of God's creation. 'Old evidence' for a theory—evidence that was, in the purely temporal sense, accommodated by that theory—sometimes supports the theory and sometimes does not.

The difference between the two types of case cannot, therefore, concern what was or was not known when theory was produced. Instead the crucial difference is the fact that, in the cases of little or no support, certain aspects of the theory concerned were fixed precisely to yield the phenomena at issue. The relative velocities around the deferent and epicyclic circles in Ptolemy's theory had to be 'read off' the phenomena of stations and retrogressions in order for that theory to yield those phenomena. The details of the fossil-accommodating version of creationism had to be read off the already known fossil record—which *particular* pretty pictures God chose to draw and what *particular* features the 'bone-like' structures have can *only* be determined by observation.

On the other hand, although the planetary stations and retrogressions had of course been observed long before Copernicus (indeed, as we just remarked, long before Ptolemy), Copernicus's theory committed him *directly* to their existence quite independently of their observation. The fact that the planets occasionally *seem* to stand still and then, for a while, move backwards before resuming their steady eastward progression round the ecliptic is a direct consequence of the Copernican theory's claim that we are on a moving observatory that will therefore periodically overtake certain planets and be overtaken by others as all move round the sun at different rates.[17]

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[17]*Of course, even here, Duhem is strictly correct. The 'direct' consequence in fact presupposes auxiliary assumptions— but ones that are 'natural' within the Copernican framework and not themselves dependent on the phenomena that they then play a part in explaining.*

In other words, the position we favour distinguishes two senses of 'accommodation'. A theory might be said to accommodate a fact merely on the grounds that the fact was already known at the time it was articulated. Or, a fact might be accommodated in the stronger sense that special assumptions need to be made within the theory on the basis of the fact so as to provide an account of it—in such a case, the fact *must* already have been known. Clearly a fact accommodated in this second sense must then have been accommodated in the first sense; but the converse implication does not hold. For ease of later exposition, call a case in which the fact happened to be already known before a theory entailed it, but in which no feature of the theory was 'read off' the fact, a case of accommodation$_1$. And call cases in which, on the contrary, the fact was both known *and used* in the construction of the theory that entails it, cases of accommodation$_2$. Our position can then be put very simply: accommodation$_1$ stands on a par with prediction so far as evidential support is concerned (other things, of course—such as the logical strength of the empirical statements concerned—being equal), and only accommodation$_2$ carries less weight.

There is no reason why a successful accommodation$_1$ should not count just as highly for a theory as a predictive success—nothing prevents the former being just as severe a test for the theory as the latter. So planetary stations and retrogressions and the precession of the equinoxes—which Copernican theory and Newtonian theory, respectively, accommodated$_1$—fully supported those theories. Or, to take another example, the precession of Mercury's perihelion, which had been known about for decades beforehand, fully supported the general theory of relativity.

The accommodation$_2$ of some piece of evidence *e* by some theory *T* undoubtedly tells us something positive about *T*—namely that it is at least *consistent* with *e*. When, as sometimes happens, it begins to seem as if there is no possible explanation for some evidence within some theory, then even finding an accommodation$_2$ of that evidence may give scientists more confidence in the theory. Something like this happened, for example, with Darwinian evolutionary theory and the widespread phenomenon of apparently altruistic behaviour—the consistency proof in that case coming in the form of the theories of kin selection and reciprocal altruism.

Something else should be said about the impact of accommodation$_2$. When the (general) theory concerned is strongly supported *independently of the fact at issue,* the accommodation$_2$ of some fact, even in this *ad hoc* way, may well still supply the best explanation that science can currently supply for that fact. So, for example, the best explanation in, say, 1700 for the observation of no stellar parallax was surely the Copernican one—that there must in fact be an apparent parallactic motion but that even the nearest stars are so far away as to make the effect too small to be detected by even the best available telescopes. (Here, as before with Ptolemy and with scientific creationism, we use the phenomenon—no observed parallax—to fix (in this case in a rather loose way) an otherwise free parameter in the theory (distance to the nearest star).)

Not only can accommodations$_2$ have this sort of impact, but it is standard scientific practice to use empirical data to fix parameter-values left free by general theoretical considerations. (Why conjecture when you can measure?) So, for example, the classical wave theory of light leaves the values of the wavelength of monochromatic light from various sources, such as a sodium arc, entirely free. However, that general theory has various consequences that characterise that wavelength as a (one-to-one) function of a set of measurable quantities—fringe distances and slit distances in some interference experiment, for example. Data from such an experiment then allow the deduction of a specific version of the wave theory, complete with a value for the theoretical parameter of wavelength of light from a sodium arc. *Of course* such data in a sense provide support—indeed *maximum* support— for that specific theory, because *given* the general theory they deductively entail it. But notice that this support judgement is ineliminably conditional—for someone who already accepts the general wave theory (with free parameter for the wavelength of light from the sodium arc), the fringe and slit distance data provide conclusive reason for accepting the specific version of the wave theory with the particular wavelength value; but those data alone give no extra reason at all for accepting that general wave framework. This is underlined by the fact that, in the case of creationism, the 'fossil' data similarly give a (near) conclusive reason for holding the gossefied version to anyone who ahead of that data holds the general creationist view. Given that you already accept that God created the universe essentially as it presently is in 4004BC, then in the light of the 'fossil' data you had better hold the specific version of the theory that has God painting pictures in the rocks and so on at the time of creation. But obviously the right judgement is that this data *only* gives you good reason for accepting the specific gossefied version of creationism *if* you already accept creationism in general—it gives no reason whatsoever for being a creationist in the first place. By contrast, the data about planetary stations and retrogressions support not just the specific Copernican models that entail that data, but also the basic general Copernican framework.

Notice one final wrinkle. Very often, once some data has been used to fix an initially free parameter, the specific theory concerned goes on to entail some further independent data. Thus, having used, for example, data from the two-slit experiment to fix the value of the wavelength of light from a sodium arc, the more specific theory will then entail results about fringe distances in other interference or diffraction experiments (for example, the one-slit experiment). Of course this further data—if it is indeed data, if the theory gets the further results correct— fully supports both the specific theory that entails it and the general framework. Such further independent data may be either predicted in the temporal sense or accommodated$_1$. This again distinguishes the wave theory case from that of creationism. In the latter, gossefying relative to particular data D produces a theory that is not testable *independently* of D. It might seem to make no difference in cases where independent testability holds whether we say that the data used to fix

some parameter supports the general theory or not. But clarity and even-handedness surely require that we say that in neither the wave theory nor the creationist case does the data used in fixing parameters support the theories concerned in the unconditional sense. However there is in the wave theory, but not the creationist, case *other* data that do provide such support.

The general methodological judgements we endorse are, then, the following. Support within a given theoretical framework must be distinguished from support for a general framework (obtained via some specific version of it). *If* some general theory is already accepted for independent reasons (in particular for independent empirical reasons), then the specific version of it that allows the accommodation$_2$ of some evidence e is (perhaps maximally) supported by e. But such a piece of evidence e supplies *no extra reason* in favour of the general theory in the first place. On the other hand, if e is either predicted as new evidence or accommodated$_1$—that is, it just happens to be already known evidence but was not used to fix any feature of the specific theory at issue—then it supplies support, not only for the specific version that entails it, but also for the underlying general theory. There is no distinction at all in this regard between prediction and accommodation$_1$.

Our account is, of course, a normative one—an account of how evidential support ought to be measured. Linking it to actual judgements by scientists and others is, then, a further matter. As several commentators have pointed out, there may, for example, be a special psychological factor about the prediction of hitherto unsuspected effects. These predictions have a special 'newsworthy' character and can perhaps be more readily and more widely appreciated amongst the educated public as important indicators of the value of the theory than simple accommodations$_1$ (the identification of which requires more knowledge of the theoretical structure of the scientific field concerned). But this psychological effect can easily be 'controlled for'—mainly by concentrating on the judgements of real experts who are actively researching in the relevant field. We would expect such judgements in fact made by experts to be in line with our normative account.[18]

So, in the Mendeleev case we would expect to find historically the following attitude—at any rate amongst the experts. Insofar as scientists were interested in applying Mendeleev's scheme or simply thinking of it as a codification of the phenomena, it should make no difference at all whether some phenomenon of interest was predicted or accommodated in either sense. However, in so far as

[18]See, for example, the discussion between Brush, Achinstein and Shimony in Forbes, Hull and Burian (1995). The eminent physicist Yuval Ne'eman, involved in the discovery of the 'eightfold way' makes the following very insightful comment about the prediction of the Ω^- particle by the eightfold way:

> the importance attached to a successful prediction is associated with human psychology rather than with scientific methodology. It would not have detracted at all from the effectiveness of the eightfold way if the Ω^- had been discovered *before* the theory was proposed. But human nature stands in great awe when a prophecy comes true, and regards the realizations of a theoretical prediction as irrefutable proof of the validity of the theory. (Ne'eman and Kirsch, 1986, p. 202)

scientists were interested in support for the underlying ideas behind the scheme—in confirming the idea that Mendeleev had discovered some real periodicities in nature—it *does* make a difference. Here we would expect *firstly* that successful predictions are of course taken as important indicators of the value of Mendeleev's ideas. But, *secondly*, we would expect such predictions to be regarded as no more important indicators than the successful, non-*ad hoc* explanation or accommodation (that is, accommodation$_1$) of any relevant already known phenomenon. And, *thirdly*, we would expect that the only known evidence whose 'explanation' might be regarded as of doubtful value in confirming Mendeleev's underlying views will be evidence which was accommodated$_2$. This consists of phenomena which could be given a place in Mendeleev's detailed scheme only by tailoring the details of that scheme to them, in a way that yielded no independent tests.

We shall see, in Section 5, that these expectations are broadly fulfilled by the history—though they are overlaid not only with the usual uncertainties about interpreting historical data, but also with a number of interesting complications which differentiate this case from other cases (taken almost exclusively from physics) that have been analysed in this regard.

Another way in which the general message that we endorse might be expressed is through clarification not of the notion of 'accommodation' but instead of that of '*prediction*'. In fact scientists often use the notion of prediction in an *atemporal* sense—that is, one which carries no implicit requirement that 'predicted' events have been hitherto unobserved. Here, for example, is a comment on Newton's theory from French's excellent textbook on *Newtonian Mechanics* (French, 1971, pp. 5–6; emphases added):

> like every other good theory in physics [Newton's theory] had predictive value; that is, it could be applied to situations *beside the ones from which it was deduced.* Investigating the predictions of a theory may involve looking for hitherto unsuspected phenomena, or it may involve *recognising that an already existing phenomenon must fit into the new framework.*

This idea is by no means unknown to philosophers. The same idea is at the heart of Whewell's notion of consilience, for example; and it was explicitly spelled out by Moritz Schlick:

> the confirmation of a prediction means nothing else but the corroboration of a formula for those data which were not used in setting up the formula. Whether these data had already been observed or whether they were subsequently ascertained makes no difference at all.[19]

Given this explication of prediction, the general message we endorse could equally well be formulated by reserving the term 'accommodation' for cases of what we have been calling accommodation$_2$, as by insisting that all predictions, if suc-

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[19]Quoted from Popper (1979), p. 112.

cessful, count—other (logical) things being equal—equally in favour of a theory whether or not they are (temporal) *pre*dictions.

3.   Brush's Account of the Reception of Mendeleev's Ideas

Stephen Brush has, in several papers (for example Brush, 1989), examined different episodes from the history of science and argued that the scientists involved in them did not in fact regard (temporal) predictive success as carrying an epistemic premium. However, in a recent paper (Brush, 1996) on the reception of Mendeleev's ideas, he claims that this case is exceptional—here temporal novelty of predictions really did count.

Brush's account can hardly be accused of being unaccompanied by serious historical data and research. He analysed much of the chemical periodical *and* chemical textbook literature from the latter part of the nineteenth century in America and Britain, and also some of the literature from France and Germany in the same period. Brush came to a conclusion that is apparently straightforwardly 'pro-predictivist':

> After spending considerable time perusing the crumbling pages of late nineteenth-century chemistry journals and textbooks, I have confirmed the traditional account: Mendeleev's periodic law attracted little attention . . . until chemists started to discover some of the elements needed to fill the gaps in his table and found that their properties were remarkably similar to those he had predicted. The frequency with which the periodic law was mentioned in journals increased sharply after the discovery of gallium, most of that increase was clearly associated with Mendeleev's prediction of the properties of the new element. (p. 617)[20]

Since we shall need to refer back to this claim quite often, let us call it (pro-predictivist) 'claim 1'.

Although critical of the precise claims of Maher and Lipton, and especially of the evidential basis they provide for their claims, Brush nonetheless holds that they may be 'broadly' correct:

> My survey of chemistry textbooks and articles . . . suggests that many chemists did give some credit for novelty; they considered that, other things being equal, the prediction of a new element and its properties counted more than fitting a known element into the table. But not thirty-one times as much! (p. 609)

(Remember that, on Maher's view, the successful prediction of two new elements counted for more than the prior successful accommodation of the then known sixty-two elements—because the two successes dispelled the scepticism that had existed despite the sixty-two successful accommodations.) Since we shall again need to

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[20]Unadorned page references throughout Section 3 are to Brush (1996).

refer later to the claim made in this passage, let us call it (pro-predictivist) 'claim 2'. So claim 1 is that little attention was paid to Mendeleev's scheme before the predictive successes were achieved; while claim 2 is that these predictive successes counted (considerably) more with the scientific community of the time than did the scheme's accommodational success.

Against this, we will argue

(a) *both* that Brush's claims 1 and 2, although individually clear, are not clearly mutually consistent *and* that he adds various concessions and details in the course of his article that make it difficult to know in the end what *precise* thesis is being propounded; and

(b) that the evidence he himself supplies, on further analysis, fails to support pro-predictivist claims 1 and 2.

3.1. Some Complications and Tensions in Brush's Analysis

In a section of his paper entitled 'The Limited Value of Novel Prediction', Brush asserts, pro-predictivist claims 1 and 2 notwithstanding, that:

> almost every discussion of the periodic law in nineteenth-century chemistry textbooks, including Mendeleev's, gives much more attention to the correlations of properties of the known elements with their atomic weights than to the prediction of new ones. (p. 612)

He also points out several times the important evidential role played by the success of Mendeleev's 'contrapredictions'—the 'corrections' of atomic weight values previously assigned to already known elements—such as beryllium, uranium and tellurium—so that they fitted into his table smoothly. And indeed the most elaborate statement of Brush's general conclusion seems to be the following:

> While chemists differed on the relative importance of prediction and accommodation, it seems fair to approximate the consensus as follows. The reasons for accepting the periodic law are, *in order of importance*, [1] it accurately describes the correlation between physicochemical properties and atomic weights of nearly all *known* elements; [2] it has led to useful corrections in the atomic weights of several elements ... ; and [3] it has yielded successful predictions of the existence and properties of new elements. (p. 612; emphases added)

But is this new claim really consistent with claims 1 and 2? Clearly this needs further investigation and we begin with the 'contrapredictions'.

First it is surely important to emphasise (as Brush does not) that there turned out to be *independent* empirical evidence for the new values assigned to these atomic weights (this re-evaluation relied, of course, on already accepted auxiliary theories—atomic weights of elements are highly theory-laden facts). It was not that chemists simply came to accept the new values because those values made those elements fit Mendeleev's table better (that would be a classic case of an *ad hoc* accommodation₂). For example, the corrected value of the atomic weight of

beryllium was confirmed independently of any consideration of its place in any table by Nilson and Petterson's discovery of one of its gaseous compounds—beryllium chloride. This discovery meant that an evaluation of beryllium's atomic weight could be made using already accepted 'background knowledge'—concerning the properties of chlorine and Avogadro's number. (Brush does mention this discovery but does not underline its significance.)

As Brush himself agrees, there is surely no general methodological reason why the empirical success of these aptly named contrapredictions should count any less in favour of Mendeleev's scheme than the success of his predictions of new elements. This becomes, we hold, uncontestable in view of the just emphasised fact that the corrections of atomic weights were independently supported rather than made simply so as to fit the table. Indeed Brush suggests that from the (correct, if only intuitive) point of view of what counts as a severe test of a theory, it might even be argued that such successful contrapredictions should count even more than successful novel predictions (since they are inconsistent with hitherto accepted 'background knowledge' rather than simply independent of it). Be that as it may, Brush certainly thinks that they count at least equally, and finds nothing in his historical researches to suggest that this intuitive methodological judgement failed to be reflected in the particular judgements of late nineteenth-century chemists.

But what, then, of the claims about the greater impact of novel predictions? Brush attempts to glide over any difficulty here by suggesting that contrapredictions should themselves count as 'novel predictions': '[Mendeleev] proposed changes in the accepted atomic weights of several elements in order to fit them into his table ... All of these may be called "novel predictions"' (p. 599). But this surely only obscures the issue. We have, of course, no complaint against the thesis that all genuine tests of a theory, if passed by that theory, count in its favour (and, other— logical—things being equal, count equally). Indeed this is an outline, pre-analytic version of precisely the general methodological thesis we endorsed in Section 2.5. This thesis entails that successful contrapredictions count fully in favour of the theory that makes them; but it also entails that accommodations—in the sense simply of explanations by the theory of already known evidence—may also count fully in a theory's favour, since they too may be genuine tests. The only evidence that counts less is evidence accommodated in the sense that it was not only already known in advance but was also bound, because of the way in which the theory was developed, to be entailed by that theory (that is, 'accommodation$_2$'). The dispute is over the issue of whether Mendeleev's *prediction of new elements* played a historically special role compared to other kinds of evidence—that is, whether novel facts here in the precise sense of temporally new evidence were especially weighty supports for Mendeleev's scheme. Brush is—we should again stress, in our view correctly—going against this thesis by admitting that successful contrapredictions counted at least as much.

We turn next to Brush's still more telling concession that the ability of Mende-

leev's periodic 'law' to yield an accurate description of 'the correlation between physicochemical properties and atomic weights of nearly all *known* elements' counted even more highly—in the aggregated consensus—than either the predictions of the new elements or the contrapredictions. (He states, remember, that his historical research shows that the reasons for accepting the periodic law were, in order of importance, first, its 'accommodation' of the known elements; second, its 'contrapredictive' success; and (only) third, its success in predicting new elements.) He points (as we have done) to the citation of the Davy Medal Award as showing that this award seems to have been made largely on the basis of the successful 'accommodations'. He also states at one point 'Frequently the reader of [nineteenth-century textbooks] is given the impression that the periodic law is *established* by these correlations [of "properties of the known elements with their atomic weights"] and then *applied* to make predictions' (p. 612; emphases in original).

But all this is surely in direct conflict with the first of the pro-predictivist assertions (claim 1) quoted earlier: if the successful accommodation of the correlation between properties and atomic weights of known elements was to be the single most important factor in the acceptance of Mendeleev's periodic law after, say, 1874, then it is difficult to see why it should be true—as Brush asserts (p. 617)—that 'Mendeleev's periodic law attracted little attention ... until chemists started to discover some of the elements needed to fill the gaps in his table'. One would, on the contrary, have expected it to attract a great deal of attention at the stage when it just explained the properties of the known elements, and then attract some more once the predictions of new elements proved successful. If it were true that, as a matter of descriptive historical fact, Mendeleev's periodic law attracted little attention and hence very little adherence before 1874, then Brush would have supplied no explanation for it.

He does mention that there was a strong pragmatic reason for a chemist to be less interested in the new elements than in the already known ones—namely their relative scarcity:

> The reason why the predicted elements were less important to chemists than the known elements that were initially correlated by the periodic law is the same reason why they had not been discovered before 1869: their abundance at the earth's surface is very small. (p. 612)

This may indeed be true of the judgments of importance made by writers of chemical textbooks (well known, after all, for a tendency towards the pragmatic and the prosaic!). But it can hardly be used to resolve the apparent conflict in Brush's account, since he explicitly states that the explanation of the properties of the known elements was chief amongst the 'reasons for accepting' the periodic law. The relative abundance of the known elements might account for some chemists being more concerned with the sections of the periodic table involving those elements, but it surely cannot account for their thinking of the explanation of the

properties of those elements as the chief reason for holding the periodic law to be some sort of general truth.

Brush's acceptance that, in the aggregate, the accommodation of the properties of the known elements was the single most important factor in the acceptance of Mendeleev's periodic law in the late nineteenth century, while inconsistent with claim 1 *above*, might seem to be vindicated by claim 2 (thus showing that these two apparently complementary pro-predictivist claims are themselves in some tension). In claim 2, Brush modifies—albeit in rather jocular fashion—Maher and Lipton's attempt to quantify the relative impacts of accommodations and predictions: 'other things being equal, the prediction of a new element and its properties counted more than fitting a known element into the table. But not thirty-one times as much!'

Brush then needs to do some work to bring claims 1 and 2, together with the various additional concessions and modifications, into a fully coherent overall view. So far as we can tell, that view would have to amount to something like the following. (i) There were, of course, marked individual differences in the support judgements of individual scientists reacting to Mendeleev's work. (ii) These individual judgements can nonetheless be aggregated to form a 'consensus' view according to which the total evidential support provided for Mendeleev's periodic 'law' by the accommodation of the properties of known elements was higher than the total evidential support provided by the success of the predictions of new elements. However, (iii) what might be called the perceived 'empirical support per single experimental/observational item' was much higher for predictions than it was for accommodations (the fact that the aggregated degree of support from accommodations was higher than the aggregated degree of support from predictions then being explained by the fact that there were, at that time, sixty-two accommodations and only two predictions).

If this is a correct analysis of it, then the chief problem with Brush's overall account—aside from any issue about the historical evidence in its favour—is that, by agreeing with Maher and Lipton that the novel predictions counted more while denying that they counted sufficiently more to outweigh the total effect of the accommodations, it ends up in no man's land. Brush may have an explanation for why special attention should have been paid to the predictive successes (they carried a lot of 'impact per unit', as it were); but this does not, despite his claims and despite, perhaps, first appearances, translate into an explanation for what he accepts is the historical fact that Mendeleev's periodic law attracted little attention before 1874—that is, before the initial success of the predictions. What his account would lead us to expect is, on the contrary, a high rate of credit for, and interest in, Mendeleev's scheme before 1874 and a somewhat higher rate afterwards.

But aside from its explanatory power is there any historical evidence for the truth of this account? And, in particular, is there evidence for the precise pro-predictivist claims 1 and 2 on which it is—somewhat shakily—built?

3.2. Does Brush's Evidence Really Show that the Predictive Successes Carried More Impact?

First, we concentrate on Brush's precise claim (the essence of 'claim 1') that his historical research

> confirm[s] the traditional account: Mendeleev's periodic law attracted little attention . . . until chemists started to discover some of the elements needed to fill the gaps in his table and found that their properties were remarkably similar to those he had predicted. The frequency with which the periodic law was mentioned in journals increased sharply after the discovery of gallium, most of that increase was clearly associated with Mendeleev's prediction of the properties of the new element. (p. 617)

Remarkably enough, Brush immediately adds to this claim the admission that 'in many cases it is difficult to prove a causal relation [between the success of the predictions and the frequency with which the periodic law is mentioned] since the authors do not mention the prediction' (*ibid.*). Two points should be made:

(a) The whole issue here is, of course, exactly about causality—no one disputes that Mendeleev's scheme attracted somewhat more attention after 1874 than before, the issue is partly over the extent of the increase but, more significantly, over what exactly underlay that increased attention. The inference simply from the premise that there was greater interest in Mendeleev's scheme after the predictive successes to the conclusion that it was the predictive successes that caused the increased interest would be, as it stands (that is, without invoking further evidence), a classic instance of the *post hoc ergo propter hoc* fallacy.

(b) The acknowledged absence 'in many cases' of any mention of the prediction of gallium is not simply an impediment to drawing a causal conclusion about the role of that prediction, it surely gives at least some *prima facie* support to the causal claim that the prediction played no significant role: it would be strange indeed for an author who had been drawn to Mendeleev's scheme in large part by its predictive success to make no mention of that success at all.

And, indeed, Brush's evidence on this issue (given in his table 1) is striking: no less than 132 of the 197 journal articles 'mentioning' the periodic law in the period 1871–1890 fail to mention the confirmed predictions of new elements.

Perhaps this is why, despite the (just quoted) claim that the evidence from frequency of mention of the periodic law in journals was 'clearly associated with Mendeleev's prediction of the properties of the new element', Brush elsewhere states that the evidence from journals is of little value one way or the other:

> The number of explicit references to the periodic law to be found in late nineteenth-century journals is small and fluctuates irregularly. From these data alone it would be difficult to judge whether the periodic law was actually accepted by the entire chemical community or was merely an exotic concept, of interest only to a few specialists. (p. 600)

And he goes on to claim that the really telling evidence comes not from journals, but from textbooks:

> If a majority of chemistry textbooks published in a country present the periodic law—
> as is the case for the United States and Britain by 1890—it is reasonable to conclude
> that the law was generally accepted in that country. (*ibid.*)[21]

But, to repeat, the extent of the diffusion of Mendeleev's scheme is not the issue here—no one disputes that this was widely (though not universally) 'accepted' by 1890 in the scientifically advanced countries. The question at issue is the relative strength of the roles played in this diffusion by evidence of various sorts and in particular by the successful predictions of new elements.

Looked at from the point of view of this question, even Brush's most vaunted evidence seems to us remarkably underwhelming. Of the total of 244 chemistry textbooks published in the period 1871 to 1890 in the USA, Britain, Germany and France that Brush examined, 76 are recorded as 'mentioning' the periodic law (that is, 168 do not mention it!). Of those 76, 43 mention the successful predictions (that is, 33 do not!); and, while it is true that there is some trend towards a higher rate of citation of the successful predictions later in the period, it is still true that 5 of the 25 textbooks published in the period 1886–1890 in the US and Britain, and 3 of the 7 published in Germany or France which mention the periodic law do not mention the successful predictions. Remember once again that what is at issue here is not whether the successful predictions carried important weight, but whether they carried an especially heavy weight relative to other confirmatory evidence. Brush's own historical evidence hardly seems to be telling for the pro-predictivist view. Indeed it seems to us, if anything, to tell in the opposite direction. If the single most weighty pieces of evidence in favour of Mendeleev's scheme were the predictions of new elements and their properties, then it surely seems very strange that, overall, more than 43% of those textbooks writers who are taken as evidence for the 'acceptance' of the scheme fail to mention the predictions. And, even allowing for the reasonable suggestion that word of the success of these predictions may take some time to get around, it seems strange, on that same supposition, that more than 25% of even the textbooks published in the period 1886–90 (that is more than twelve years after the discovery of gallium) that present Mendeleev's 'law' still fail to mention the successful predictions.

The only remaining evidence in Brush's paper is a series of isolated quotations from chemists of the time—such as Pattison Muir, Hell, Crookes, Cooke and others (pp. 610–611). It is unclear just how much weight Brush puts on these himself; but objectively they can surely carry very little.

Many of them are uncontroversial: for example, the Stuttgart chemist Carl Hell

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[21]There are surely difficulties even with this claim. Would not the most telling evidence in fact be instances in *research articles* of explicit assertions by scientists that what especially recommended Mendeleev's scheme to its author as a basis for further research was that scheme's success in predicting the properties of new elements?

is quoted (p. 610) as holding that the agreement of gallium's properties with those predicted by Mendeleev 'has contributed to the recognition and confirmation of the periodic law'. Only someone who inclined to the strange view that successful prediction carried no confirmatory weight at all could find this any sort of telling remark.

Perhaps the two most striking passages quoted by Brush are from William Crookes and from Mendeleev himself. Brush claims that the latter 'stressed the importance of predictions when he reviewed the status of his periodic law in 1879' (*ibid.*) in the following remark (to which we have added the emphasis):

> No natural law acquires any scientific importance unless it introduces, so to speak, some practical conclusions, or, in other words, unless it admits of logical conclusions capable of *explaining what has before remained unexplained*, and, above all, unless it raises questions which can be confirmed by experience.[22]

But Mendeleev's talk of 'explaining what has before remained unexplained' is perfectly consistent with the phenomena at issue being already known phenomena—such as the similarities between the *known* elements in corresponding positions in the table. Thus Mendeleev certainly allows that the fact that known valency relationships, for example, 'follow' from his scheme can count significantly in its favour. It is true that 'raising questions' might refer to making predictions about initially unknown matters, and also true that he does say that these count 'above all'. Notice, however, that, even then, his message seems to be that it is the fact that the 'natural law' makes predictions ('raises questions') at all that is its really significant virtue and not whether these predictions turn out to be empirically confirmed. After all, if a theory makes predictions about matters that scientists had not even thought about hitherto, then science learns something significant from their investigation either way—that is, whether or not the predictions turn out to be correct. Moreover, 'raising questions' could at least equally plausibly refer to the 'contrapredictions'—'does beryllium really have the atomic weight that chemists have hitherto believed it has?' Finally, there is no explicit mention of the specific role of the newly predicted elements.[23]

The other apparently telling quotation comes from William Crookes (1877, p. 292):

> The prevision of phenomena not yet observed has been rightly declared by methodologists to be one of the principal distinctions between science, in the strict sense of the term, and a mere accumulation of unorganised knowledge; the discovery of gallium thus shows the value of Mendeleev's theory.

But, once again, no one denies that successful prediction 'shows the value' of Mendeleev's theory, the issue is whether *only* such evidence shows its value or

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[22]Mendeleev (1879a), p. 292 (quoted from Brush, 1996, p. 610).

[23]We would not, however, want to deny that Mendeleev elsewhere does make fairly unambiguous claims about the special power of these predictive successes—but then of course he had his own personal reasons for doing so.

whether, at any rate, such evidence is much more telling than the systematic explanation (not of course the 'unorganised' 'accumulation') of known phenomena. Crookes in fact expressed a definite view on this issue, apparently unnoticed by Brush:

> Mendeleeff considers that all the functions by which the dependencies of the elements on the atomic weights are expressed are periodic. The properties change in accordance with the increasing atomic weights, and are then repeated in a new period with the same regularity as in the former. If we examine his scheme we must admit that it brings admitted relations into a very prominent light. Such groups as fluorine, chlorine, bromine, and iodine; as sulphur, selenium, and tellurium; as nitrogen, phosphorus, arsenic, and antimony . . . fall into positions which well agree with their respective analogies . . . A further study of Table II [a version of Mendeleeff's table] will bring to light many more curious instances of such representation, *which we submit, lend a powerful support to M. Mendeleeff's arrangement.* (Crookes, 1877, p. 303; emphasis added)

Notice that Crookes is here talking about already known ('admitted') relations between *already known* elements—fluorine, chlorine, nitrogen, and so on.

4.   The Periodic Table and the 'Periodic Law'

Having argued that neither Peter Lipton nor Patrick Maher nor Stephen Brush supplies any convincing evidence that the successful predictions were the, or even a, major factor in changing attitudes towards Mendeleev's table, nor indeed much in the way of evidence for the existence of any radically changed attitudes, the next stage is clearly to provide our own analysis of the evidential situation and its evolution from 1869 onwards. We shall provide this in the following, final section. However, one further preliminary clarification is necessary. There is at least one sense in which the Mendeleev case is indeed significantly different from others that have been analysed from the point of view of the general prediction versus accommodation debate—though not the sense indicated by Brush.

As already mentioned, the Periodic Table is patently not itself a theory and therefore does not in itself have any logical consequences. Mendeleev saw his Table (indeed, significantly, Tables—he produced a total of sixty-five different ones through the course of his career) as embodying, or as underpinned by, something he called the 'periodic law'. The predictions of the existence of the new elements are, then, if logical consequences of any general claim, presumably logical consequences of this periodic law. Mendeleev himself wrote:

> *if all the elements be arranged in the order of their atomic weights a periodic repetition of properties is obtained.* This is expressed by the *law of periodicity; the properties of the elements, as well as the forms and properties of their compounds, are in periodic dependence or, expressing ourselves algebraically, form a periodic function of the atomic weights of the elements.* (Mendeleev, 1891, p. 16)

The rows and columns of Mendeleev's table are meant to reflect the 'periodic function' asserted to exist by this periodic law.

It is no surprise that Mendeleev never gave precise mathematical expression to this 'periodic function'. In fact, it would be impossible, we claim, to state at all precisely the content of Mendeleev's 'periodic law'. (We are, of course, referring here to the law as articulated by Mendeleev himself and as understood by his contemporaries. There is no doubt that the subsequent development of chemistry has seen at least great progress toward the articulation of a precise version of the periodic law, based ultimately on quantum mechanics.[24])

Mendeleev clearly believed (along with others) that there is a whole set of dependencies of chemical properties on atomic weight and that some of these properties recur at regular intervals. The 'periodic law' amounts, essentially, to a commitment to look for such dependencies and recurrences, and the suggestion that something of importance will emerge from this search.

Mendeleev admitted that the basic idea of two elements having 'analogous' properties was a difficult and 'relative' one:

> it is easy to fall into error in the formation of the groups because the notions of the degree of analogy will always be relative, and will not present any accuracy or distinctness. Thus lithium is analogous in some respects to potassium and in others to magnesium; or beryllium is analogous to both aluminium and magnesium. (Mendeleev, 1891, p. 15)

His argument seems to have been that the fact that one could make a case for periodic dependencies of properties of elements *on the basis of such a natural ordering principle as that of atomic weight* lent objectivity to the analogies thus revealed. That is, Mendeleev was so inclined to regard the ordering by atomic weights as natural that he took this as evidence for 'lower level' claims about real similarities between elements, rather than following the usual methodological process whereby lower level empirical results, usually thought of as relatively more certain, are taken as evidence for higher level laws and theories.

Notice that the lack of specificity of the 'periodic law' as then conceived does not entail that Mendeleev failed to operate in a precise way *locally*. For example, he himself gave a clear account of his approach to working out some of the main relationships between the properties of the elements in his textbook *The Principles of Chemistry*. The method consists of simultaneous interpolation within groups or columns as well as within periods or rows of the periodic table. The average of the values of the numerical properties of the four elements flanking the element in question are taken to determine the latter's properties. So Mendeleev wrote:

[24]See Scerri (1998), where it is argued that, while still no one has succeeded in giving a mathematically precise version of the periodic law, and while the law has not *exactly* been reduced to quantum mechanics, sufficient progress has been made to suggest that a precise version of the law *may* eventually be possible (if only 'in the limit'). (See also Scerri, 1999, where further clarification is provided.)

> If in a certain group there occur elements, R1, R2, R3, and if in that series which contains one of the elements, for instance R2, an element Q2 precedes it and an element T2 succeeds it, then the properties of R2 are determined by the mean of the properties of R1, R3, Q2 and T2. (Mendeleev, 1891, p. 692)

In the various editions of his textbook, and in the publications dealing specifically with his predictions, Mendeleev repeatedly gives the example of calculating the atomic weight of the element selenium, a value that was known at the time and which could thus be used to test the reliability of his method.

$$S \ (32)$$

$$As \ (75) \qquad Se \qquad Br \ (80)$$

$$Te \ (127.5)$$

$(32+75+80+127.5)/4=78.65$, which is approximately the correct value for the atomic weight of Se (79).

But there are two points to stress. The first is that Mendeleev did not always operate according to this clear procedure. This is true—surprisingly enough—even in the case of some of his famous predictions. For example, if his method is applied to predict the atomic weights, atomic volumes, densities and other properties of gallium, germanium and scandium, it produces values which differ significantly from those that Mendeleev actually published. Employing Mendeleev's stated method of taking an average of the four flanking elements around gallium, for instance (using, of course, the atomic weights available at the time), gives a prediction of 70.9. Mendeleev modifies this value to 'about 69' without any form of explanation. The accepted value of the atomic weight of gallium at the time of its discovery was 69.35. Since Mendeleev did not of course know this value when he produced his table, and assuming he did not simply make a crude calculational error, this suggests that he had some further theories which operated on some occasions to 'correct' what the above method would otherwise yield. But he never divulged these extra assumptions—he seems, in other words, not to have found it necessary to specify how and why he departed from the simple method of interpolation.

The second point to be stressed about this 'simple' method is that it in fact hides a good deal of vagueness (or rather, theoretical *Spielraum*). Which other elements 'flank' a particular one depends, of course, on (i) which other elements exist, (ii) what properties (in particular, atomic weights) they possess, and (iii) how the table is constructed (in particular, when a new row was begun).

Concerning (iii): Mendeleev, as is well known, produced different tables at different times. In fact, and as already mentioned, approximately sixty-five periodic tables were devised by Mendeleev not including partial tables and simple lists of elements. These sixty-five tables consist of published as well as unpublished manu-

script forms and tables devised by Mendeleev for the purposes of giving public lectures. They show considerable variation indicating the gradual evolution of the periodic system.[25] This again shows that Mendeleev was groping his way towards the best form of the periodic table and that his method, although based, importantly, on the atomic weight ordering, was augmented by numerous, probably rather vague and certainly never fully articulated, heuristic devices.

As for (ii), Mendeleev was, as indicated, quite ready to change atomic weight assignments from those accepted at his time to avoid significant discrepancies in his tables. This may sound *ad hoc*, but in fact, and as we already pointed out, some of these 'contra-predictions' could be independently tested and their success in independent tests played an important evidential role—one which, as Brush allows, there is no reason (either historical or methodological) to suggest was any less significant than that played by the prediction of new elements.

There were more difficulties. In hindsight, Mendeleev was, of course, operating with the 'wrong' ordering principle. The 'correct' ordering principle from the point of view of later science is that based on atomic number, first shown by Moseley in 1914. The atomic weights of the various elements simply reflect purely contingent truths about the relative amounts of various isotopes of those elements in 'typical' samples from the earth. This explains why Mendeleev and his contemporaries met various difficulties. (Notice that we do not need hindsight to identify the difficulties, but only to understand the explanation of them.)

First, the sequence of non-integer atomic weights, consisting of weighted averages over all the isotopes of any particular element, is highly irregular. As a result it was not clear whether any gaps or indeed how many gaps existed between any two consecutive values of known atomic weights. This sort of problem may be illustrated by reference to any of the periods or series in the periodic table. The following data is taken from a periodic table produced by Mendeleev in 1904 and corresponds to series 4 in his scheme:

Ar=38 K=39.1 Ca=40.1 Sc=44.1 Ti=48.1 V=51.4 Cr=52.1 Mn=55

The gaps between the values of atomic weights are irregular, thus giving no clear indication as to whether one should expect any missing elements within this or other sequences of elements.

Hence, although Mendeleev in particular was committed to ordering the elements according to increasing atomic weights, the use of this 'incorrect' ordering principle (along with various other difficulties) produced much ambiguity in the prediction of missing elements—which resulted, as we already pointed out, in a whole series of failed predictions by Mendeleev about unknown elements and their properties.

One of the problems that further compounded these difficulties was the fact that many of the atomic weights with which Mendeleev was operating—that is, aside

[25]See Smith (1975), pp. 199–202 for a complete list of Mendeleev's 65 documented periodic tables.

from those that he 'corrected'—were incorrect (because of mistaken techniques and auxiliary assumptions used by his predecessors). Still further difficulties in this regard were produced by the existence of so-called 'pair reversals'. As we can see with hindsight, there are, scattered throughout the periodic table, pairs of elements E and E' (iodine and tellurium form one such pair) such that E has lower atomic weight than E' (that is, lower atomic weight when measured correctly) but, because E' has the lower atomic number (that is, the lower number of protons in its nucleus), it 'ought' to come before E in the table. As before, although hindsight is needed to identify the anomalous cases as ones of 'pair *reversals*' and also needed in order to explain why they appeared anomalous, no hindsight was needed to identify them as problems for Mendeleev's scheme. These cases can indeed be regarded as cases of *failed 'contrapredictions'*—that is, cases where Mendeleev's table would have been better served, given that he was ordering by atomic weight, if the then accepted values for atomic weights of, say, iodine and tellurium were wrong; but they were not: the problem was rather that the concept being used— that of atomic weight—is not the fundamental one that Mendeleev and his contemporaries took it to be.

In sum, there is a clear and methodologically highly significant difference between, say, Fresnel's prediction of the 'white spot' at the centre of the shadow of an opaque disc held in light diverging from a point source, and Mendeleev's prediction of the existence of new elements. In the Fresnel case (see Worrall, 1989) and others like it from physics, there is a very definite mathematically derived entailment from a precise theory. Mendeleev, on the contrary, was operating within a general and rather loose framework, underpinned by no very definite theory, and was feeling his way towards making particular predictions rather than being in possession of a theory that makes them willy nilly. This may indeed be a distinguishing mark between physics and chemistry more generally.

A further important aspect of this difference between the case of Mendeleev and the cases from physics should also be noted. While Fresnel's theory (and the general theory of relativity and so on) make precise conditional predictions—to the effect that if certain conditions are instantiated, then a certain effect will be observed—Mendeleev at best made a direct non-conditional prophecy: that there are other elements to be found; though without directing the search for them (or at any rate not directing the search in anything like such a precise way). It is true that in the Fresnel and similar cases, auxiliary assumptions are always involved in underwriting the claim that some particular experiment instantiates the relevant conditions and still further auxiliary assumptions are involved in underwriting the claim that the predicted outcome has indeed occurred. (These are aspects of the 'Duhem Problem'.) But in these cases, the theory certainly directs us quite straightforwardly towards an experiment that will—subject to these further auxiliary assumptions—be decisive as to whether or not its prediction is fulfilled. The 'predictions' made by Mendeleev, aside from the fact that they are not the logical

consequences of any well defined theory, are not of conditional form and hence involve no *direct* indications as to how they are to be verified or falsified. Mendeleev tells us that some element with a certain atomic weight and bearing certain analogies to already known elements exists—is out there to be found. The atomic weight prediction and the analogies, of course, provided investigators with important guidance;[26] but, quite unlike the normal 'predictive case' from physics there is nothing in Mendeleev's 'theory' that entails anything like as precise a statement as that if an experimenter instantiates certain conditions then the relevant element will appear. (Notice that further developments in chemistry moved the field towards the physics case. Once it is understood that what differentiates the elements is atomic number—that is, the number of protons in a nucleus—then the prediction is that there are elements (not necessarily long-lived ones) for all integer atomic numbers, and hence that new elements will be found whenever a certain number of protons, a different number from any known element, are stuck together to form a (perhaps *very* temporarily) stable configuration.)

5. Evidence and the Periodic Table

We have now assembled all the material that allows us finally to outline our own positive view of the role of evidence in the reception of Mendeleev's work.

Firstly, although we have said it several times already, it may be as well to emphasise yet again that of course we agree that the predictive successes played an important role. As we indicated earlier, Mendeleev's prediction played no part in the actual discovery of gallium, the first 'new' element. But in the case of scandium, the second new element, its discoverer, Cleve, remarked:

> The great interest of scandium is that its existence had been predicted. Mendeleef, in his memoir on the law of periodicity, had foreseen the existence of a metal which he named ekabor, and whose characteristics agree fairly well with those of scandium. (Cleve, 1879, p. 419)

Secondly, we agree with Brush that there is no doubt that the success of what he calls the 'contrapredictions'—corrections of hitherto assigned atomic weights to known elements—played an important role. We can find nothing in the historical record that suggests that the impact of the contrapredictions, amongst the relevant experts, was any less than that of the prediction of new elements. Had these contrapredictions been a question of assigning a different atomic weight to certain elements simply so that they fitted more neatly into Mendeleev's scheme, then the historical fact that they seem to have counted just as strongly for that scheme as did the novel predictions would, of course, be a counterexample to our own thesis

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[26] And other heuristic guides could kick in to give plausible, but never deductively derived, 'predictions'. (So, for example, Paneth in the 1920s used simple reasoning based on the Periodic Table to predict that then undiscovered hafnium would occur in the same ores as zirconium. This is nonetheless a considerably looser notion of prediction than applies to standard cases from physics. See Scerri, 1994).

about empirical support. However, this was not the case. It was recognised, for instance, that beryllium's assigned atomic weight made it somewhat anomalous for Mendeleev's scheme. However, far from the fact of it fitting better being the only evidence for the newly assigned value, the discovery of one of beryllium's gaseous compounds—beryllium chloride—made a recalculation of its atomic weight possible using standard methods (essentially using Avogadro's number and the known properties of chlorine). This recalculation confirmed the new value independently of any consideration connected with Mendeleev's table.

But, *thirdly*, and contrary both to Maher and Lipton's story of scepticism giving way to general credence and to Brush's more sophisticated account, the real story of the reception of Mendeleev's ideas was a complicated affair with at least the following aspects:

(a) There were elements not predicted by Mendeleev whose successful accommodation into his tables played as big a role in the reception of his ideas as the successful predictions—these included the rare earths and the noble gases; and

(b) The imprecise nature of the underlying ideas, and the highly tentative nature of the details of at least some parts of Mendeleev's table meant that there was no real sense in which the table or the ideas were 'accepted' at any stage: rather there was a tentativity about, and an evolving character to, the tables and the underlying ideas quite different from anything in the standard cases from physics; and these features clearly informed the reaction to various pieces of evidence.

5.1. Accommodation and the Periodic Table

There is strong historical counterevidence to the predictivist thesis in the form of elements—indeed two whole 'families' of them—whose existence neither Mendeleev nor anyone else had predicted and yet whose eventual 'accommodation' within his scheme provided strong evidence for it. These families are the 'rare earths' and the 'noble gases'. We can again find no suggestion in the historical sources that the impact of these successes was in any way lessened on the grounds that the elements concerned were known before being found a place in Mendeleev's scheme. Since we believe that the same methodological lessons could be drawn from the accommodation of either family of elements, and since the story of the 'noble gases' is less complex, we concentrate on it here.

The story of argon—the first of the noble gases to be identified—begins with some work by Rayleigh and Ramsay in 1894 (reported in Rayleigh and Ramsay, 1895). A specially convened meeting was held at the Royal Society on 31st January 1895 at which Rayleigh and Ramsay presented their findings and responded to criticisms and comments from a variety of major scientists at the time. The record of this meeting provides a fascinating insight into the uncertainties surrounding the evidence about argon and the periodic table.

As always, and as Mendeleev had continually stressed, the crucial quantity in placing argon in his table was its atomic weight. Atomic weight determinations, of course, require an assumption about the atomicity of the element. The molecular weight of (standard samples of) argon was fairly readily determined to be close to 40, and this would make its atomic weight 40 if argon is monatomic, 20 if it is diatomic etc. Since all gases discovered up that point—N_2, O_2, Cl_2 and so on— were diatomic and since the only example of monatomicity then known was vaporised mercury, chemists were naturally initially inclined towards the diatomic option for argon, but in any case an atomic weight of either 20 or 40 failed to fit Mendeleev's table. There seemed to be no conceivable gaps in the early part of the table for argon to fill.

One obvious suggestion was that the way that argon was standardly prepared might in fact be producing a *mixture* of gases of different atomic (or molecular) weights so that the measured molecular weight of around 40 represented merely an average. Ramsay and Rayleigh tried to investigate these issues systematically in the following way.

Clausius had shown in 1857 that if K is the translational energy of molecules of a gas and H is the total kinetic energy, then

$$K/H = 3(C_p - C_v)/2C_v$$

where C_v is the specific heat capacity of the gas at constant volume and C_p its specific heat capacity at constant volume. Rayleigh and Ramsay had arrived at values for C_v and C_p for argon based on measurements of the speed of sound through it under various conditions (Rayleigh and Ramsay, 1895).

Notice that it straightforwardly follows from Clausius's equation that if the ratio C_p/C_v is 1.66 then K/H=1, that is, K=H: all the kinetic energy of the molecules is taken up by the translation movement. Hence, such a ratio, to say the least, strongly suggests monoatomicity—since some of the energy in a polyatomic molecule would surely be taken up by rotation of the molecules about their common centre of mass. Ramsay and Rayleigh's measurements produced a value of 1.66 for the ratio C_p/C_v for argon. They—somewhat cautiously—inferred that the gas was monatomic and therefore consisted either of a single element or a mixture of elements. The caution was due to the *logical possibility* that the molecules of a polyatomic molecule might—mysteriously—never acquire any relative motion, either vibrational or rotational.

As for the issue of purity of the sample, Rayleigh and Ramsay again discuss the possibilities and the evidence rather than taking a very definite position. At the same meeting, Crookes had produced spectral evidence that was consistent with the gas being a mixture, but Rayleigh and Ramsay also reminded the meeting of Olszewski's results, which indicated sharp boiling and melting points, as well as constant pressure during boiling—all strong evidence for a single pure substance.

Rayleigh and Ramsay decided that overall 'the balance of evidence seemed to

point to simplicity'—that is, towards the ideas that their samples of argon were pure and that argon is monatomic. They explicitly pointed to the conclusion that, since this assigns a value of around 40 (in fact they gave 39.9) for the atomic weight of argon, the element cannot be fitted into the periodic table:

> If argon be a single element then there is reason to doubt whether the periodic classi-
> fication of elements is complete; whether in fact elements may not exist that cannot
> be fitted among those of which it is composed. (Rayleigh and Ramsay, 1895, p. 58)

There were certainly commentators at the Royal Society meeting who were ready to contemplate a polyatomic structure for the gas: Armstrong (1985) suggested, for example, that the gas might consist of (individually reactive) atoms so firmly bonded into molecules that it appeared inert—the atoms being 'so firmly locked in each other's embrace' that they are 'perfectly content to roll on together without taking up any of the energy that is put into the molecules'. Rucker and Kelvin (1895) and Fitzgerald (1895) were both also ready to at least contemplate this possibility (though both also saw massive difficulties), while Lord Kelvin (1895) categorically dismissed it.

It seems clear that Armstrong's motivation for taking the polyatomic structure hypothesis seriously was indeed to defend the periodic table. Even on this score, however, there is nothing of the feeling of a Kuhnian 'commitment' to a paradigm. For example, Rucker, the President of the Royal Society, while ready to consider non-rotating polyatomic molecules, was, like Rayleigh and Ramsay themselves, also ready to see the periodic table rejected if necessary:

> whatever the effect may be on the great generalisation by Mendeleef, that is, after
> all, an empirical law which is based at present on no dynamical foundation. If it holds
> its own in this case, it will, of course, strengthen our belief in it, but, on the other
> hand, I do not think that it stands on the footing of those great mechanical generalis-
> ations which could not be upset without upsetting the whole of our fundamental
> notions of science. (Rucker and Kelvin, 1895, p. 62)

Notice, then, two points in Rucker's perceptive remark: first, the successful accommodation of argon 'will, of course, strengthen our belief in' Mendeleev's scheme; second, the whole spirit is very much investigative rather than committed to Mendeleev's scheme, whose lack of a 'dynamical foundation' and therefore whose tentativity and eminent revisability are emphasised.

Unsurprisingly, Mendeleev (1895, p. 543) himself was more committed: Rayleigh and Ramsay's gas had to fit in the table somehow, and an atomic weight of 40 meant it did not fit—his favoured hypothesis was that the gas consists of triatomic nitrogen, N_3, with the hypothesis of an hexatomic element the runner-up.

The eventual resolution of the issue was that argon was fitted into a *new group* within the table, between the halogens and the alkali metals. In the meantime, the properties were being investigated of a gas first detected in 1868 by Frankland and Lockyer by spectroscopic analysis of solar radiation. Shortly after the argon episode, it was discovered that this gas, appropriately named 'helium', could be

evolved terrestrially by heating certain minerals, notably those containing uranium. This allowed empirical investigation of its properties, and it was decided, for evidential reasons unconnected with the periodic table, that it is an inert, monoatomic element with atomic weight 4—an inert 'noble gas' like argon. Helium too had to fit into the new section of the Periodic Table.

The idea of a new group within the table was suggested to Mendeleev by Ramsay during a meeting in Berlin in the spring of 1900. The suggestion was warmly welcomed by Mendeleev and was soon regarded as the solution of the argon problem and very much another feather in the Periodic Table's cap. As Mendeleev himself commented two years later:

> This was extremely important for [Ramsay] as an affirmation of the position of the newly discovered elements, and for me as a glorious confirmation of the general applicability of the periodic law.[27]

He elsewhere spoke of the 'magnificent survival' of the periodic system in what had been a 'critical test'.

Mendeleev had personal reasons for indulging in hyperbole, of course, but the general response of the chemical community does indeed seem to have been that this accommodation of argon within Mendeleev's scheme was a major feather in its cap—no less major than any other empirical success, whether predictive in the temporally novel sense or not.

The evidential weight that seems to have been accorded to the 'accommodation' of argon (and then of helium) within the Periodic Table undermines the straightforwardly pro-predictivist view that accommodations always count less than (otherwise equal) predictions. (Notice that helium in particular was first discovered in 1868—before even Mendeleev's first published paper on the Periodic Table.) But the weight accorded to this accommodation might seem equally to undermine the more nuanced view we endorsed earlier. At first sight, the accommodation of argon and helium by inventing a new group looks exactly like the sort of *ad hoc* accommodation$_2$ that we insisted ought to carry less evidential weight. Surely inventing a new group for these elements is exactly a case of 'writing already known phenomena into' a pre-accepted theory without any independent testiblity?

This may indeed appear true at first sight, but appearances are deceptive. It is not simply a question of inventing a new section of the table to fit the noble gases into; it must then also be checked that the periodicities previously noted in terms of valencies, 'analogous' properties and the like among the already accommodated elements are preserved. The atomic weights of the four newly discovered noble gases have to be such that each one would fit into a particular space in each successive period of the table. That is, each of these atomic weights had to be intermediate between two other elements in each period. In addition, this insertion of the four new elements had to result in all of them lying vertically below one another in

[27]Mendeleev (1879a); quoted from Smith (1975), p. 460.

the newly created group. These are stringent (and ultimately empirically based) constraints: it is perfectly conceivable that there was no way of placing the noble gases into the table that simultaneously satisfied all those constraints. In effect, creating a new group for the noble gases leads to a new series of predictions (in the atemporal sense) about already known analogies between elements.[28]

Indeed, as well as 'predicting' already known analogies between already known elements, this invention of a new group turned out to lead to a further temporally novel prediction—that of the existence of a third 'noble gas', neon. As Ramsay explained in his (1897) address to the British Association for the Advancement of Science (published in *Nature*), the periodicities amongst the properties of the known elements would be restored in more convincing fashion after the introduction of the new group if there were a further inert gas with atomic weight 20.[29] Neon, which indeed has an atomic weight of 20, was identified in the following year, 1898, by Ramsay himself and his co-worker Travers. There is, so far as we

[28]In a comment on a distant relative of the present paper, an anonymous referee suggested that 'the "accommodation" within the periodic table of the newly discovered facts about rare earths, noble gases ... are actually grist to the predictivist mill'. According to this referee, accommodation 'for the purposes of the predictivist/anti-predictivist debate concerns the devising of a theory to accommodate *known* facts. It does not concern the "accommodation" of *newly-discovered* facts (whether they have been explicitly predicted or not)' (italics in original). The reason why accommodation of newly [later] discovered facts, as opposed to the accommodation of already known facts, should involve no evidential discount seems to be that 'the periodic table "predicts", or rather, logically implies, that future discoveries will be found to fit with it, find "accommodation" in it', and it therefore deserves credit when this turns out to be the case.

It is easy to see that the referee's claim must be wrong. To take the example of Creationism again, many of the facts—about so-called fossils, for example—that are relevant to its rivalry with Darwinian theory were of course discovered only (long) after the basic Creationist hypothesis had been formulated. It then follows from the position advocated that, since the Creationist hypothesis in effect predicted that these future discoveries would find accommodation within it, and they indeed did via the 'Gosse dodge', that hypothesis is confirmed by those discoveries. But this is of course absurd. In general, the correctness of the Duhem thesis implies that this so-called prediction on behalf of a 'core' theory that future discoveries will be accommodatable is trivially satisfied. Given that the core theory makes no direct empirical predictions, there is always *some way* of accommodating any relevant fact that is discovered within a theoretical framework based on that core idea—that's the whole problem.

Research programmes, paradigms, theoretical frameworks—call them what you will—of course develop over time. The basic ('paradigm-forming' 'hard core') theory makes no predictions (Duhem). The issue of when some evidence was produced relative to when the hard core theory was first articulated is quite irrelevant to any confirmational question—hence the fact that argon was discovered only after Mendeleev's underlying ideas were formulated while sulphur, say, had long been known is of no significance at all. What needs to be asked *at each stage* in the development of a programme is whether the latest specific theory produced within it is, or is not, supported by various bits of evidence. The temporal view can only sensibly be understood to entail that the chief question is whether some evidence was known, not when the hard core was articulated, but rather when the specific theory that entails that evidence was first articulated. Argon had already been discovered when the specific version of the 'periodic law' that accommodates it was first produced. It nonetheless supports that 'law', not of course because it was still *un*discovered when the first version of the 'periodic law' was articulated, but instead because the particular accommodating move, leading to the particular version of the periodic law at issue was *independently testable*.

[29]This article is reprinted in Knight (1970). It gives further insight into the tentative, probing nature of prediction in this area compared to the clear-cut predictions often made by theories in physics. It is also interesting to note Ramsay's remark in this paper that 'to the general public ... novelty is often more of an attraction than truth [and consequently for them it is] the prophetic aspect [of science that] excites most interest.' (See above note 18.)

can tell, again no support in the historical record for the idea that the prediction of neon played any particularly 'crucial' role here or that it counted for any more than the 'accommodation' of argon—if anything, the contrary. In fact the whole episode of the 'accommodation of the noble gases' seems to us to underline the lack of any serious distinction between accommodation (accommodation$_1$, of course!) and prediction.

This episode did involve proposed shifts in the table and in associated theoretical ideas that indeed amount simply to writing evidence into the table—that is, to cases of accommodation$_2$. And just as we would expect, these shifts were, precisely on this account, not taken to be well supported—there was no independent evidence in their favour. For example, Rayleigh and Ramsay (1895) suggested that the gas they investigated might consist not of a single element but of a 93.3% to 6.7% mixture of elements with atomic weights 37 and 82. Needless to say the 93.3% to 6.7% split was exactly designed to give atomic weights that might fit into the table—a classic case of parameter-adjustment. (These atomic weights would in fact place the proposed two elements in the eighth group, one after chlorine and the other after bromine.) This suggestion was never taken up—precisely because the *only* evidence in its favour was accommodated$_2$ evidence.

Similarly, the hypothesis about argon that Mendeleev originally favoured—that it consists of 'superbonded' triatomic nitrogen—together with the various other 'superbonded', non-rotational polyatomic hypotheses, were not taken seriously because all that they did was save the existing periodic table from *prima facie* negative evidence: the *only* reason to think that there might be such polyatomic molecules all of whose energy was translational was that this might reconcile Rayleigh and Ramsay's data with Mendeleev's table.

Another case—quite separate from the argon affair—in which Mendeleev produced an entirely *ad hoc* non-independently testable response to an initial difficulty concerns one of his failed predictions about the properties of gallium that we mentioned briefly earlier. In his paper of 1871 Mendeleev predicted that eka-aluminium, subsequently known as gallium, would in all respects have properties intermediate between those of the elements above and below it, namely aluminium and indium. However, the melting point of gallium (30°C) is nowhere close to being intermediate between those of aluminium (660°C) and indium (155°C). In 1879 Mendeleev gave the following *ad hoc* rationalisation of the anomalously low value for gallium:

> we should pay heed to the fact that the melting-point of gallium is so low that it melts at the temperature of the hand. It might appear that this property is unexpected; but this is not so. It suffices to look at the following series—
>
> | Mg | Al | Si | P | S | Cl |
> |----|----|----|----|----|----|
> | Zn | Ga | ... | As | Se | Br |
> | Cd | In | Sn | Sb | Te | J |

It is evident that in the group Mg, Zn, Cd, the most refractory metal has the lowest atomic weight; but in the groups beginning with S and Cl, the most difficultly fusible

simple bodies are, on the contrary, the heaviest. In a transitory group such as Al, Ga, In, we must expect an intermediate phenomenon; the heaviest (In) and the lightest (Al), should be less fusible than the middle one, which is as it is in reality. I turn attention to the fact that properties such as the melting-point of bodies depend chiefly upon molecular weight, and not on atomic weight. If we were to have a variety of solid sulphur not in the form of S_6 (or, perhaps, of still heavier molecules S_n), but in the form S_2, which it assumes at 800°C, then its temperature of melting and of boiling would undoubtedly be much lower. In just the same way, ozone, O_3, condenses and solidifies much more readily than does ordinary oxygen, O_2. (Mendeleev, 1879b, p. 62)

Not only had such an argument never been given before by Mendeleev as a means of predicting trends in properties, but it also runs contrary to the spirit of his method of simple interpolation used so successfully in many other instances. Finally, the completely *ad hoc* nature of the argument is compounded by the fact that it is by no means clear that it truly represents an intermediate phenomenon to those in the other groups mentioned; nor is it clear why this contrived trend should begin at this particular place in the periodic table. In spite of his use of the word 'must' there is nothing in the least bit compelling about Mendeleev's argument. And, unsurprisingly and in agreement with the methodological thesis we defend, there is absolutely no evidence that this piece of accommodation$_2$ was considered satisfactory or as supplying any support for the periodic law.

5.2. Exploring Periodicity

We have already commented at some length on the lack of any precise version of the periodic law (the lack of a 'dynamical foundation' for the periodic classification, as Rucker put it) and indicated that this had a major impact on the way in which the relevant evidence was treated. The whole notion of the 'acceptance' of theories, even in physics, although often taken for granted by philosophers, is a complex and difficult one. But usually there is, in physics, a set of basic theories that are relatively sharp and that are taken, for some period, as relatively inviolable or at any rate as the last theories to be questioned in case the whole theoretical framework in which they are embedded runs into empirical difficulties (see, for example, Worrall, 1985a). In the case of Mendeleev's table, however, largely because of the vagueness of the underlying theoretical claims, the attitude seems always to have been more questioning and exploratory. There was some commitment to the idea that there are underlying periodicities to be found, but no commitment to any particular set of periodicities: rather these were to be discovered as a result of investigation. Hence we find a rather different attitude to evidence here than we generally do in physics.

Some indication of the differences can be found by analysing some 'criticisms ... upon the periodic classification' solicited in 1881 by the editor of the *Chemical News* from Adolphe Wurtz, a celebrated Parisian chemist of the time. (Wurtz's note follows notes from Mendeleev and from Lothar Meyer forming their famous priority dispute.)

Wurtz (1881, p. 16) allowed that Mendeleev's system forms a 'powerful generalisation and must in future be taken into account whenever we regard the facts of chemistry from a lofty and comprehensive point of view'. However, he pointed out that the system still contained many imperfections—the rare earths in particular at that time had no satisfactory home in the system. He also pointed out a problem with tellurium and iodine, whose atomic weight ordering is inconsistent with their chemical properties (one of the problems caused, as we can see in hindsight, by the fact that atomic number rather than atomic weight yields the important ordering principle). Moreover, cobalt and nickel have almost identical atomic weights and so their properties ought, on Mendeleev's scheme, to coincide—quite contrary to the truth. He added that the alleged gradations in properties did not in fact progress smoothly or regularly as Mendeleev would have had us believe.

Wurtz then turned specifically to an analysis of the famous predictions:

> In Mendelejeff's table we are chiefly struck with the gaps between two elements, the atomic weights of which show a greater difference than two or three units, thus marking an interruption in the progression of the atomic weights. Between zinc (64.9) and arsenic (74.9) there are two, one of which has been lately filled up by the discovery of gallium. But the considerations by which Lecoq de Boisbaudran was led in the search for gallium have nothing in common with the conception of Mendelejeff. Though gallium has filled up a gap between zinc and arsenic, and though other intervals may be filled up in future, it does not follow that the atomic weights of such new elements will be those assigned to them by this principle of classification. The atomic weight of gallium is sensibly different from that predicted by Mendelejeff. It is also possible that the future may have in reserve for us the discovery of a new element whose atomic weight will closely coincide with that of a known element, as do the atomic weights of nickel and cobalt. Such a discovery would not fill any foreseen gap. If cobalt were unknown it would not be discovered in consequence of Mendelejeff's classification. (Wurtz, 1881, p. 16)

Wurtz's point about cobalt and nickel is well taken: given that classification was by atomic weight there would have been no basis for the prediction of two elements between iron and copper, had neither cobalt or nickel been known, and no basis for predicting the existence of the other had only one of them been known.

His whole attitude is also, it seems to us, well justified and reflects quite well a general view: Mendeleev is 'on the right track' at a very general level, but the details are unreliable. Given this, all predictions are to some extent 'shots in the dark'—in this situation neither predictive successes nor predictive failures (as we noted, there were many of these) are as significant as they might otherwise be and as they generally are in science. And indeed, the historian Brock (1992, p. 325) refers to Mendeleev's vaunted predictive successes as 'fortuitous guesses'; while his failures, 'like astrologers' failures are commonly forgotten'. Perhaps they did tend to be forgotten later by some historians—hagiography makes for gripping, if scarcely accurate, history; but there is no evidence that they were not noted and taken into account at the time.

In sum,

(i) there is no support from this episode for any temporal version of predictivism: we saw earlier that the famous three predictions of new elements, while certainly important, were very much only part of the story and we have seen now that the successful accommodation of the noble gases (and also the rare earths) also formed important evidence for the ideas underlying Mendeleev's scheme;

(ii) there *is* support for the important distinction being between accommodation$_2$, on the one hand, and *either* accommodation$_1$ *or* prediction on the other: the successful prediction of the new elements, the 'contrapredictions' of revised atomic weights, and the accommodation$_1$ of the noble gases and rare earths were all treated as definite successes for the scheme—more or less on a par, so far as we can see; while various non-independently testable accommodations—such as the suggestion that argon might be a mixture of two gases each of which individually fitted the original Mendeleev table—were correspondingly downgraded; and

(iii) there are interesting differences in the impact of evidence in this case compared with the standard cases from the history of physics that have previously been analysed in the attempt to shed light on the predictivism issue: these result from the relative vagueness of the 'periodic law' underlying Mendeleev's table and involve, amongst other things, greater tentativity and greater tolerance of predictive failure than in those other cases, and a corresponding (relative) downgrading of predictive success.

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LOWDIN'S REMARKS ON THE AUFBAU PRINCIPLE AND A PHILOSOPHER'S VIEW OF AB INITIO QUANTUM CHEMISTRY.

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1. Introduction.

It is indeed a great honor to be invited to contribute to this memorial volume. I should say from the outset that I never met Löwdin but nevertheless feel rather familiar with at least part of his wide-ranging writing. In 1986 I undertook what I believe may have been the first PhD thesis in the new field of philosophy of chemistry. My topic was the question of the reduction of chemistry to quantum mechanics. Not surprisingly this interest very soon brought me to the work of Löwdin and in particular his analysis of rigorous error bounds in ab initio calculations (Löwdin, 1965).
I later discovered a short article in which Löwdin made some interesting remarks that resonated with me (Löwdin, 1969).

> The energy rule for the neutral atoms was obviously in contradiction to Bohr's calculation on the hydrogen atom, which indicated that the energies should be increasing with increasing n. It is typical of the nature of "frontier-research" that Bohr abandoned this rule for the higher atoms, since it led to the wrong structure of the periodic system, and the modified rule $[(n + \ell, n)]$ seems to have been obtained in a more intuitive way. Bohr himself was never too explicit about his "Aufbau" -principle, and [the rule] is sometimes referred to as the Goudsmit-rule or the Bose-rule. It is perhaps remarkable that, in axiomatic quantum

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theory, the simple energy rule has not yet been derived from first principles. (p.332).

Bohr's quantum numbers (n, ℓ, m) have fully entered chemistry, and every chemistry student learns about the symbols *1s, 2s, 2p, 3s, 3p, 3d* etc. It is hence a startling fact that the simple energy rule has not entered any major chemistry textbooks, as far as I know, and it is still this rule which gives the first explanation of the occurrence of the transition metals, the rare-earth metals, and the over-all structure of the electronic shells of atoms. (p.334).

It would certainly be worth while to study the energy rule from first principles, i.e. on the basis of the many-electron Schrödinger equation. (p.334).

In the case of the second excerpt I think I can safely say that Löwdin is wrong. The simple energy rule regarding the order of filling of orbitals in neutral atoms has now entered *every* textbook of chemistry, although his statement may have been partly true in 1969 when he wrote his article.[1] Although Löwdin can be excused for not knowing what was in chemistry textbooks I think it is also safe to assume that he is correct in his main claim that this important rule has not been derived. Nor as I have claimed in a number of brief articles has the rule been derived to this day (Scerri, 1998).

The examination of this idea has subsequently formed an integral part of my research in the philosophy of chemistry. This has also led to a certain amount of disagreement with other authors who appear to interpret Löwdin's remark in a somewhat different manner (Ostrovsky, 2001). I now deeply regret not having contacted Löwdin directly in order to seek his own clarification. In the present contribution I intend to revisit this question and to take the opportunity to respond to some critics as well as hopefully injecting some new ideas into the discussion.

2. General approach of this study and ab initio calculations in science generally.

Quantum Mechanics has been the most spectacularly successful theory in the history of science. As is often mentioned the accuracy to which the anomalous magnetic moment of the electron can be calculated is a staggering nine decimal places. Quantum Mechanics has revolutionized the study of radiation and matter since its inception just over one hundred years ago. The impact of the theory has been felt in

such fields as solid state physics, biochemistry, astrophysics, materials science and electronic engineering not to mention chemistry.

Quantum Mechanics offers the most comprehensive and most successful explanation of many chemical phenomena such as the nature of valency and bonding as well as chemical reactivity. It has also provided a fundamental explanation of the periodic system of the elements which summarizes a vast amount of empirical chemical knowledge. Quantum Mechanics has become increasingly important in the education of chemistry students. The general principles provided by the theory mean that students can now spend less time memorizing chemical facts and more time in actually thinking about chemistry.

My project is not to critique of the power of quantum chemistry that I regard to be a self-evident fact. But with the triumph of quantum mechanics I believe there has been some tendency to exaggerate its success, especially on the part of some practicing quantum chemists and physicists. As a philosopher of chemistry I have the luxury of being able to examine the field as an outsider and of asking the kinds of questions which true practitioners might not even contemplate. The approach I take in this article is a philosophical one in the sense that I am concerned with principles and not just with technical details, although I try to be as accurate as possible with the latter.

Quantum mechanics is part of the reductionist tradition in modern science, and the general claim, often just made implicitly as in any branch of reduction, is that the highest ideal one can aspire to is to derive everything from the theoretical principles. The less experimental data one needs to appeal to, the less one is introducing measured parameters the purer the calculation and the closer it approaches to the ideal of Ockham's razor of being as economical as possible (Hoffman, Minkin, Carpenter, 1996).[2]

Of course there is no such thing as a completely *ab initio* calculation and if one looks far enough back at the history of any scientific theory one finds that it began with the assumption of at least some experimental data. But it is also fair to say that once the basic principles of a theory have been arrived at the theorist may 'kick away' the historical-experimental scaffolding. The modern student of quantum mechanics, for example, is not obliged to follow the tortuous route taken by Planck, Einstein, De Broglie, Schrödinger and others. She can go directly to the postulates of quantum mechanics where she will find a procedure for doing all kinds of calculations and she can safely ignore the historical heritage of the theory. Indeed many argue, and correctly in my view, that it is actually a hindrance for the practitioner to get too involved in the historical aspects of the theory although it may of course be culturally enriching to do so.

The epitome of the ab initio approach in science is something like Euclidean geometry where one begins with a number of axioms and one derives everything from this starting point without any recourse whatsoever to empirical data. Needless to say geometry, Euclidean or otherwise, has its origins in the dim distant past when agrarian people needed to think about lines and angles and areas of land. But once the concepts of line, angle and distance had been sufficiently abstracted the agrarian heritage could be completely forgotten.

In a similar way, my question in this article will be to be to ask to what extent the periodic table of the elements can be explained strictly from first principles of quantum mechanics without assuming any experimental data whatsoever. I suspect that some readers and fellow contributors to this volume might well experience some irritation at the almost perverse demands which I will make on what should be derivable from the current theory. If so, then I apologize in advance.

By adopting a perspective from the philosophy of science I will attempt to cross levels of complexity from the most elementary chemical explanations based on electron shells to those based on ab initio methods. Such a juxtaposition is seldom contemplated in the chemical literature. Textbooks provide elementary explanations which necessarily distort the full details but allow for a more conceptual or qualitative grasp of the main ideas. Meanwhile the research literature focuses on the minute details of particular methods or particular chemical systems and does not typically examine the kind of explanation that is being provided. To give a satisfactory discussion of explanation in the context of the periodic table we need to consider both elementary and deeper explanations within a common framework.

One of the virtues of philosophy of science is that it can bridge different levels in this way since it primarily seeks the 'big picture' rather than the technical details. In fact supposedly elementary explanations often provide this big picture in a more direct manner. Of course what is also needed is to connect the elementary explanation to the technical details in the deeper theories.

The question of whether or not different levels of explanation for any particular scientific phenomenon are in fact consistent and whether they form a seamless continuum has been the subject of some debate. For example the philosopher of science Nancy Cartwright goes to some lengths to argue that many different explanations can be found for the action of lasers and suggests that these explanations are not necessarily consistent with each other (Cartwright, 1983). In other writings she has expressed some support for the thesis that the various special sciences are dis-unified (Galison, Stump, 1996).

My own view differs from Cartwright's in that I think that the sciences are unified and that explanations given for the same scientific

phenomenon at different levels are essentially consistent, although the connection if frequently difficult to elaborate in full (Scerri, 2000). In this paper I will attempt to draw such connections for the various explanations of the periodic table given at different levels of sophistication. Another way of regarding the present project is to consider typical 'chemical explanations', full of visualizations and sometimes naïve realism, and contrast them with the more abstract mathematical explanations favored by the theorist.

3. What do the terms ab initio and first principles really mean in current quantum chemistry?

It is interesting to consider the meanings of the terms of "ab initio" calculations as well as the closely related term "first principles calculations". How are these terms currently used by the computational chemistry community? Do these terms mean the same thing?

The answer to this question as well as the question of the precise meaning of the term ab initio itself in the context of quantum chemistry seems to differ considerably according to the particular researcher that one might consult.[3] Some authors I have questioned claim that the two terms are used interchangeably to mean calculations performed without recourse to any experimental measurement. This would include Hartree-Fock, and many of the DFT functionals, along with quantum Monte Carlo and CI methods.

Others report that the term first principles is being increasingly used because the Latin term "ab initio" can been seen as unnecessarily elitist and that there is no scientific significance in using one term rather than the other one. Others disagree, suggesting that first principles is favored by the DFT community since in this kind of work it is quite clear that some semi-empirical elements are introduced whereas the wavefunction or traditional ab initio approaches are less semi-empirical.

Turning to the question of exactly what is implied by the term ab initio, I have encountered an even larger variety of opinions. According to some sources the origin of the term is purely accidental. They claim that the term was originally applied to the Roothaan-Hall approach through an amusing accident. Robert Parr was apparently collaborating in some work of this kind with a group in England and in reporting one of his calculations, is said to have described it as "ab initio", implying that the whole of that particular project had been carried out from the beginning in his laboratory. Very soon the term was being used for all kinds of accurate theoretical work which, at least at first sight, did not involve any fixing of paramenters.

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Regarding current ab initio calculations it is probably fair to say that they are not really ab initio in every respect since they incorporate many empirical parameters. For example, a standard HF/6-31G* calculation would generally be called "ab initio", but all the exponents and contraction coefficients in the basis set are selected by fitting to experimental data. Some say that this feature is one of the main reasons for the success of the Pople basis sets. Because they have been fit to real data these basis sets, not surprisingly, are good at reproducing real data. This is said to occur because the basis set incorporates systematical errors that to a large extent cancel the systematical errors in the Hartree-Fock approach. These features are of course not limited to the Pople sets. Any basis set with fixed exponent and/or contraction coefficients have at some point been adjusted to fit some data. Clearly it becomes rather difficult to demarcate sharply between so-called ab initio and semi-empirical methods.[4]

To some other experts the meaning of the term ab initio is rather clear cut. Their response is that "ab initio" simply means that all atomic/molecular integrals are computed analytically, without recourse to empirical parametrization. They insist that it does not mean that the method is exact nor that the basis set contraction coefficients were obtained without recourse to parametrization. Yet others point out that even the integrals need not be evaluated exactly for a method to be called ab initio, given that, for instance, Gaussian employs several asymptotic and other cutoffs to approximate integral evaluation.
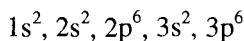
But regardless of these disagreements as to what exactly the term ab initio means I want to presume to define a new term that I shall call "super ab initio". In the rest of this article I would like to suggest the kind of explanations which might be possible when we arrive at the point of being able to perform super-ab initio calculations in which no feature whatsoever is introduced by recourse to experimental data. This will be done especially regarding attempts to explain, or reduce, the periodic system of the elements by using quantum mechanics.

4. First the elementary approach.
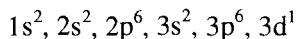
Let us start at an elementary level or with a typically "chemical" view. Suppose we ask an undergraduate chemistry student how quantum mechanics explains the periodic table. If the student has been going to classes and reading her book she will respond that the number of outer-shell electrons determines, broadly speaking, which elements share a common group in the periodic table. The student might possibly also add that the number of outer-shell electrons causes elements to behave in a particular manner.

Suppose we get a little more sophisticated about our question. The more advanced student might respond that the periodic table can be explained in terms of the relationship between the quantum numbers which themselves emerge from the solutions to the Schrödinger equation for the hydrogen atom.[5]
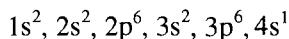
But does the fact that the third shell can contain 18 electrons, for example, which emerges from the relationships among the quantum numbers, also explain why some of the periods in the periodic system contain eighteen places? Actually not exactly. If electron shells were filled in a strictly sequential manner there would be no problem and the explanation would in fact be complete. But as everyone is aware, the electron shells do not fill in the expected sequential manner. The configuration of element number 18, or argon is,

$$1s^2, 2s^2, 2p^6, 3s^2, 3p^6$$

This might lead one to think that the configuration for the subsequent element, number 19, or potassium, would be

$$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^1$$

since, up to this point, the pattern has been to add the new electron to the next available orbital in the sequence of orbitals at increasing distances from the nucleus. However spectroscopic evidence shows quite clearly that the configuration of potassium should be denoted as,

$$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$$

As many textbooks state this can be explained from the fact that the 4s orbital has a lower energy than the 3d orbital. In the case of element 20 or calcium the new electron also enters the 4s orbital and for the same reason.

5. Transition metal configurations.

The interesting part is what happens next. In the case of the following element, number 21, or scandium, the orbital energies have reversed so that the 3d orbital has a lower energy. Textbooks almost invariably claim that since the 4s orbital is already full there is no choice but to begin to occupy the 3d orbital. This pattern is supposed to continue across the first transition series of elements, apart from the elements Cr and Cu where further slight anomalies are believed to occur.

In fact this explanation for the configuration of the scandium atom and most other first transition elements is inconsistent. If the 3d

orbital has a lower energy than 4s starting at scandium then, if one were really filling the orbitals in order of increasing energy, one would expect that all three of the final electrons would enter 3d orbitals. The argument which most textbooks present is incorrect since it should be possible to predict the configuration of an element from a knowledge of the order of its own orbital energies (Scerri, 1989, Vanquickenborne, 1994). It is incorrect to consider the configuration of the previous element and assume that this configuration is carried over intact on moving to the next element, especially in cases where orbital energies cross over each other as they do in this case. It should be possible to predict the order of orbital filling for the scandium atom on its own terms. If one tries to do so however one predicts a configuration ending in $3d^3$ contrary to the experimental facts.

The full explanation of why the $4s^2 3d^1$ configuration is adopted in scandium, even though the 3d level has a lower energy, emerges from the peculiarities of the way in which orbital energies are defined in the Hartree-Fock procedure. The details are tedious but have been worked out and I refer anyone who is interested in pursuing this aspect to the literature (Melrose, Scerri, 1996).[6,7]

6. How are configurations derived from the theory?

But let me return to the question of whether the periodic table is fully and deductively explained by quantum mechanics. In the usually encountered explanation one assumes that at certain places in the periodic table unexpected orbital begins to fill as in the case of potassium and calcium where the 4s orbital begins to fill before the 3d shell has been completely filled. This information itself is not derived from first principles. It is justified *post facto* and by some tricky calculations (Melrose, Scerri, 1996; Vanquickenborne, Pierloot, Devoghel, 1994).

But if we ignore the conceptual paradox of why 4s fills preferentially even though it has a higher energy than 3d we can just concentrate on calculations aimed at determining the ground state configuration. The Hartree-Fock method[8] can be used to compare the energies of the scandium atom with two alternative configurations, [Ar] $4s^2 3d^1$ and [Ar] $4s^1 3d^2$.

configuration $4s^2 3d^1$

Non-Relativistic -759.73571776 (in Hartrees)
Relativistic   -763.17110138

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configuration $4s^1\ 3d^2$

Non-Relativistic   -759.66328045
Relativistic   -763.09426510

It would appear that both non-relativistic and relativistic ab initio calculations correctly compute that the $4s^2$ configuration has the lowest energy in accordance with experimental data. But these calculations, including the ones for subsequent elements must be done on a case-by-case basis. As Löwdin has pointed out, there is not yet a general derivation of the formula which governs the order of filling, that is the $n + \ell$, or Madelung rule, which states that given a choice of filling any two orbitals the order of filling goes according to increasing values of $n + \ell$.

But similar calculations do not fare as well in other atoms. Consider the case of the chromium atom for example.[9]

configuration $4s^1\ 3d^5$

Non-Relativistic   -1043.14175537
Relativistic   -1049.24406264

configuration $4s^2\ 3d^4$

Non-Relativistic   -1043.17611655
Relativistic   -1049.28622286

It appears that both non-relativistic and relativistic calculations at this level of accuracy fail to predict the experimentally observed ground state which is the $4s^1\ 3d^5$ configuration. Of course I do not deny that if one goes far enough in a more elaborate calculation then eventually the correct ground state will be recovered. But in doing so one knows what one is driving at, namely the experimentally observed result. This is not the same as strictly predicting the configuration in the absence of experimental information.

In addition, if one goes beyond the Hartree-Fock approximation to something like the configuration interaction approach there is an important sense in which one has gone beyond the picture of a certain number of electrons into a set of orbitals.[10] If one insists on picturing this, then rather than just every electron being in every possible orbital

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in the ground state configuration, every electron is now in every one of the orbitals used to express the thousands or even millions of contributing configurations.

But I want to return to my claim that quantum mechanics does not really explain the fact that the third row contains 18 elements to take one example. The development of the first of the period from potassium to krypton is not due to the successive filling of 3s, 3p and 3d electrons but due to the filling of 4s, 3d and 4p. It just so happens that both of these sets of orbitals are filled by a total of 18 electrons. This coincidence is what gives the common explanation its apparent credence in this and later periods of the periodic table. As a consequence the explanation for the form of the periodic system in terms of how the quantum numbers are related is semi-empirical, since the order of orbital filling is obtained form experimental data. This is really the essence of Löwdin's quoted remark about the $(n + \ell, n)$ rule.

| *Closing of shells,* |
| Occurs at Z = 2, 10, 28, 60, 110, etc. |
| |
| *Closing of periods,* |
| Occurs at Z = 2, 10, 18, 36, 54, etc. |

It is the second sequence of Z values shown above that really embodies the periodic system and not the first.[11] For all we know electron shells or orbitals may not even exist or may be replaced by some other concept in a future theory. But the fact that chemical repetitions occur at Z = 2, 10 18, 36, for example, are chemical facts which will never be superceded.

Only if shells filled sequentially, which they do not, would the theoretical relationship between the quantum numbers provide a purely deductive explanation of the periodic system. The fact the 4s orbital fills in preference to the 3d orbitals is not predicted in general for the transition metals but only rationalized on a case by case basis as I have argued. Again, I would like to stress that whether or not more elaborate calculations finally succeed in justifying the experimentally observed ground state does not fundamentally alter the overall situation.[12]

To sum-up, we can to some extent recover the order of filling by calculating the ground state configurations of a sequence of atoms but nobody has yet deduced the n + ℓ rule from the principles of quantum mechanics.[13]

7. Choice of basis set.

There is another general problem which mars any hope of claiming that electronic configurations can be fully predicted theoretically and that quantum mechanics thus provides a purely deductive explanation of what was previously only obtained from experiments. In most of the configurations we have considered, with the exception of cases mentioned above, it has been possible to use a quantum mechanical method to calculate that this particular configuration does indeed represent the lowest energy possibility. However, in performing such calculations the candidate configurations which are subjected to a variation procedure are themselves obtained from the aufbau principle and other rules of thumb such as Hund's principle or by straightforward appeal to experimental data. There is a very simple reason for this state of affairs. The quantum mechanical calculations on ground state energies involve the initial selection of a basis set, which in its simplest form is the electronic configuration of the atom in question.

Quantum mechanical calculations are not capable of actually generating their own basis sets that must therefore be put in "by hand". So whereas the correct ground state electronic configurations can in many cases be selected among a number of plausible options, the options themselves are not provided by the theory. I suggest this is another weakness of the present claims to the effect that quantum mechanics explains the periodic system and it is an aspect that might conceivably corrected by future developments.[14]   In addition the commonly used basis sets are almost invariably constructed in a semi-empirical manner by reference to experimental data on some particular chemical system. This is rather undeniable given that the exponents and contraction coefficients in the basis set are generally selected by fitting to experimental data as mentioned above in section 3.[15]

8. Qualitative explanation of PT in terms of electrons in shells.

I will now attempt to take stock of the various senses of the claim that the periodic system is reduced, or fully explained, by quantum mechanics and to extend the scope of this work to more elaborate theoretical approaches. As any student of chemistry knows, the approximate recurrence of elements after certain regular intervals is explained by the possession of a certain number of outer-shell

electrons. This form of explanation appears to be quantitative to some people because it deals in number of electrons but in fact turns out to be rather qualitative. It cannot of course be used to predict quantitative data on a particular atom with any degree of accuracy.

Whereas the crude notion of a particular number of electrons in shells or orbitals does not produce very accurate calculations the process can be refined in several well known ways. The first refinement is perhaps the use of the Hartree method of calculating self-consistent orbitals while at the same time minimizing the energy of the atom.[16] The next refinement lies in making the method consistent with the notion that electrons are indistinguishable. By appealing to the Hartree-Fock method and by performing a permutation of all the electrons in the atom each electron finds itself simultaneously in all occupied orbitals at once to put it in pictorial terms. A third refinement might be to include any number of excited state configurations for the atom, in a configuration interaction calculation. Having reached this level of abstraction we have really left behind the homely picture of electrons in particular shells. If one still insists on visualization, each electron is now in every orbital of every single configuration which we choose to consider.

There is still a connection with the elementary homely model but it is also fair to say that the move towards greater abstraction has somewhat invalidated the naïve model. This now raises the question as to whether the elementary model really does have explanatory power. I would argue that it does not. It may have led historically to these more sophisticated approaches but it has been rendered vastly more abstract in the process. But if we are considering the general question of explanation it is not essential to retain the homely picture that can be grasped by the general chemist of the beginning student of physical chemistry. We must move on to enquire about how the more abstract approaches actually fare. The short answer I believe is much better but still not in strictly, or super, ab initio fashion.

9. Ab initio calculations based on wavefunctions.

Of course the Hartree-Fock method and the configuration interaction approaches fare much better and are a serious contenders for the claim of a full explanation of the periodic system than the elementary and qualitative notion of electrons in shells.

Within these ab initio approaches the fact that certain elements fall into the same group of the periodic table is not explained by recourse to the number of outer-shell electrons. The explanation lies

in calculating the magnitude of a property such as the first ionization energy and seeing whether the expected periodicity is recovered in the calculations. For example Clementi shows a diagram of the experimental ionization energies for the first 53 elements in the periodic table, along with the values calculated using ab initio quantum mechanical methods (Clementi, 1980, p. 12). The periodicity is captured remarkably well, even down to the details of the anomalous sections of the graph occurring between elements in groups II and III in each period of the table where ionization energies show a decrease with increasing Z. Clearly the accurate calculation of atomic properties can be achieved by the theory. The quantum mechanical explanation of the periodic system within this approach represents a far more impressive achievement than merely claiming that elements fall into similar groups because they share the same number of outer-electrons.

And yet in spite of these remarkable successes such an ab initio approach may still be considered to be semi-empirical in a rather specific sense. In order to obtain calculated points shown in the diagram the Schrödinger equation must be solved separately for each of the 53 atoms concerned in this study. The approach therefore represents a form of "empirical mathematics" where one calculates 53 individual Schrödinger equations in order to reproduce the well known pattern in the periodicities of ionization energies. It is as if one had performed 53 individual experiments, although the "experiments" in this case are all iterative mathematical computations. This is still therefore not a general solution to the problem of the electronic structure of atoms.

10. Density Functional Approach.

In 1926 Llewellyn Thomas proposed treating the electrons in an atom by analogy to a statistical gas of particles. Electron-shells are not envisaged in this model, which was independently rediscovered by Enrico Fermi two years later. For many years the Thomas-Fermi method was regarded as a mathematical curiosity without much hope of application since the results it yielded were inferior to those obtained by the method based on electron orbitals.[17]

On the other hand the Thomas-Fermi method, which treats the electrons around the nucleus as a perfectly homogeneous electron gas, yields a mathematical solution that is universal, meaning that it can be solved once and for all. This feature already represents an improvement over the method which seeks to solve Schrödinger equation for every atom separately. This was one of the features that made people go back to the Thomas-Fermi approach in the hope of

making progress. As is well known much progress has now been achieved and the current density functional theories, that are modern descendants of the Thomas-Fermi method have become as powerful as methods based on orbitals and wavefunctions and in many cases can outstrip the wavefunction approaches in terms of computational accuracy.

An important conceptual, or even philosophical, difference between the orbital/wavefunction methods and the density functional methods is that, at least in principle, the density functional methods do not appeal to orbitals. In the former case the theoretical entities are completely unobservable whereas electron density invoked by density functional theories is a genuine observable. Experiments to observe electron densities have been routinely conducted since the development of X-ray and other diffraction techniques (Coppens, 2001).[18]

Meanwhile orbitals cannot be observed either directly, indirectly since they have no physical reality contrary to the recent claims in Nature magazine and other journals to the effect that some d orbitals in copper oxide had been directly imaged (Scerri, 2000). Orbitals as used in ab initio calculations are mathematical figments that exist, if anything, in a multi-dimensional Hilbert space.[19] Electron density is altogether different since it is a well-defined observable and exists in real three-dimensional space, a feature which some theorists point to as a virtue of density functional methods.

11. Density Functional Theory in Practice.

But alas most of what has been described so far concerning density theory applies in theory rather than in practice. The fact that the Thomas-Fermi method is capable of yielding a universal solution for all atoms in the periodic table is a potentially attractive feature but is generally not realized in practice. The attempts to implement the ideas originally due to Thomas and Fermi have not quite materialized. This has meant a return to the need to solve a number of equations separately for each individual atom as one does in the Hartree-Fock method and other ab initio methods using atomic orbitals.

In addition most of the more tractable approaches in density functional theory also involve a return to the use of atomic orbitals in carrying out quantum mechanical calculations since there is no known means of directly obtaining the functional that captures electron density exactly.[20] The work almost invariably falls back on using basis sets of atomic orbitals which means that conceptually we are back to square one and that the promise of density functional methods to work with observable electron density, has not materialized.

To make matters worse, the use of a uniform gas model for electron density does not enable one to carry out good calculations. Instead a density gradient must be introduced into the uniform electron gas distribution. The way in which this has been implemented has typically been in a semi-empirical manner by working backwards from the known results on a particular atom, usually the helium atom (Gill, 1998). It has thus been possible to obtain an approximate set of functions which often serve to give successful approximations in other atoms and molecules. As far as I know, there is no known way of yet calculating, in an ab initio manner, the required density gradient which must be introduced into the calculations.

By carrying out this combination of semi-empirical procedures and retreating from the pure Thomas-Fermi notion of a uniform electron gas it has actually been possible, somewhat surprisingly, to obtain computationally *better* results in many cases of interest than with conventional ab initio methods. True enough, calculations have become increasingly accurate but if one examines them more closely one realizes that they include considerable semi-empirical elements at various levels. From the purist philosophical point of view, or what I call "super - ab initio" this means that not everything is being explained from first principles.

As readers of this volume are also aware, the best of both approaches have been blended together with the result that many computations are now performed by a careful mixture of wavefunction and density approaches within the same computations (Hehre et al., 1986). But the unfortunate fact is that, as yet, there is really no such thing as a pure density functional method for performing calculations. The philosophical appeal of a universal solution for all the atoms in the periodic table based on observable electron density, rather than fictional orbitals, has not yet borne fruit.[21, 22]

12. Conclusions.

My aim has not been one of trying to decide whether or not the periodic system is explained by quantum mechanics. Of course broadly speaking quantum mechanics does provide an excellent explanation and certainly one better than was available using only classical mechanics. But the situation is more subtle.

Whereas most chemists and educators seem to believe that all is well, I think that there is some benefit in pursuing the question of how much is strictly explained from the theory. It is indeed something of a miracle that quantum mechanics explains the periodic table to the

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extent that it does at present. But we should not let this fact seduce us into believing that it is a completely ab initio explanation. We have not yet arrived at the super – ab initio phase of quantum chemistry and nor are we even close. If anything, the compromises that have been struck with the acceptance of parametrization as well as the mixing of wavefunction and DFT approaches begin to question the earlier promise of ab initio quantum chemistry.

One thing that is sure is that the attempt to explain the details of the periodic table continues to challenge the ingenuity of quantum physicists and quantum chemists. For example, a number of physicists are trying to explain the periodic table by recourse to group theoretical symmetries in combination with quantum mechanics (Ostrovsky, 2001). Meanwhile Dudley Herschbach and colleagues have worked on a number of approaches which aim at obtaining a global solution to the energies of the atoms in the periodic table by drawing analogies with the work of physicists on second-order phase transitions (Kais, Sung, Herschbach, 1994)

But to return to the general question of explaining the periodic table, perhaps philosophers of chemistry have a role to play here. Unconstrained by what can presently be achieved, or even what might be achieved in the foreseeable future, one can point out the limitations of the current state of the art. One may thereby place the research in the wider context of scientific reductionism in general and what it might mean for a calculation to be really ab initio. This is not a denial of the progress achieved in quantum chemistry but is more of an unrestrained look at what more could conceivably be done. Of course this might require a deeper theory than quantum mechanics or maybe a cleverer use of the existing theory. There is really no way of telling until the next significant advance has been achieved.

NOTES

[1]   I doubt whether Löwdin's claim was even true of textbooks in 1969, although I have not conducted any survey on this point.

[2]   Although actually in this article Hoffman et al. argue that using Ockham's razor may not always be the ideal approach to take in chemistry.

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3   I would like to thank the many subscribers to the Computational Chemistry Listserver (CCL) who responded to my questions on this topic.

4   Meanwhile others object to the suggestion that the optimization of basis sets are carried out by reference to experimental data. While accepting that the exponents and contraction coefficients are generally optimized in atomic calculations, they insist that these optimizations are in themselves ab initio.

5   In fact the fourth quantum number does not emerge from solving Schrödinger's equation. It was initially introduced for experimental reasons by Pauli, as a fourth degree of freedom possessed by each electron. In the later treatment by Dirac the fourth quantum number emerges in a natural manner but the extension of this theory to many-electron system has proved to be difficult. The Schrödinger approach is still the most commonly used one. Spin is thus generally added to the functions derived from the Schrödinger equation.

6   It is gratifying to see that this article has now been cited by about ten chemistry textbooks including those by Atkins, Huheey, Levine, Zumdahl etc.

7   Very briefly, the issue is resolved by recognizing that the energies of the 4s and 3d orbitals vary depending on the configuration in question (Melrose, Scerri, 1996).

8   In a recent paper Ostrovsky has criticized my claiming that electrons cannot strictly have quantum numbers assigned to them in a many-electron system (Ostrovsky, 2001). His point is that the Hartree-Fock procedure assigns all the quantum numbers to all the electrons because of the permutation procedure. However this procedure still fails to overcome the basic fact that quantum numbers for individual electrons such as ℓ in a many-electron system fail to commute with the Hamiltonian of the system. As aresult the assignment is approximate. In reality only the atom as a whole can be said to have associated quantum numbers, whereas individual electrons cannot.

9   These calculations were carried out using the Internet web pages constructed by Charlotte Froese-Fischer, http://hf5.vuse.vanderbilt.edu/hf.html

10 Broadly speaking it is still an orbital based method of course but not one that corresponds to the elementary concept of a particular number of electrons in the shells of an atom.

11 I thank Professor Henry Bent for pointing out an error in an earlier draft of this paper.

12 Although the C.I. approach it is capable of calculating the energy of the entire atom, given that the calculation involves a mixture of so many different configurations, it could be argued that it does not calculate the ground state configuration as such. In any case this will depend on the weighting coefficients which result from each calculation.

13 Of course the calculations can be improved by adding extra terms until this failure is eventually corrected. However, these additional measures are only taken after the facts are known. In addition, the lengths to which theoreticians are forced to go to in order to obtain the correct experimental ordering of terms

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does not give one too much confidence in the strictly predictive power of quantum mechanical calculations in the context of the periodic table. For example, the very accurate calculations on nickel include the use of basis sets which extend up to 14s, 9p, 5d as well as f orbitals (Raghavachari, Trucks, 1989).

[14] It is not inconceivable that this procedure could be automated but I am not aware that it has yet.

[15] Details can be found in chapter 4 of the book by Hehre et al. as cited in the references. As a further aside, it is worth noting that despite of the title of this book which is "Ab Initio Molecular Orbital Theory", the authors admit on the very first page that most of the book is devoted to calibrated work!

[16] I am doing a certain amount of back-tracking given that this method was mentioned above when some results were quoted for tranition metals.

[17] Edward Teller showed that the Thomas-Fermi method cannot predict binding in atoms.

[18] This is why I and some others have been agitating about the recent reports, starting in Nature magazine in September 1999, that atomic orbitals had been directly observed. This is simply impossible unless one is using the word "orbital" rather perversely to mean charge density (Scerri, 2000).

[19] I have tried to stress the educational implications of the claims for the observation of orbitals in other articles and will not dwell on the issue here (Scerri, 2000 in Science and Education).

[20] The fact that an exact density functional exists is known from a theorem proved by Hohenberg and Sham and Kohn. However, this is a non-constructive proof since it does not actually give the form of the exact functional. DFT theorists must try to approximate this functional as well as they can.

[21] Some preliminary work aimed at developing pure density methods has been carried out (Wang, Carter, 2000).

[21] Peter Gill has recently given a more accurate as well as more witty account of what he regards as the demise of the DFT approach (Gill, 2001).

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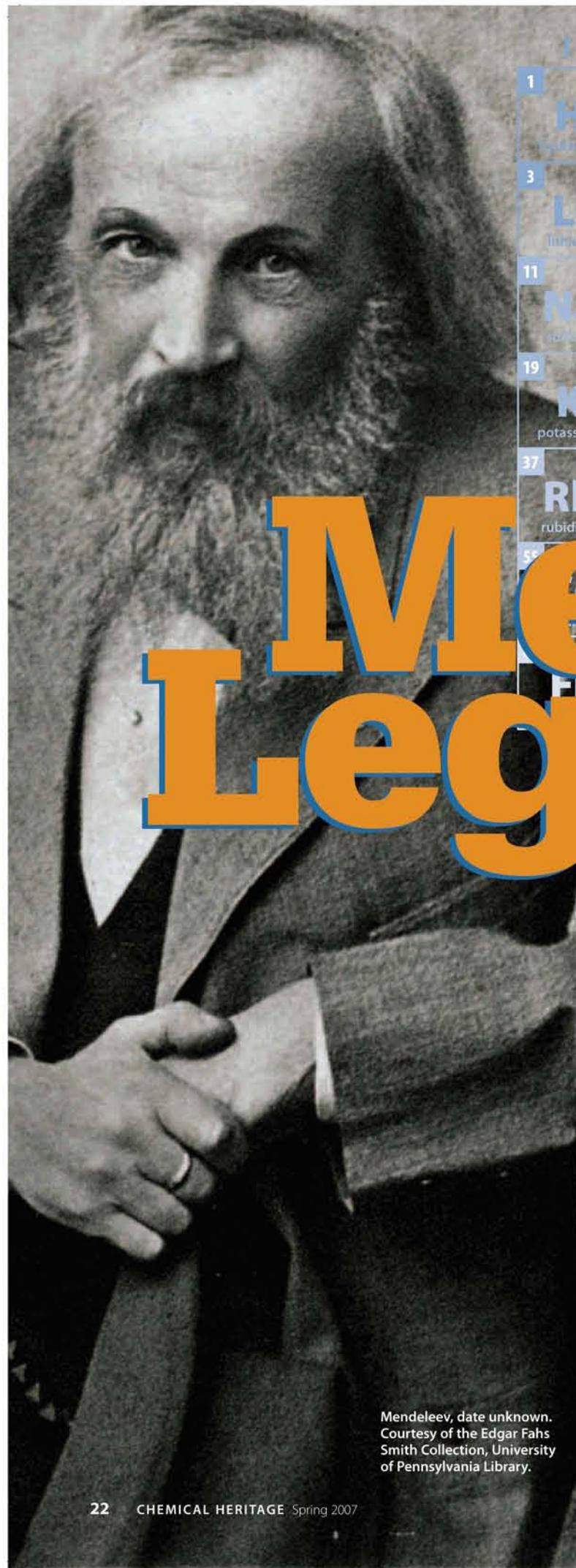
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Mendeleev's Legacy

THE PERIODIC SYSTEM

By Eric R. Scerri

Mendeleev, date unknown. Courtesy of the Edgar Fahs Smith Collection, University of Pennsylvania Library.

This year marks the 100th anniversary of the death of one of the most famous scientists of all time, the Russian chemist Dmitri Ivanovich Mendeleev (1834–1907). The periodic table that he introduced in 1869 was a monumental achievement— a wonderful mnemonic and a tool that serves to organize the whole of chemistry. No longer were students of chemistry obliged to memorize the properties of all the known elements; hereafter they could learn the properties of at least one element from each column and could, in principle, make sound predictions about the other elements in the column.

Arguably, however, Mendeleev's greatest achievement was not the periodic table so much as the recognition of the periodic system on which it was based. Of the nearly 1,000 variations that have been published since, all are attempts to represent the fundamental rule that after certain but varying intervals, the chemical elements show an approximate repetition in their properties.

Mendeleev in his library, 1904. Courtesy of the Edgar Fahs Smith Collection, University of Pennsylvania Library.

Mendeleev was hardly the first to arrive at a periodic system. The observation that certain types of elements prefer to combine with certain other types prompted early chemists to classify the elements in tables of chemical affinities. In 1817 the German chemist Johann Wolfgang Döbereiner noticed the existence of groupings of elements in threes, subsequently called triads. The elements in these groupings displayed an important numerical relationship to each other: the equivalent weight (an early substitute for atomic weight) of the middle element had the approximate mean of the values of the two flanking elements. Although Döbereiner worked with the rather crude approximations of atomic weight available at the time, he successfully identified four such groups: calcium, strontium, and barium; iodine, bromine, and chlorine; lithium, sodium, and potassium; and sulfur, selenium, and tellurium. His triads—which would eventually appear on the periodic table in vertical columns—represented the first step in fitting the elements into a system that would account for their chemical properties and reveal their physical relationships.

By the 1860s a number of scientists had moved beyond the triad concept to produce some very respectable periodic systems. The French geologist Alexandre-Émile Béguyer de Chancourtois achieved the first true periodic system in 1862 by arranging the elements by atomic weight in a spiral line wrapped around a metal cylinder. Periodic relationships could be seen by moving vertically down the screw. In 1863 and 1864 two British chemists, John Newlands and William Olding (both born in the same London borough of Southwark), independently published periodic tables that used atomic weight to arrange the elements into groups with analogous properties. A more eccentric spiral periodic system was created by the Danish-born polymath Gustavus Hinrichs in 1864. Hinrichs was intrigued that atomic spectral frequencies, like planetary distances, show whole number ratios, and he concluded that atomic spectra must therefore be an indication of atomic size.

The closest precursor to Mendeleev's table in both chronological and philosophical terms was developed by Julius Lothar Meyer, a German chemist, in 1864. Although Meyer stressed physical rather than chemical properties, his table bears remarkable similarity to the one that Mendeleev would develop five years later. For a number of reasons, Meyer's prominence in the history books never matched Mendeleev's. There was an untimely delay in the publication of his most elaborate periodic table, and, perhaps more important, Meyer—unlike Mendeleev—hesitated to make predictions about unknown elements.

Notwithstanding these earlier scientists' contributions to the idea of periodicity, Mendeleev remains the undisputed champion of the periodic system as a defender, propagator, and elaborator. Mendeleev's version of the periodic table left the greatest impact on the scientific community, both at the time it was produced and thereafter. In the popular imagination the periodic system invariably and justifiably connects to his name, to the same extent that the theory of evolution connects to Darwin's name and the theory of relativity to Einstein's. But what really set Mendeleev's contribution apart?

From Simple Substances to Abstract Elements.
By organizing the elements as he did, Mendeleev took a stand on the centuries-old question of the philosophical status of the elements. Unlike some of his contemporaries, Mendeleev rejected the suggestion that the periodic system implied the existence of any form of primary matter of which all the elements were composed. He maintained that all elements were strictly individual, indestructible, and irreducible, yet he acknowledged the seeming challenge posed by chemical reactions. Consider the familiar example of sodium chloride: common white table salt does not seem to include either poisonous grey metallic sodium or poisonous green gaseous chlorine.

Aristotle had maintained that all matter was composed of some combination of four abstract elements: earth, fire, water, and air. Although the four elements were themselves unobservable, their relative proportions within a specific substance governed its properties. Antoine-Laurent Lavoisier and his contemporaries challenged this view in the 18th century with new concepts of simple substances. They created a list of 37 simple substances that could be isolated from the decomposition of compounds and could not be further decomposed by any known means. More than any of the other discoverers of the periodic system, Mendeleev was concerned with the philosophical status of the elements. At the beginning of the first volume of his landmark *Principles of Chemistry* (first English translation, New York, 1891; *Osnovy Khimii*, first edition, Saint Petersburg, 1869), he wrote, "It is useful in this sense to make a clear distinction between the conception of an element as a *separate* homogenous substance and as a *material* but invisible *part* of a compound" (p. 23). For Mendeleev an element was an entity that was essentially unobservable but formed the inner essence of simple bodies. Whereas a particular element was to be regarded as unchanging, its corresponding simple-body aspect could take many forms, such as charcoal, diamond, and graphite in the case of carbon. His periodic table classified abstract elements, not simple substances.

Mendeleev's genius lay in recognizing that just as it was the element in the abstract sense that survived intact in the course of compound formation, so atomic weight was the only quantity that survived in measurable amounts. He therefore took the step of associating these two features: an element was to be characterized by its atomic weight. In a sense an abstract element had acquired a single measurable attribute that would remain unchanged in all its chemical combinations. Here, then, was a profound justification for using atomic weight as the basis for the classification of the elements, unlike any of the precursors to the periodic system.

Isotopes.
Toward the end of Mendeleev's life a growing body of evidence began to challenge his conception of the nature of the elements. Several revolutionary discoveries in physics showed that atoms were, in fact, reducible and that there was a sense in which all elements are composed of the same primary matter: protons, neutrons, and electrons. Most alarmingly, there was even evidence to suggest that certain elements could be transformed into others through radioactivity.

In 1879 J. J. Thomson identified electrons as the particles constituting cathode rays. By repeating his experiments with cathode rays produced by different elements, he concluded that the same particle was produced in every case and that this particle was therefore a fundamental constituent of all matter. Shortly thereafter Henri Becquerel and the Curies began to explore the phenomenon of radioactivity. One of the most talented researchers attracted to the study of radioactivity was Ernest Rutherford, who suggested in 1902 that radioactive reactions had the power to transform certain elements into entirely different elements. While fully aware of the possible criticism that such a notion might bring, Rutherford and his colleague Frederick Soddy went so far as to describe this new phenomenon as chemical transmutation, thus evoking the age-old dream of the alchemists.

As if the threat of transmutation were not enough, the discovery of isotopy nearly unraveled the entire periodic system. Scientists' failure to separate radioisotopes by chemical means threatened both the traditional notion of the elements and the utility of atomic weight as an elemental characteristic. Reflecting on this sad situation in the *Annual Report to the London Chemical Society* in 1911, Soddy wrote, "Chemical homogeneity is no longer a guarantee that any supposed element is not a mixture of several different atomic weights, or that any atomic weight is not merely

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Precursors

Early attempts at visualizing the relationships between the elements focused on reactivity and mathematical coincidence. "Tables of affinity" arranged elements that reacted with one another in vertical lists. Those elements that reacted most strongly with a given element appear at the top of the column, those with the weakest affinity at the bottom. This particular table (1) was created by a French apothecary named De Fourcy around 1773. In the early 19th century a number of chemists noticed that several groups of three elements with chemical similarities showed an interesting mathematical relationship: the atomic weight of the middle element is the approximate mean of the atomic weight of the other two elements (2). In 1862 Alexandre-Émile Béguyer de Chancourtois extended the idea of periodicity into three dimensions. The elements were arranged in a continuous spiral in order of atomic weight around a metal cylinder so that elements with similar properties—for instance, oxygen, sulfur, and selenium—appeared in vertical lines. Since tellurium appeared in the center of the spiral, it became known as the "telluric screw" (3).
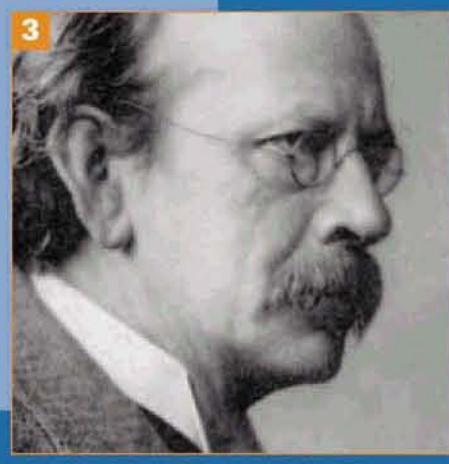
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$$Na = \frac{Li + K}{2}$$

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Discoveries

Ernest Rutherford (1) and Frederick Soddy's (2) discovery of chemical transmutation through radioactive decay undermined the utility of a periodic system based on atomic weight. A way out was eventually found by using atomic numbers rather than weight as the organizing principle. J. J. Thomson's (3) discovery of the electron in 1897 would eventually allow chemists to draw connections between the physical structure of the atom and periodic behavior. As more sophisticated models of the atom would later explain, many of an element's chemical properties are determined by the number of electrons in the outermost shell.

ALL PHOTOS COURTESY OF THE EDGAR FAHS SMITH COLLECTION, UNIVERSITY OF PENNSYLVANIA LIBRARY.

a mean number. The constancy of atomic weight, whatever the source of the material, is not a complete proof of homogeneity."

This situation was clarified somewhat when Soddy and Kasimir Fajans, a Polish-born chemist, independently suggested what became known as the group displacement laws in 1913. Each found that the emission of an alpha particle from an element produces an element located two places to the left on the periodic table, while the emission of a beta particle resulted in a movement one position to the right. For example, if an atom of uranium-235 undergoes alpha decay, it forms an atom of thorium-231; meanwhile, an atom of actinium-230 can undergo a beta decay to form an atom of thorium-230. Today we would recognize both products as atoms of the same elements with different atomic weights, but at the time the matter of elemental identity had not yet been settled.

By the 1920s the periodic system was in crisis. Many new isotopes had been discovered over a short period of time so that the number of "atoms," or fundamental units, suddenly seemed to have mu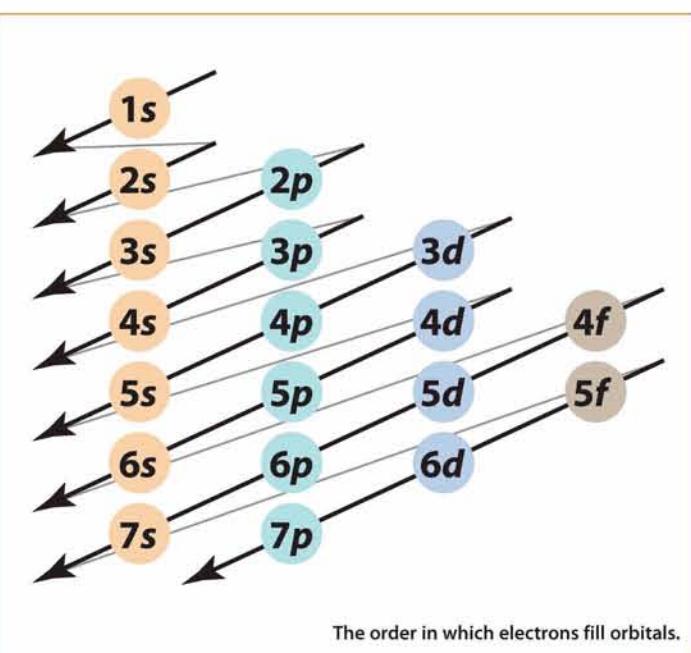ltiplied. At this point some chemists, including Fajans, called for abandoning Mendeleev's periodic system in favor of a more complicated table of isotopes. A way out appeared in the form of atomic numbers assigned by nuclear charge. The Austrian chemist Fritz Paneth championed the atomic number—instead of atomic weight—as the primary characteristic of the elements. Paneth, along with Hungarian chemist György Hevesy, showed that the chemical properties of isotopes of the same element were, for all intents and purposes, identical. Chemists could therefore regard the isotopes of any element as being the same simple substance, even though individual atoms might appear in different isotopic forms.

Electrons.
If the discovery of isotopes threatened to undermine the periodic system, the discovery of the electron explained many of the periodic properties on which the table was based. J. J. Thomson attempted to explain the periodic system by postulating rings of electrons embedded in the positive charge that made up his plum pudding model of the atom. Thomson's model was quickly superseded by more sophisticated and elaborate mod-

The order in which electrons fill orbitals.

els of atomic structure. However, the origin of our current conception of electronic configurations—an explanatory paradigm in much of chemistry—can be traced to his ideas. Because of Thomson we know that the key to an atom's properties lies in the number of outer-shell electrons, which in turn can be deduced—with some exceptions—from an element's position on the periodic table.

The origin of electronic configuration is frequently and inaccurately attributed to Niels Bohr, who introduced quantum theory to the study of the atom. But Bohr essentially tidied up Thomson's pre-quantum configurations and took advantage of a more accurate knowledge of the number of electrons each of the elements actually possessed. Further developments in quantum theory, including Pauli's exclusion principle and Schrödinger's equation,

led to a more rigorous theoretical explanation of the form of the periodic system.

Collectively, these theories established the basic principles by which electronic configurations are assigned: as one moves from left to right on the periodic table, each element contains one additional electron (Bohr's *aufbau* principle); each additional electron, with certain exceptions, is added to the atom's outermost electron shell; only two electrons can fill a single orbital; when electrons fill orbitals of equal energy, they occupy as many different orbitals as possible; and no two electrons in an atom can share the same set of quantum numbers. The rules that govern the assignment of quantum numbers are rigorously explained by quantum theory, with the outcome that the first 2 shells contain a maximum of 2 and 8 electrons—at long last an explanation for the lengths of the first two periods of the table! Similar considerations for the 3rd and 4th shells predict 18 and 32 electrons respectively, but this is not in accordance with the arrangement of the elements in the periodic table.

The problem is this: the third row of the periodic table contains 8, not 18, electrons. It turns out that while quantum numbers provide a satisfying deductive explanation of the total number of electrons that any shell can hold, the correspondence of these values with the number of elements that occur in any particular period is something of a coincidence. The familiar sequence in which the s, p, d, and f orbitals are filled (see diagram, left) has essentially been determined by empirical means. Indeed, Bohr's failure to derive the order for the filling of the orbitals has been described by some as one of the outstanding problems of quantum mechanics.

The simple textbook explanation—that orbitals are filled in the order of their relative energies—has its limitations, as illus-

trated by the cases of chromium and copper. Both are anomalies in that electrons are added to the 3d orbital before the 4s orbital is closed; that is, their outer shells have configurations of $4s^1 3d^5$ and $4s^1 3d^{10}$ instead of the expected $4s^2 3d^4$ and $4s^2 3d^9$. Scholars have offered various simple explanations for this experimental finding, the most common of which is that the stability of a half-filled or fully filled *d* shell offers the most energetically stable arrangement of electrons. However, since the configurations of the elements in the second transition series follow an even more "anomalous" pattern—not necessarily involving half-filled or fully filled shells—it is clear that the explanation is specific to chromium and copper. Quantum mechanics can generally be used to explain a particular atom's empirical electronic configuration, but that configuration usually cannot be deduced from quantum mechanics alone.

It is something of a miracle that quantum mechanics explains the periodic table to the extent that it does; we should not let this fact seduce us into believing that it is a deductive explanation. Attempts to explain the details of the periodic table continue to challenge the ingenuity of quantum physicists and quantum chemists, and the periodic table will continue to present a test case for the adequacy of new methods developed in quantum chemistry.

A Lasting Legacy.
Our story has now been brought up to date. From its humble beginnings as a set of isolated triads of elements, the periodic system has grown to embody well over 100 elements, and it has survived the discovery of isotopes and the quantum revolution in the study of matter. Rather than being swept aside, it has continued to provide a challenge to the development of ever-more-accurate means of calculating the basic properties of the atoms of the chemical elements. A century's worth of science has consolidated rather than chipped away at the periodic system's central role in modern chemistry.
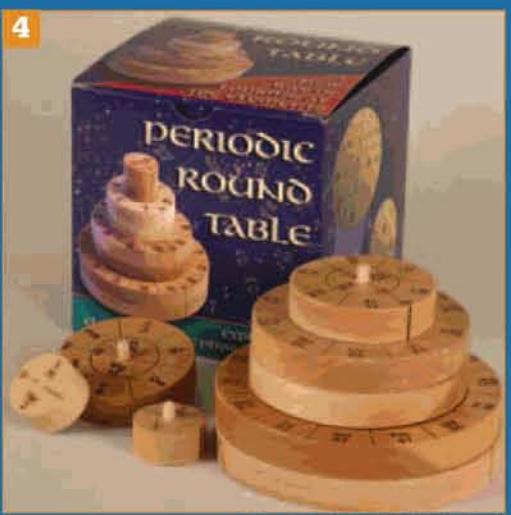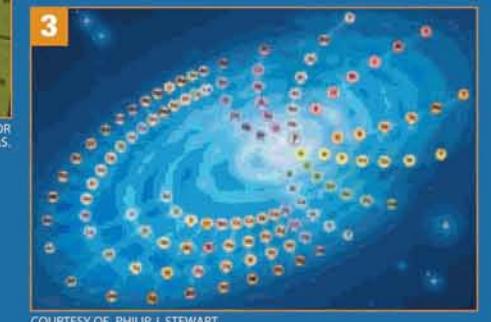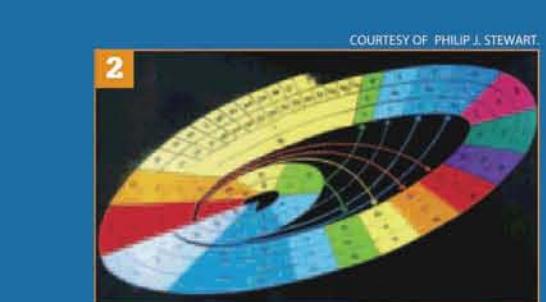
The problem is no longer the validity of Mendeleev's system, but the best way to represent it. Should it be the original short-form table with 8 columns, the familiar medium-long form with 18 columns, or perhaps even a long-form table with 32 columns, which more naturally accommodates the rare earth elements into the main body of the table? Alternatively, some favor pyramidal tables, while others advocate the left-step form proposed by Charles Janet in the 1920s. Theodor Benfey and Philip Stewart have proposed continuous spiral models. Hundreds, possibly even thousands, of periodic systems have been proposed, and each has its ardent supporters.

Is there one best periodic table? Many chemists argue that the form of the table is of little importance and that one's choice depends on what particular aspect of periodicity one wants to depict. But surely this is not the case if, for example, rival versions put helium and hydrogen in radically different places. Such debates will continue for a long time. However, the debate would not exist without Dmitri Ivanovich Mendeleev, and for the very legacy of periodicity we are indebted to him. ○

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Variations

Twentieth-century chemists and designers have created hundreds—if not thousands—of variations on the familiar medium-form periodic table. This spiral periodic table (1) was developed by Theodor Benfey while he was serving as the editor of *Chemistry* magazine. As Benfey explains, "When reporting on, say, the alkali metals, we would highlight that section of the spiral table. The idea was to show that the elements really do show a fascinating periodicity, something largely obscured by the standard table." Other spiral variants, such as Edgar Longman's mid-century model (2) and Philip Stewart's more recent one (3), suggest the elegance of the spiral. Gary Katz's "Periodic Round Table" (4) updates the three-dimensional periodic table with a modern understanding of electronic configurations. Four pairs of wooden disks are arranged around a central axis, with each disk divided into bands representing electron orbitals. The disks rotate so students can discover relationships between the elements.

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COURTESY OF THEODOR BENFEY AND INSTRUMENTS FOR RESEARCH AND INDUSTRY. PHOTO BY GREGORY TOBIAS.

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The Role of Triads in the Evolution of the Periodic Table: Past and Present

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It has been suggested by various authors that an improved form of the periodic table might be the left-step form, as first proposed by Charles Janet, in which helium is placed among the alkaline earths *(1)*. The present author's previous support for this form of representation was not motivated by any chemical intuition concerning the element helium, but rather by a desire for greater regularity in the form of the periodic table. In common with other authors, the present author has also suggested that the left-step table reflects the manner in which electrons occupy atomic orbitals more directly than the conventionally used medium-long form table *(2)*.

The left-step table (Figure 1) allows one to display the $n + \ell$ rule very prominently contrary to the medium-long form. Successive periods are identified with increasing values of $n + \ell$, the sum of the first two quantum numbers denoting the atomic orbital in which the differentiating electron is located. Meanwhile, the medium-long form is based on numbering successive periods with increasing values of just the first quantum number, n. Consequently, when using the medium-long form, one encounters complications starting with the fourth period, which involves the filling of the 4s orbital followed by the 3d and 4p orbitals successively.

Dual Sense of the Concept of "Element"

In our previous work the justification for ignoring the apparent clash with chemical intuition regarding helium, was essentially philosophical and formed the main motivation for that proposal. Although it is not well known, Mendeleev repeatedly argued that the periodic system is not primarily a classification of the elements regarded as simple substances (Lavoisier's elements) but, more correctly, a classification of elements regarded as basic substances. The terminology being used here is not Mendeleev's but rather due to Paneth who, sometime later, wrote,

> I suggested that we should use the term "basic substance" whenever we want to designate that which is indestructible in compounds...and that we should speak of a "simple substance" when referring to the form in which such a basic substance, not combined with any other, is presented to our senses *(3)*.

Mendeleev himself makes the distinction between the two senses of the term element in a number of passages, including the following,

> It is useful in this sense to make a clear distinction between the conception of an element as a *separate* homogeneous substance, and as a *material* but invisible *part* of a compound. Mercury oxide does not contain two simple bodies, a gas and a metal, but two elements, mercury and oxygen, that, when free, are a gas and a metal. Neither mercury as a metal nor oxygen as a gas is contained in mercury oxide; it only contains the substance of the elements, just as steam only contains the substance of ice, but not ice itself, or as corn contains the substance of the seed but not the seed itself *(4)*.

To state the distinction otherwise, simple substances are the manifestation of the elements considered as basic substances, the latter being the more fundamental of the two senses of the term "element". Admittedly the terminology is a little unfortunate since the labels "basic" and "simple" appear to place the two senses of the term element on the same epistemological level. The intention however is that basic substances are to be regarded as more fundamental. Be that as it may, we will retain Paneth's terminology in view of the importance of the writings of this author in which the distinction is perhaps more clearly established than elsewhere in the literature *(5)*.

We have previously suggested that concentrating on elements as basic substances means that one could ignore the apparent absurdity of placing helium among the alkali earths since elements as basic substances do not possess properties in the macroscopic sense. Strictly speaking an element as a basic substance possesses no properties but as Mendeleev suggested it should be attributed just one characteristic—atomic weight, or in present day terms—atomic number.

However, one aspect, having to do with triads of elements, is troubling in this otherwise elegant left-step periodic system. The use of the left-step table results in the loss of a triad involving helium, neon, and argon.

																		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	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	Rb	Sr
			Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	Cs	Ba
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	Fr	Ra
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg

Figure 1. Left-step periodic table.

Triads

Although triads were highly instrumental in the discovery of the periodic system, the concept of atomic weight triads became somewhat neglected following the accurate determination of atomic weights.

But as argued in a recent book, once one accepts that the more correct ordering principle for the elements is atomic number the concept of triads makes a significant return, at least in about half of all conceivable triads in the modern table (6). Using the atomic numbers of chlorine, bromine, and iodine for example the middle element is not just the approximate mean of the atomic numbers of the flanking elements but the exact mean.

If one looks for an atomic number triads among the elements helium, beryllium, and magnesium within the left-step table one encounters a serious discrepancy. Moreover, the conventional placing of helium among the noble gases gives a perfect atomic number triad. So why would one want to lose an atomic number triad by adopting the left-step table? This we suggest now is a serious objection against the repositioning of helium in the way that is carried out in the left-step table. As will be argued, the existence of atomic number triads represents a fundamental aspect of periodic classification because it depends just on atomic number which, as mentioned above, is the one essential criterion for the characterization of elements as basic substances.

A Brief History of Triads

Perhaps the earliest hints of any numerical regularity among the atomic weights of the elements was discovered as early as 1817 by Döbereiner. He was the first to notice the existence of various groups of three elements, subsequently called triads, that showed chemical similarities. In addition, such elements displayed an important numerical relationship, namely that the equivalent weight, or atomic weight, of the middle element is the approximate mean of the values of the two flanking elements in the triad.

In 1817 Döbereiner found that if certain elements were combined with oxygen in binary compounds, a numerical relationship could be discerned among the equivalent weights of these compounds. Thus when oxides of calcium, strontium, and barium were considered, the equivalent weight of strontium oxide was approximately the mean of those of calcium oxide and barium oxide. The three elements in question, strontium, calcium, and barium were said to form a triad.

$$SrO = \frac{CaO + BaO}{2} = \frac{59 + 155}{2} = 107$$

Though Döbereiner was working with weights that had been deduced with the relatively crude experimental methods of the time, his values compare rather well with current values for the triad:

$$104.71 = \frac{56.08 + 153.33}{2}$$

Döbereiner's observation had little impact on the chemical world at first but later became very influential. He is now regarded as one of the earliest pioneers of the development of the periodic system. Very little happened regarding triads

until twelve years later, in 1829, when Döbereiner added three new triads. The first involved the element bromine, which had been isolated in the previous year. He compared bromine to chlorine and iodine, using the atomic weights obtained earlier by Berzelius:

$$Br = \frac{Cl + I}{2} = \frac{35.470 + 126.470}{2} = 80.970$$

The mean value for this triad is reasonably close to Berzelius' value for bromine of 78.383. Döbereiner also obtained a triad involving some alkali metals, sodium, lithium, and potassium, which were known to share many chemical properties:

$$Na = \frac{Li + K}{2} = \frac{15.25 + 78.39}{2} = 46.82$$

In addition he produced a fourth triad:

$$Se = \frac{S + Te}{2} = \frac{39.239 + 129.243}{2} = 80.741^{1}$$

Once again, the mean of the flanking elements, sulfur (S) and tellurium (Te), compares well with Berzelius' value of 79.5 for selenium (Se).

Döbereiner also required that, in order to be meaningful, his triads should reveal chemical relationships among the elements as well as numerical relationships. On the other hand he refused to group fluorine, a halogen, together with chlorine, bromine, and iodine, as he might have done on chemical grounds, because he failed to find a triadic relationship between the atomic weights of fluorine and those of these other halogens. He was also reluctant to take the occurrence of triads among dissimilar elements, such as nitrogen, carbon, and oxygen, as being in any sense significant even though they did display a triadic numerical relationship.

Suffice it to say that Döbereiner's research established the notion of triads as a powerful concept, which several other chemists were soon to take up with much effect. Indeed, Döbereiner's triads, which would appear on the periodic table grouped in vertical columns, represented the first step in fitting the elements into a system that would account for their chemical properties and would reveal their physical relationships.

Later Work on Triads

It is probably fair to say that much time was wasted by other researchers in trying to uncover triads where they simply did not exist. Some pioneers, including Mendeleev, made it a point to turn their backs on numerical approaches such as Prout's hypothesis and the search for triads. This attitude certainly seems to have paid dividends for Mendeleev in that he made progress where others had failed to do so.

The problem with triads, as well as the other important numerical hypothesis due to Prout, is easy to discern in retrospect. It is simply that atomic weight, which both concepts draw upon, is not the most fundamental quantity that can be used to systematize the elements. The atomic weight of any element depends on the particular geological origin of the sample examined. In addition, the atomic weight of any particular element is an average of several isotopes of the particular element.

Mendeleev's Path to Mature Periodic System

Many historians have examined in detail the path that Mendeleev took in arriving at his early periodic tables. It seems to be agreed that the first key document, which still exists, consists of a letter sent to Mendeleev. On the back of the letter Mendeleev sketched some rudimentary ideas on how best to arrange the elements into a coherent system.

This letter, which is held in the Mendeleev archives, is dated February 17, 1869, which is also the date of the famous first table that Mendeleev produced. The letter is from one Alexei Ivanovich Khodnev, secretary of the Free Economic Society in St. Petersburg, inviting Mendeleev to visit a cheese factory where he was due to conduct an inspection. On the back of the letter Mendeleev has made a comparison of the following atomic weights:

23	39	85	133
7 or 14	24	65	112
16 or 9	15	20	21

Historians differ regarding the precise assignment of elements to these values. In particular they disagree with respect to the identity of the element depicted as 7 or 14. According to some it is twice the atomic weight of lithium, while others maintain that it is beryllium using an older value for its atomic weight.

Na	K	Rb	Cs
2 Li?	Mg	Zn	Cd

Kedrov, and after him Dimitriev, conclude that the first entry in the second row should be twice the weight of lithium (7). In any case it is clear that Mendeleev is groping his way towards a horizontal relationship by examining differences in atomic weights and is starting to see hints of almost constant differences in some cases such as Rb/Zn and Cs/Cd. We suggest that his endeavor was in the same spirit as the search for triads. The only difference being that in the case of a triad one seeks two differences between the weights of three elements rather than just two as Mendeleev was doing in these early attempts.

A similar activity is found in Mendeleev's first attempt at a periodic system as presented in a hand-written table. If one examines the calculations that he is carrying out one finds again an attempt to compute differences between the atomic weights of elements in the columns of his table. For example Mendeleev writes the number 27 in smaller writing below the symbols for potassium (Zn − K = 65 − 39 = 27) and again below rubidium (Cd − Rb = 112 − 85 = 27).

It appears that, in the space of a single day, February 17th 1869, Mendeleev not only began to make horizontal comparisons but also produced the first version of a full periodic table that included most of the known elements. Moreover, Mendeleev's overall approach consists of looking at atomic weight differences in conformity with the general principle of triads even though he was not specifically identifying triads in the manner of Döbereiner.

Mendeleev's Use of Triad-Like Concepts To Make Predictions

Mendeleev went to some length to distance himself from the use of numerical relationships such as Prout's relationship and the notion of triads. However, it is quite clear that many of his predictions of the properties of new elements involve the notion of triads. The triads he considered were sometimes vertical, or horizontal, or at times the combination of both vertical and horizontal triads.

In the various editions of his textbook, and in the publications dealing specifically with his predictions, Mendeleev repeatedly illustrates his method using the known element selenium as an example. The atomic weight of selenium was known at the time and so could be used to test the reliability of his method. Given the position of selenium and the atomic weights of its four flanking elements,

$$
\begin{array}{ccc}
 & S\ (32) & \\
As\ (75) & Se\ ? & Br\ (80) \\
 & Te\ (127.5) &
\end{array}
$$

the flanking atomic weights can be averaged to yield approximately the correct value for the atomic weight of selenium:

$$\frac{32 + 75 + 80 + 127.5}{4} = 79$$

Atomic Number Triads

The atomic weight of any particular elements is not a fundamental property in that it depends upon terrestrial contingencies concerning isotopic abundances. Atomic number, on the other hand, is fundamental and more correctly characterizes the distinction between one element and the next. The adoption of atomic number has an intriguing consequence on triads that has seldom been discussed. This is the fact that approximately 50% of all vertical triads based on atomic number, rather than atomic weight, are mathematically exact. This remarkable result is easy to appreciate by referring to the long-form of the modern periodic table (Figure 2).

Figure 2. Long-form periodic table.

By considering elements from rows 1, 2, and 3, such as helium, neon, and argon one obtains a perfect atomic number triad,

He	2
Ne	10 = (2 + 18) / 2
Ar	18

or from rows 3, 4, and 5, for example,

P	15
As	33 = (15 + 51) /2
Sb	51

or from rows 5, 6, and 7,

Y	39
Lu	71 = (39 + 103) / 2
Lr	103

Alternatively any triads taken from combinations of elements in rows 2, 3, 4 or 4, 5, 6 and so on, do not give perfect triads. The reason why this works so perfectly, albeit in only about 50% of possible triads, is because the length of each period repeats just once in the long-form periodic table, with the exception of the very first short period. The full sequence is 2, 8, 8, 18, 18, 32, presumably 32, and so forth.

So if one selects any element at random there is a 50% chance that the element above and below the selected element, in the same column of the periodic table, will have atomic numbers at an equal interval away from the original element. If this is the case, then it follows trivially that the second element in the sequence will lie exactly mid-way between the first and third elements. In numerical terms, its atomic number will be the exact mean of the first and third elements, or in other words the atomic number triad will hold perfectly. All one needs to do is to pick a middle element from the first of a repeating pair of periods. Thus about half of all the elements are good candidates for beginning a triad. This phenomenon is therefore a mathematical consequence of the fact that all periods repeat (except for the first one) and that the elements are characterized by whole number integers.

It would appear that the original discoverers had accidentally stumbled upon the fact that the length of most periods of elements repeat. What held them back was that these repeat distances vary in length and, of course, the fact that they were operating with the vagaries of atomic weight data. It is somewhat amusing to think that the ancient notion triads of elements, which was initially so productive but later and later came under criticism, should now emerge as being essentially correct, and that the reason for its correctness is now fully understood. It might also be mentioned that a recent article in this *Journal* has proposed using atomic weight triads to predict the atomic weights of the trans-lawrencium elements *(8)*.

The aim of the present article is to elevate the role of triads to an even greater extent. Since triads are now expressed in terms of atomic numbers they coincidentally characterize the elements as basic substances. In other words they characterize the true basis for periodic classification compared with the elements as simple substances, as argued by Mendeleev and more recently by Paneth and other authors.

The New Proposal

Finally let us turn to the new periodic table, which it is claimed restores a fundamental role to triads. Rather than relocating helium to the alkaline earths and thereby losing a perfect triad (He, Ne, Ar), we propose to relocate hydrogen into the halogen group, thereby gaining one completely new perfect triad (H, F, Cl) as shown in Figure 3.

In chemical terms this proposal is certainly more conservative and more generally plausible to chemists, than the relocation of helium, although this is not the reason for suggesting it here. In addition, the relocation of hydrogen is supported in some respects on chemical grounds as has been argued previously by many authors *(9)*.

Conclusion

We are not under any illusion that chemical educators or governing bodies of chemistry will readily accept this new proposal. It is being suggested to promote further discussion on the presentation of the periodic system and because it appears to rest on the fundamental criterion of elements as basic substances. Of course even the medium-long form table (not shown) utilizes atomic number for the purposes of ordering the elements in what might be termed primary classification. What is being proposed here is that triadic relationships between atomic numbers can also serve for the purpose of secondary classification, namely the placement of elements in groups or columns.

Figure 3. New proposed periodic table. Numbers at the right of table denote values of n + ℓ for each period and not principal quantum numbers.

As suggested in the title of the present article, we believe that the periodic table, which initially arose from the discovery of atomic weight triads, can now be further enhanced by recognizing the fundamental importance of atomic number triads. In addition one should recognize the more fundamental nature of the elements as basic substances rather than as simple substances, and that the periodic system is primarily a classification of the former. Whereas we previously suggested that these aims were best served by the left-step table we now favor the revised left-step table shown in Figure 3.

The proposed new table retains most of the feature of the Janet left-step table but does not commit one to placing helium in the alkaline earths. The regular form of the table represents an advantage over the medium-long form and the closer connection with electron-shell filling that the left-step table offers is maintained with the small disadvantage that two values of $n + \ell$, namely 1 and 2, appear in the same first row.

The new proposed version does not alleviate the concern that some authors voice in wanting to maintain the metals on the left and non-metals on the right of the table. We suggest that such a desideratum does not necessarily reflect the most fundamental aspects of the elements as basic substances whereas the left-step and its new variant do. The latter two forms aim to represent elements as basic substances as well as establishing a closer connection with fundamental aspects of electron-shell filling, and consequently with quantum mechanics, than the medium-long form table does. Finally, we have recently published another new table that differs only in shape from the one proposed here *(10)*.

Note

1. This seems to be a printer's error since the mean should be 84.241.

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Supporting *JCE Online* Material

The Past and Future of the Periodic Table

This stalwart symbol of the field of chemistry always faces scrutiny and debate

Eric R. Scerri

I t graces the walls of lecture halls and laboratories of all types, from universities to industry. It is one of the most powerful icons of science. It captures the essence of chemistry in one elegant pattern. The periodic table provides a concise way of understanding how all known chemical elements react with one another and enter into chemical bonding, and it helps to explain the properties of each element that make it react in such a fashion.

But the periodic system is so fundamental, pervasive and familiar in the study of chemistry that it is often taken for granted. A century after the death of the leading discoverer of the periodic system, the Russian chemist Dimitri Mendeleev, it seems time to revisit the origins and modern status of this now-standard chemical classification. There were a number of historic precursors to Mendeleev's periodic system. But there are also current ongoing debates regarding the best way to display the periodic system, and whether there is really a "best way" of doing so.

The periodic system of elements gets its moniker because it graphs how certain properties of chemicals repeat after regular intervals. In the modern table of 117 elements, each is placed across rows in order of increasing atomic number—the number of protons in the nucleus of one atom of each element. There are seven rows, each

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making up one period. The lengths of periods vary: The first has two elements, the next two eight each, then 18 and 32, respectively, for the next pairs of periods. Vertical columns make up groups, of which there are 18, based on similar chemical properties, related to the number of electrons in the outer shell of the atoms, also called the valence shell. For instance, group 17, the halogens, all lack one electron to fill their valence shells, all tend to acquire electrons during reactions, and all form acids with hydrogen.

The Classics

There have been many changes to the table since Mendeleev's first, which showed eight groups, 12 rows and 66 elements, was published in 1869. But neither did Mendeleev's table spring from a vacuum. Historians of chemistry have long recognized two ideas that contributed to the evolution of the periodic system: the notion of triads of elements and Prout's hypothesis, whereby the atomic weights of the elements are integral multiples of the atomic weight of hydrogen, the lightest of all the elements.

In 1817 the German chemist Johann Döbereiner noticed that several groups of three elements formed triads with two interesting features. Not only was the middle element of a triad of intermediate chemical reactivity, but it also had an intermediate atomic weight. Differing from atomic number, a value that had not yet been ascertained, atomic weight had been measured since the start of the 1800s. The idea was to determine the weight of each indivisible unit of matter relative to hydrogen, whose weight was taken as 1.00. Because formulas for many compounds were unknown, atomic weights remained imprecisely measured for some time. But in triads of

elements, Döbereiner found that the weight of the middle element—such as selenium in the triad formed by sulfur, selenium and tellurium—had an atomic weight that was the approximate average of the weights of the other two elements. Sulfur's atomic weight, in Döbereiner's time, was 32.239, whereas tellurium's was 129.243, the average of which is 80.741, or close to the then-measured value for selenium, 79.264.

The importance of this discovery lay in the marrying of qualitative chemical properties, such as degree of reactivity, with numerical data on the elements. It suggested that there might be some underlying numerical order that could serve to relate the elements to one another in a systematic way.

Döbereiner also discovered other triads, such as calcium, strontium and barium, and lithium, sodium and potassium. Other chemists discovered yet more triads and began to make tables that also attempted to relate triads among one another. But some of these contributions degenerated into mere numerology, especially when they neglected chemical relations between the elements. For example, in his 1857 article, German chemist Ernst Lenssen suggested the existence of a triad consisting of silicon, boron and fluorine, even though there was no conceivable chemical connection between these elements. Nevertheless, the lure of the search for triads encouraged chemists to determine atomic weights more accurately, a pursuit that served chemistry in many other ways.

A little earlier, in 1815, the London based physician, William Prout, proposed another general principle. In a few papers, which he published anonymously, Prout wrote that the fact that the atomic weights of many elements seemed to be integral multiples of the weight of hydrogen suggested that all

Figure 1. With its compact form displaying a wealth of information about the elements, the periodic table has long been a standard-issue reference in the field of chemistry. Theodore Gray created this museum display to improve on the appeal of the table by adding samples of each element behind its entry. (This close-up shows, at left, the triad sulfur, selenium and tellurium, studies of which were a precursor to the periodic system.) The story of the periodic table is one of gradual improvements, from early measurements of atomic weight to current-day proposals for new layouts of the elements that look nothing like a two-dimensional chart.

the elements were composite multiples of hydrogen. He also went on to claim that this would imply the essential unity of all matter. But some elements such as nitrogen, which then had a value of 12.6 relative to hydrogen, seemed to point against Prout's hypothesis. Prout's supporters regarded such facts as anomalies that would eventually disappear with the more accurate determination of atomic weights.

As in the case of triads, attempts to confirm or refute Prout's hypothesis contributed to renewed efforts on the part of chemists to measure atomic weights. However, although these ideas were fruitful in some ways, they were also found wanting as more ac-

curate atomic-weight data began to accumulate. The notion of triads was found to be too approximate and even then only applied to carefully selected groups of three elements. Meanwhile, Prout's hypothesis showed too many nonintegral exceptions. In the language of philosopher of science Karl Popper, both ideas had been refuted by the second half of the 19th century.

At the start of the 20th century, it was found that atomic number, rather than atomic weight, serves as the more correct criterion for ordering the elements in a linear sequence. Researchers such as the British physicist Henry Moseley found that they could use x-ray diffraction to relate atomic number

to positive charge, or the number of protons in the nucleus of any atom. On re-examining the notions of triads and Prout's hypothesis in the light of atomic number, one finds a remarkable sense in which both notions have made what another famous philosopher of science, Imre Lakatos, has termed a theoretical comeback. In terms of atomic number, the elements have exact multiples of the number of protons in the hydrogen atom—as hydrogen has only one proton, everything is a multiple of it. And perhaps in a deeper sense, modern astrophysics has shown that almost all of the elements are literally formed from hydrogen and helium atoms, which combined together
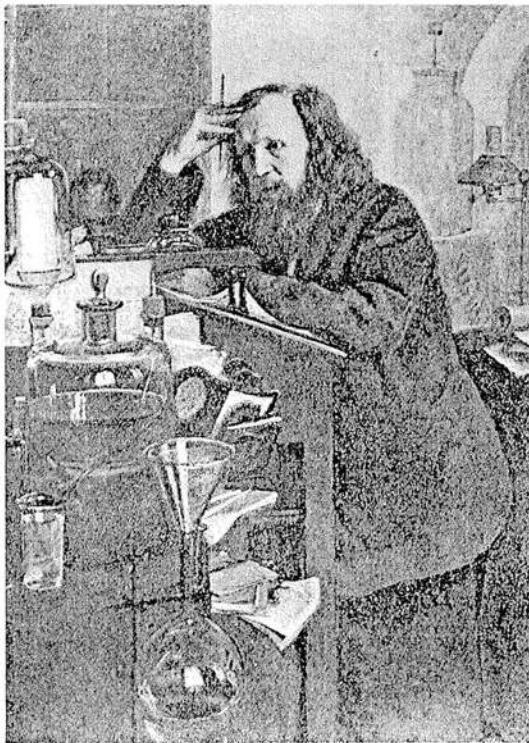
during the Big Bang at the start of the universe, as well as in the interiors of stars and supernovae.

Moreover, if we consider atomic numbers instead of atomic weights for the triads discovered in the 19th century, it turns out that the atomic number of the middle element is *exactly* the average of the other two elements. Indeed, about half of all the possible triads in the modern periodic table are exact in this sense. However, many other potential triads are not even approximately correct in that the atomic number of the middle element is nowhere near the average of the other two elements.

The reason for this behavior is that the periodic table shows a repetition in the length of all periods (with the exception of the first very short period which consists of just the elements hydrogen and helium). The second period consists of eight elements (lithium to neon) followed by another period of eight elements (sodium to argon), followed by two periods of 18 elements, presumably followed by two periods of 32 elements and so on. As a result of these repetitions, atomic number triads are exact in half of all possible cases. Take the element chlorine as an example. In order to encounter another element with similar chemical properties we need to advance 18 places to get to the element bromine. To reach yet another element sharing these same chemical properties it is necessary to advance a further 18 places to the element iodine. Bromine lies exactly between chlorine and iodine in terms of atomic number, precisely because the length of the two periods between these elements is exactly the same—18 elements. But in other cases of potential triads, the second and third elements are not in periods of the same length, so the triads don't work.

Bridging the Gaps
Despite this modern reprieve and explanation, in the mid-1800s, Men-

Corbis

Figure 2. Dimitri Ivanovich Mendeleev was born in 1834 in Tobolsk, Siberia, the youngest of 14 children. He studied in St. Petersburg, Russia, where he became a professor of chemistry at the university in 1863. He published his initial periodic table in 1869. Although his table was not the first, his version is the one that had the biggest impact on the scientific community. He also championed the system, defending its validity and devoting time to its elaboration. Mendeleev died just over 100 years ago, in 1907. A statue of him with his table stands in St. Petersburg.

deleev—the undisputed champion of the periodic table—was a critic of the use of triads and especially of Prout's hypothesis concerning the existence of primary matter. Mendeleev was firmly convinced of the individuality and distinct existence of the elements. He is rightly famous for having left gaps in his periodic tables for elements that had not been isolated and for successfully predicting many of their properties, especially in the case of gallium, germanium and scandium.

There are aspects of Mendeleev's system that are not very well known but that nevertheless were quite fundamental to his approach. Mendeleev repeatedly emphasized that there is a dual sense of the concept of element. In the first case, elements are the final stage of chemical analysis, or something that can be isolated and that can-

not be further simplified. This is the notion of elements as first emphasized by Antoine Lavoisier in the 1700s, when he called them "simple substances."
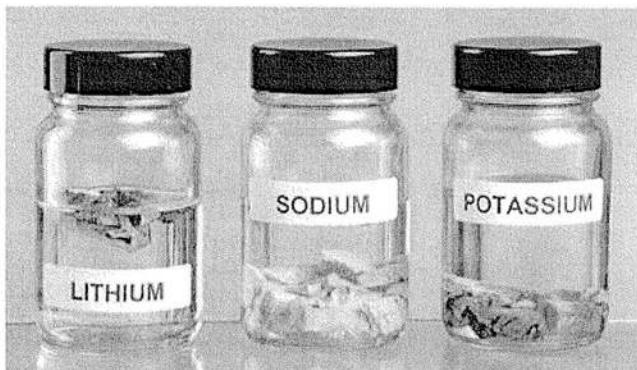
But there is a second notion, which Mendeleev sometimes called "real elements," in order to indicate their more fundamental status. In this sense, the elements represent abstract substances that lack what we normally regard as properties and that represent the form that elements take when they occur in compounds. For example, sodium and chlorine as simple substances—a grey metal and a greenish gas respectively—are not literally present in the compound sodium chloride (table salt). Mendeleev would have said that sodium and chlorine are present in the compound as the abstract or "real elements."

Let me emphasize that these abstract elements are still real, and indeed should be regarded as somehow being more fundamental than the elements as simple substances that can actually be isolated. Mendeleev gave just one attribute to the abstract element, namely atomic weight. It is the atomic weight of sodium, for example, that preserves its identity when sodium enters into chemical combination. Just as Mendeleev implied that the abstract version of the concept of element was more real, so he emphasized that his periodic classification was primarily concerned with the abstract elements.

As some authors have argued, this more philosophical view of the elements may have been the crucial sense in which Mendeleev went further than his competitors, who restricted their attention to the elements as simple substances. It also seems to provide a means of understanding how Mendeleev was able to challenge the values of the atomic weights of many elements and the manner in which several elements had been accommodated into the periodic system. This was achieved

element	atomic weight	chemical reactivity toward water
lithium Li	6.94	little reactivity, no flame, no explosion
sodium Na	22.99	intermediate reactivity, produces yellow flame and mild explosion
potassium K	39.10	greatest reactivity, produces lilac flame and considerable explosion

Figure 3. The elements lithium, sodium and potassium form a triad of the kind studied by chemist Johann Döbereiner in 1817. Elements formed a triad when the average of the then-known atomic weights of the first and third ones closely approximated that of the center member. The reactivity of the middle element was also known to be intermediate to that of the first and last. In the modern periodic table, this particular triad is part of the group of alkali metals. Actual samples of these elements (right) are stored in oil because they are highly reactive with water and air.

by ignoring, to some extent, the more obvious, more superficial properties of the elements as simple substances.

Mendeleev is often given most credit for his fame as the "father of the periodic table" because he predicted elements that were undiscovered at the time. But just how impressive were those predictions? As far as the elements gallium, germanium and scandium are concerned, they were quite outstanding—so much so that Mendeleev was even able to correct some of the initial experimental findings on these new elements.

On the other hand, if one considers all of Mendeleev's many predictions of new elements, his powers of prophecy appear somewhat less impressive, even to the point of being a little worrying. In all Mendeleev predicted a total of 18 elements, of which only nine were subsequently isolated. As one historian of chemistry has wondered, how is it that we are prepared to forgive Mendeleev so many failures?

In addition, it is by no means clear that successful predictions were in fact so decisive in the acceptance of the periodic table by the scientific community in Mendeleev's era. For example, the Davy medal, which predates the Nobel Prize as the highest accolade in chemistry, was jointly awarded to Mendeleev and Julius Lothar Meyer, his leading competitor, who did not make any predictions. Indeed, there is not even a mention of Mendeleev's predictions in the published speech that accompanied the joint award of the Davy prize. It therefore seems that this prize was awarded for the manner in which the

two chemists has successfully accommodated the then-known elements into their respective periodic systems rather than for any foretelling.

Theoretical physics has provided a partial explanation for the form and existence of Mendeleev's table and its modern descendents. From the viewpoint of physics, the electrons orbiting the nucleus of an atom are responsible for its chemical properties. Atoms of elements that lie in the same group or vertical column of the table do so because they share the same number of outer-shell electrons. The very idea of electrons in shells is a quantum-mechanical concept. The energy of electrons is said to be quantized in the sense that electrons occupy a set of energy levels or orbitals, each level having a specific and discrete energy value.

In addition, solutions to Austrian physicist Erwin Schrödinger's famous equation for the electron can be characterized by a set of quantum numbers. When this set is supplemented with an additional quantum number for spin, it is possible to predict that subsequent main shells of the atom can contain a maximum of 2, 8, 18 or 32 electrons. This

is in perfect agreement with the lengths of periods in the chemist's periodic table. The simple quantum mechanical theory does not, however, account for the repetition of all period lengths except for the first one. Indeed, this problem has continued to elude theoretical

element	atomic weight
hydrogen (H)	1.0
beryllium (Be)	10.9
boron (B)	11.7
carbon (C)	12.0
nitrogen (N)	12.6
oxygen (O)	16.0
fluorine (F)	9.6
sodium (Na)	93.3
magnesium (Mg)	50.0
aluminium (Al)	55.0
silicon (Si)	49.0
phosphorus (P)	27.0
sulfur (S)	32.0
chlorine (Cl)	70.0
potassium (K)	156.0
calcium (Ca)	82.0
titanium (Ti)	28.8
chromium (Cr)	113.0
manganese (Mn)	113.0
iron (Fe)	111.0
cobalt (Co)	117.0
nickel (Ni)	117.0
copper (Cu)	128.0
zinc (Zn)	128.0
arsenic (As)	134.0
strontium (Sr)	178.0

Figure 4. One early attempt at a classification system for the elements related their atomic weights to that of hydrogen, whose weight was taken to be 1.0. Around 1815 London physician William Prout hypothesized that, because the atomic weights of many elements seemed to be integral multiples of that of hydrogen, perhaps all elements were, in fact, composite multiples of hydrogen. The atomic weights shown in this table were typical values that were available in Prout's time, but they are not accurate by modern standards.

physicists until quite recently. Appropriately enough, it was a Russian physicist, the late Valentin Ostrovsky, who recently published a theory to explain this feature, although it is not yet generally accepted. Although the theory is too mathematically complicated to explain here, Ostrovsky's work and some other competing accounts demonstrate that the periodic table continues to be an area of active research by physicists as well as chemists even though it has existed for nearly 140 years.

Fertile Ground

Chemists, physicists and philosophers of science continue to debate the relative virtues of different forms to display the periodic table itself. Some even question whether a two-dimensional table is the best way to arrange the elements. Chemists frequently express the view that there is no one best representation and that the question of representation is a matter of convenience and convention. More recently this view has been questioned by philosophers of science,

Figure 5. The standard modern periodic table, called the medium-long form *(top)*, shows the elements in rows in order of increasing atomic number, or the number of protons in the nucleus of an atom of each element. Each row makes up a period, the lengths of which vary. Each column represents a group in which the elements have similar chemical properties, related to the number of electrons in the outer, or valence, shell of their atoms. The lanthanides and actinides, in the separated bottom two rows, are pulled out after the elements barium (Ba) and radium (Ra), for the sake of compactness. Highlighted on this table *(pink)* are triads, originally related by their atomic weights, but that work in terms of atomic numbers *(beige)*. An alternate table is the left-step form *(middle)*, which puts helium in the alkaline earth group as these all have two electrons in their valence shells. It also more naturally follows the order of the filling of electron shells. The author has proposed another form *(bottom)* that puts hydrogen in the halogens group and places this group at the leftmost edge of the table. This form dispenses with the anomalous-seeming two-element period in the medium-long table and is based on maximizing atomic-number triads, such as the new one formed by hydrogen (H), fluorine (F) and chlorine (Cl) *(pink)*.

some of whom believe that there may be one best way to arrange the elements in groups of columns. They argue that disputes concerning the placement of certain troublesome elements, such as hydrogen and helium, in the periodic system have one correct solution, even if this is not yet apparent to current-day science.

Consequently, they maintain that some displays of the periodic system may, in truth, be superior to others. Whereas the conventionally displayed table, called the medium-long form, has many virtues, it places helium among the noble-gas elements. Some have argued that in spite of appearances, helium should in fact be placed at the head of group 2, the alkaline earth group, which includes beryllium, magnesium and calcium. Helium has two outer-shell electrons as do the elements in the alkaline earth group.

In addition, the filling of electron shells follows a particular ordering, which is more naturally displayed with this grouping, called the left-step periodic table. This form of the periodic system was first proposed by the Frenchman Charles Janet in the 1920s and has recently been revived by U.S. chemical educator Gary Katz, among others. Further support for this representation also lies in the fact that it renders the periodic system more orderly than the conventional layout. In the left-step table there are two very short periods of two elements, instead of one, with the result that *all* period lengths, without fail, are repeated.

In a recently-accepted paper, I have proposed another periodic table in which hydrogen is placed at the head of the halogen group. Moreover, this table has been rearranged so that the group that is now headed by hydrogen appears at the left-hand edge of the table. The main outcome of this arrangement is to introduce greater regularity into the display of the periodic system, which may reflect the regularity of the periodic law more faithfully. This modified periodic table displays two periods of eight elements at the start of the periodic system and dispenses altogether with the anomalous-seeming very short period of two elements.

The main motivation for this layout is that it leads to the formation of a new perfect triad involving hydrogen. In addition, the perfect triad involving helium is retained, unlike in the left-step table, where it is lost. But why

should one even seek to create any new perfect triad? This feature is rather important because it is based solely on atomic number, the only criterion of the elements regarded as basic substances rather than simple substances. As mentioned earlier, Mendeleev went to great lengths to emphasize that the periodic system was primarily a classification of the elements as basic substances ("real elements").

This more-philosophical view of the elements has come to the rescue of chemistry as its own field, rather than simply a part of physics, on more than one occasion. It suggests that chemistry possesses an essential philosophical foundation even though it is popularly presumed to reduce to quantum physics and thus to be devoid of a philosophical character. In the early years of the 20th century, when isotopes of many elements were discovered, it suddenly seemed as if the number of "elements," in the sense of simplest substances, that can be isolated had multiplied. Some chemists believed that this proliferation would signal the demise of the periodic table, which would give way to a table of the isotopes.

However, some chemists such as Austrian Friedrich Paneth reconceptualized the notion of elements in such a way as to avoid the abandonment of the chemist's periodic table. Paneth appealed to Mendeleev's distinction between "real elements" and elements as simple substances. By concentrating on the "real elements" as Mendeleev had done, but now characterizing them by their atomic numbers, the chemist could ignore the fact that the "elements" occur as many hundreds of isotopes. The isotopes could be regarded as mere simple substances. Moreover, isotopes of the same element, with a few exceptions such as those of hydrogen, tend to show identical chemical properties, thus justifying this approach.

Perhaps the most radical development to take place in contemporary research on the periodic table has been a willingness to challenge tradition by questioning whether the periodic system should be displayed in a two-dimensional form and whether it should even be displayed as a table. At least three distinct three-dimensional periodic systems have been developed and successfully marketed as educational tools. In some cases, such as Canadian chemist Fernando Dufour's
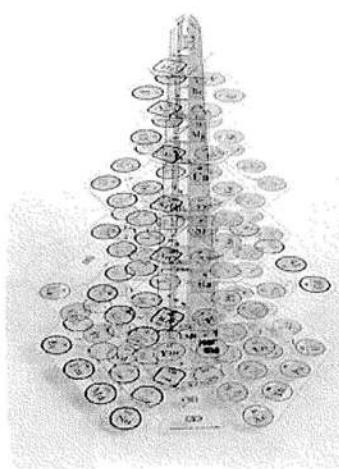
Figure 6. Canadian chemist Fernando Dufour has taken the periodic system from two to three dimensions, dispensing with the idea of a table altogether. His system, produced in 1990 and called the ElemenTree, emphasizes chemical similarities that span different groups on the standard table. (Photo courtesy of the author.)

"ElemenTree," they also serve to emphasize chemical similarities that are not embodied in the conventional two-dimensional table.

For example, the elements in group 13 of the conventional-format table, such as boron, aluminum and gallium, all display a combining power, or valence, of three. However, there are a number of other elements that also show this property, such as the elements in group 3 of the conventional table, including scandium, yttrium and lutetium. In Dufour's system all these elements fall onto the same two-dimensional plane which may be pictured as a slice through the three-dimensional classification system.

Another design that Philip Stewart of the University of Oxford has revived and argued for is the spiral-form periodic system, and it has received a good deal of recent attention. As Stewart contends, the conventional table fails to emphasize the continuity in the sequence of the elements. Spiral systems stress continuity rather than implying breaks between the noble gases at the right-hand edge and the alkali metals at the left edge.

Hindsight

Could it be that our reliance on the

Figure 7. Philip Stewart of Oxford University has championed a spiral format for the periodic system. Such continuous forms get rid of the implied breaks between periods in the conventional table. Spiral forms have been considered for more than 100 years, but this poster shows Stewart's adaptation, which he calls a "chemical galaxy," as the increasing length of the periods can be accommodated by a format similar to the radiating arms of a spiral galaxy. (Image courtesy of Philip Stewart and Carl Wenczek of Born Digital Ltd.)

two-dimensional forms of the periodic table are due to the predominance, until recently, of the two-dimensional textbook page surface and the two-dimensional nature of the walls of lecture theaters? After all, a three-dimensional system is not so easily displayed in a book or indeed on the wall of a lecture hall. But could it also be that with the rise of new technologies in the 21st century, Mendeleev's famous icon might be transformed into something that even he might not recognize if he were still here to see it?

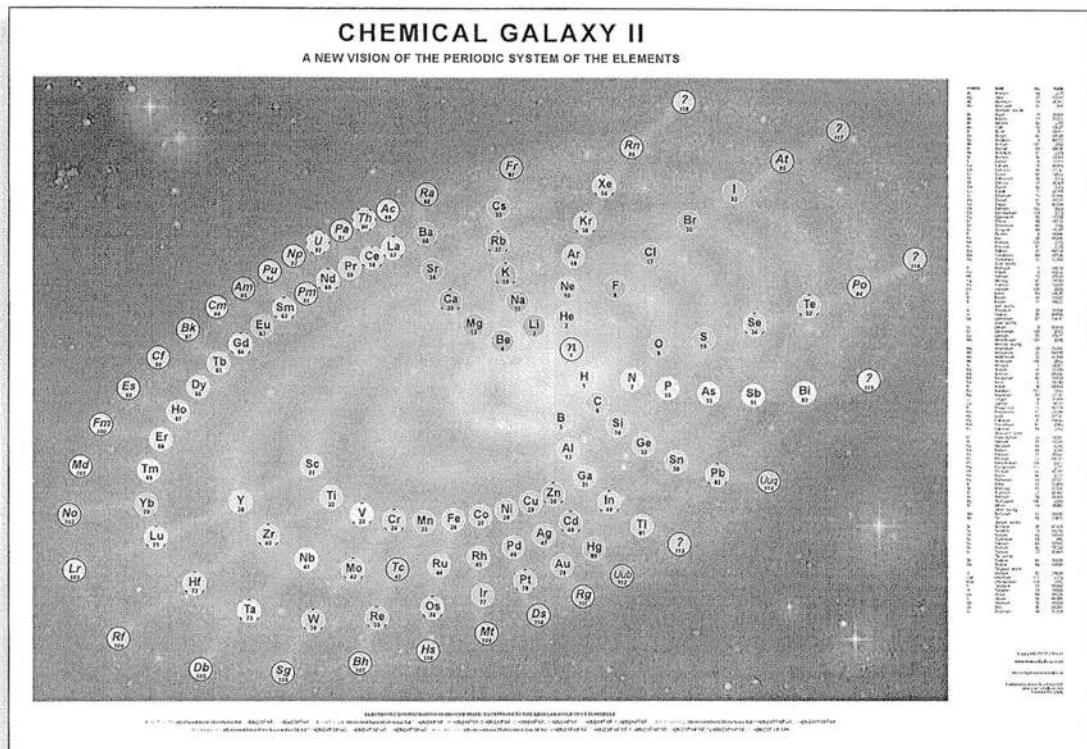In fact, as far as spiral forms are concerned, Mendeleev did consider such arrangements but did not devise a successful version. As Stewart has written, if Mendeleev had paid more attention to spiral forms, he might have added the prediction of the whole family of noble gases to his other famous predictions of isolated elements. If one uses a spiral display of the elements, the possible existence of the noble gases be-

comes rather obvious, as was noted by the English chemist William Crookes more than 100 years ago.

The periodic table began with the recognition of triads of elements and arose at the time of Prout's hypothesis of the unity of all matter. From these numerical and philosophical origins it has evolved into an enormously practical tool used not just by chemists, but by all scientists and engineers. But its philosophical aspects have not been completely eclipsed, and, as I argue here, they continue to underwrite the periodic system and sometimes surface to assist in the solution of practical issues concerning its identity and graphical representation.

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The Dual Sense of the Term "Element," Attempts to Derive the Madelung Rule, and the Optimal Form of the Periodic Table, If Any

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ABSTRACT: This article concerns various foundational aspects of the periodic system of the elements. These issues include the dual nature of the concept of an "element" to include element as a "basic substance" and as a "simple substance." We will discuss the question of whether there is an optimal form of the periodic table, including whether the left-step table fulfils this role. We will also discuss the derivation or explanation of the $[n + \ell, n]$ or Madelung rule for electron-shell filling and whether indeed it is important to attempt to derive this rule from first principles. In particular, we examine the views of two chemists, Henry Bent and Eugen Schwarz, who have independently addressed many of these issues. © 2008 Wiley Periodicals, Inc. Int J Quantum Chem 109: 959–971, 2009

Key words: elements; periodic table; Madelung rule; left-step table

The Nature of the Concept of an "Element"

Discussions concerning the fundamental importance of the concept of "element" have been published by a number of historians and philosophers of chemistry in recent years [1–5]. In addition, some chemists have begun to elaborate their

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views on the subject [6, 7]. Much of this work appeals to the published views of Mendeleev in the late 19th century and also to the work of Paneth in the 1920s and 30s [8]. Some authors began at the dawn of ancient Greek philosophy, in which there was considerable discussion upon the most fundamental components of the nature [9].

However, this article will take as its starting point the seminal work of Lavoisier [10]. It is generally agreed that Lavoisier was among the first chemists to turn their backs on regarding the elements as unobservable principles or as literally substances which

stand underneath all matter.[1] In common with the growing positivism that characterized the scientific revolution in general, Lavoisier's approach was to eschew any notions of elements as principles in favor of regarding the elements as "simple bodies" to use an English translation of his own term *corps simples*.[2] These "elements" were regarded as substances which could actually be isolated and which were the final stage of any attempts to break them down into further components.

In 1789, Lavoisier and his collaborators famously published their list of elements as simple bodies. In doing so they continued to include a number of "principles" such as chaleur and lumière, but it seems to be widely held that their intention was to concentrate on the truly simple bodies. As is the case in many revolutionary changes, including co-incidentally the French revolution that took the life of Lavoisier, such tumultuous changes have a tendency to be excessive in their early stages. It was not until the writings of Mendeleev, a good 80 years later, that the more abstract sense of the term "element" was to return and to receive a clear elaboration, although it became rather different from the "principles" of the ancient Greek philosophers and the alchemists. For example, Mendeleev wrote

It is useful in this sense to make a clear distinction between the conception of an element as a *separate* homogeneous substance, and as a *material* but invisible *part* of a compound. Mercury oxide does not contain two simple bodies, a gas and a metal, but two elements, mercury and oxygen, which, when free, are a gas and a metal. Neither mercury as a metal nor oxygen as a gas is contained in mercury oxide; it only contains the substance of the elements, just as steam only contains the substance of ice, but not ice itself, or as corn contains the substance of the seed but not the seed itself [12, 13].

The subsequent development of atomic theory and quantum mechanics has provided an explana-

tion for the periodic table and a shift of attention away from macroscopic chemical properties to the properties of the neutral atoms of the elements. One result of this shift in attention has been that Mendeleev's distinction, having to do with macroscopic chemical elements, has been all but completely forgotten.

However, an important development within atomic physics, namely the discovery of isotopy in the 1910s, led some philosophically minded chemists to reexamine Mendeleev's distinction and to rehabilitate it in a modified form. With the rapid discovery of isotopes it began to seem as though there were far more "elements" than the ~90 or so which were displayed on periodic tables at the time. The work of Soddy [14], in particular, served to clarify the situation, and one that had been anticipated by Crookes,

I conceive that when we say the atomic weight of calcium is 40, we really explain the fact, while the *majority* of calcium atoms have an actual atomic weight of 40, there are not a few which are represented by 39 or 41, a less number by 38 or 42, and so on [15].

But what would become of Mendeleev's periodic system which now seemed to consist of 300 or so "elements"? To some chemists, the discovery of isotopes implied the end of the periodic system as it was known.[3] These chemists suggested that it would be necessary to consider the individual new isotopes as the new "elements." But the chemist Paneth adopted a less reductionist approach, arguing that the periodic table of the familiar chemical elements should be retained because it dealt with the "elements" that were of interest to chemists. A justification for this view was provided by the fact that, with a few exceptions, the chemical properties of isotopes of the same element are indistinguishable.[4] Moreover, Paneth appealed to Mendeleev's distinction between the two senses of the concept of an "element" in order to provide a philosophical rationale for the retention of the chemist's periodic table. Paneth argued that the discovery of isotopes of the elements represents the discovery of new elements as simple substances, whereas periodic

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[1]There has been some discussion as to whether the word "substance" is appropriate in this context. For example, Earley believes it is not because it implies a form of materiality which is not intended [2]. In this article, the word "substance" will be used, however, because of the terminology coined by Paneth when he drew his distinction between the two senses of the term "element." However, Paneth actually uses the German words "grundstuff" and "einfacherstuff" which were translated as basic substance and simple substance, respectively, in the article that appeared in the *British Journal for the Philosophy of Science* and which has been most widely read.

[2]This view is opposed by [11].

[3]This kind of argument was given by Ida Noddack, for example, as described by Van Tiggelen [16].

[4]This fact was verified experimentally by Paneth and Hevesy, who found that the redox potentials of bismuth cells containing different isotopes of the metal produced indistinguishable values.

classification à la Mendeleev should be concerned with elements as basic substances.[5]

Much more recently it has been suggested that the key to Mendeleev's success, when compared with his competitors like Lothar Meyer, lay precisely in the former's adherence to this philosophical distinction [17]. Even more recently some authors have suggested that the distinction might play a role in the question of the placement of the elements hydrogen and helium in the periodic system [6, 18].[6]

Optimal Form, If Any, of the Periodic Table

There have been, quite literally, over 1,000 different periodic tables published since the early forms by Lothar Meyer, Mendeleev, and other early pioneers [18]. Amateur and professional scientists alike, frequently debate the "best form" of the periodic table. On the other hand, many chemists adopt a somewhat condescending attitude to such activities while maintaining that there is no such thing as an optimal periodic table, adding that different forms only serve to highlight different aspects of the properties of the elements. These chemists thus seem to be placing a greater premium on utility than on "truth" for want of a better word. Such apparent conventionalism, among many chemists, not to say relativism, is surprising at least to the present author. This is especially so because these same chemists are quick to pour scorn on any suggestion of relativism in science in general, of the type that was so well criticized by Gross and Levitt and more recently by Sokal [19, 20]. While the relativists are frequently perceived as being on the losing side of the Science Wars and are ridiculed by the majority of the scientific community, the notion that periodic classification is a matter of subjectivity does not generally meet with any criticism. This ambivalent tendency is even true among authors who argue strenuously for one particular form of the periodic table such as that of Bent, of whom more will be said presently [21].[7]

Of course it is important to distinguish between the shape of the periodic table, which is admittedly a matter of choice or convention, from tables that actually place certain elements in different groups. The point is not whether one should favor a tabular form, in which periods end abruptly, over circular displays which emphasize the continuity of the sequence of the elements for example. The question is rather whether to favor a table that places the element helium among the noble gases, when compared with tables that place this element among the alkaline earths. The wider question is whether elemental classification is an objective matter of fact or whether it is a matter of convention. It is the question of whether helium, for example, has a natural kinship with the noble gases or with the alkaline earths. Or as philosophers of science are apt to say, it is the question of whether or not groups, or families of elements, represent *natural kinds*.

In this article it will be argued that the classification of the elements is an objective feature of the world and not open to conventional choice and relativism. It will also be argued that the element helium belongs objectively and most naturally either to the alkaline earths or the noble gases regardless of whether such a question may be settled at present.[8]

The Left-Step Table

This form of the periodic table is shown in Figure 1. Although it is often assumed to have a quantum mechanical origin it was first proposed on purely esthetic grounds by the Frenchman, Charles Janet [23]. But in a quantum mechanical guise it takes on a new lease of life, as will be explained shortly.

If one accepts the modern reductionist tendency that explanations of chemical facts are to be found at the level of electronic configurations, it is tempting to regard the element helium as an s-block element and perhaps to move it into the s-block of the periodic table. This change in the position of helium represents one important feature of the left-step table. A second feature is a movement of the entire s-block, complete with relocated helium, to the right edge of the conventional periodic table. In this way one achieves a pleasingly regular shape with no apparent gaps between sets of elements such as beryllium and boron, or magnesium and

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[5]Indeed, the terminology of element as basic substance as opposed to as simple substance, which has been used throughout this article, originates with this work of Paneth.

[6]However, I believe that Bent's understanding of elements as basic substances is incorrect because he insists on identifying them with neutral atoms of the elements.

[7]See review of Bent's book by Schwartz [22].

[8]The answer to this question favored by the present author is postponed for the time being.

FIGURE 1. Left-step periodic table.

aluminum, as normally found on the medium-long form table. In addition the elements are numbered sequentially, unlike in the case of the medium-long form. More significantly, one obtains a more faithful correspondence with the order of electron shell filling in the neutral atoms of the elements as given by the Madelung or $n + \ell$ rule. This rule corresponds to the empirical order of sub-shell filling in gas-phase atoms, namely,

$$1s < 2s < 2p < 3s < 3p < 4s < 3d \ldots$$

where the sum of $n + \ell$ refers to the sum of the values of the first two quantum numbers for each of the above listed orbitals. For example, the rule accounts for the fact that the 4s orbital ($n = 4$, $\ell = 0$, or $n + \ell = 4$) is occupied before the 3d orbital ($n = 3$, $\ell = 2$, or, $n + \ell = 5$). The left-step table has the additional feature that each row coincides precisely with increasing values of $n + \ell$, as shown on the right-side of Figure 1.

By contrast, the commonly used periodic table or medium-long form as shown in Figure 2, involves a certain amount of 'hopping around' in terms of values of the n quantum number as one proceeds horizontally across periods. For example, in the fourth period one encounters elements corresponding to the filling of the 4s orbital, followed by the 3d orbitals and then the 4p orbitals. It would appear that the medium-long form table is predicated on the false notion that electron shells fill sequentially in order of increasing values of n, a feature that then needs to be corrected by what I have called 'hopping around' within any single period. Nevertheless, the medium-long form arose well before the

left-step table. It was originally based on chemical similarities and not on the electronic structure of atoms of the elements, thus accounting partly for its continued widespread use.

Derivation of the $n + \ell$ Rule

Given the generalizing power of so simple a relation as the $n + \ell$ rule, it is natural to wonder whether a theoretical derivation or explanation for it can be given. If such a derivation from quantum mechanics were available it would strengthen the view that we possess a good theoretical understanding of the periodic system. What is not generally appreciated in this context is that the frequently encountered textbook explanation of the periodic system has some important limitations.

As many textbooks correctly report, the number of electrons that can be accommodated into any electron shell coincides with the range of values for the three quantum numbers that characterize the solutions to the Schrödinger equation for the hydrogen atom and the fourth quantum number as first postulated by Pauli.

The first quantum number n can adopt any integral value starting with 1. The second quantum number which is given the label ℓ can have any of the following values related to the values of n. In the form, $\ell = n - 1, \ldots, 0$. In the case when $n = 3$ for example, can take the values 2, 1, or 0. The third quantum number labeled m_ℓ can adopt values related to those of the second quantum numbers by the relationship, $m_\ell = -\ell, -(\ell + 1), \ldots, 0, \ldots, (\ell - 1), \ell$. For example, if $\ell = 2$ the possible values

																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	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

FIGURE 2. Medium-long form periodic table.

of m are -2, -1, 0, $+1$, $+2$. Finally, the fourth quantum number labeled m_s can only take two possible values, either $+1/2$ or $-1/2$ units of spin angular momentum. We thus have a hierarchy of related values for the four quantum numbers, which are used to describe any particular electron in an atom. These relationships are derived theoretically and do not involve the use of any experimental data.

For example, if the first quantum number is 3 the second quantum number ℓ can take values of 2, 1, or 0. Each of these values of ℓ will generate a number of possible values of m_ℓ and each of these values will be multiplied by a factor of two since the fourth quantum number can adopt values of $1/2$ or $-1/2$. As a result there will be a total of $2n^2$ or 18 electrons in the third shell. This scheme thus explains why there will be a maximum total of 2, 8, 18, 32, etc., electrons in successive shells as one moves further away from the nucleus.

But does the fact that the third shell can contain 18 electrons also explain why some of the periods in the periodic system contain eighteen places? Actually not exactly. If electron shells were filled in a strictly sequential manner the explanation would be complete. But as anyone who has studied even just high school chemistry is aware, the electron shells do not fill in the expected sequential manner. The configuration of element number 18, or argon is

$$1s^2, 2s^2, 2p^6, 3s^2, 3p^6$$

This might lead one to think that the configuration for the subsequent element, number 19, or potassium, would be

$$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^1$$

because up to this point the pattern has been to add the new electron to the next available orbital in the sequence of orbitals at increasing distances from the nucleus. However, experimental evidence shows that the configuration of potassium should be denoted as

$$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$$

One of the authors to ask whether a theoretical derivation of the $n + \ell$ rule might be found was the late Per Olov Löwdin, who wrote

> The energy rule for the neutral atoms was obviously in contradiction to Bohr's calculation on the hydrogen atom, which indicated that the energies should be increasing with increasing n. It is typical of the nature of "frontier-research" that Bohr abandoned this rule for the higher atoms, since it led to the wrong structure of the periodic system, and the modified rule $[(n + \ell, n)]$ seems to have

been obtained in a more intuitive way. Bohr him-self was never too explicit about his "Aufbau" -principle, and [the rule] is sometimes referred to as the Goudsmit-rule or the Bose-rule. It is per-haps remarkable that, in axiomatic quantum the-ory, the simple energy rule has not yet been derived from first principles ([24], p 332).

There have been a number of attempts to meet the "Löwdin challenge," as it has been called. Allen and Knight published an explanation in the *International Journal of Quantum Chemistry*, which has turned out to be rather problematic as I have re-cently argued [25–27]. In addition, Ostrovsky has published an account in which he claims to explain the $n + \ell$ rule, but this account is far from trans-parent, or convincing, at least to this author [28].

Recent Developments

The preceding survey will serve as background for two recently published accounts which touch on all four of the various aspects of the periodic system that have been reviewed above.

In the July 2007 issue of the *Journal of Chemical Education* Bent and Weinhold, an inorganic and a theoretical chemist, respectively, published an ex-tensive paper on the left-step periodic table. One rather noticeable feature of their article is the overtly reductionist stance that the authors adopt. They wrote

Only with Bohr's 1913–1923 introduction of the "old quantum theory" (itself strongly inspired by chemical periodicity patterns; vide infra) and the final discovery of Schrödinger's wave mechanics in 1925 would the periodic table be supplanted as the deepest expression of current chemical un-derstanding ([21], p 2).

It seems a little excessive, at least to this author, that the periodic table is being regarded as some-how supplanted by quantum mechanics. This is something that is simply not the case on closer examination, as I have argued in some previous articles [29, 30].

Or to cite another passage, Bent and Weinhold wrote

Modern ab initio calculations daily confirm the usefulness of the orbital-based quantal perspec-tive as a basis for predicting complex chemical phenomena. In this framework the fundamental descriptors of the orbital filling sequence are the

radial (n) and angular (l) quantum numbers. Thus, one may conclude that the most profound characterization of the chemical properties of a given atom is in terms of quantum numbers or equivalent descriptors that allow the relative en-ergy, angular shape, radial diffuseness, or other properties of its occupied and unoccupied va-lence orbitals to be inferred ([21], p 3).

It is not easy to see why the authors believe that the success of orbital calculations should lead one to think that the most profound characterization of the properties of atoms implies such an importance to quantum numbers as they are claiming. As is well known in quantum chemistry, successful mathematical modeling may be achieved via any number of types of basis functions such as plane waves. Similarly, it would be a mistake to infer that the terms characterizing such plane wave expan-sions are of crucial importance in characterizing the behavior of atoms.

A third quotation to illustrate the naively reduc-tionist approach of Bent and Weinhold is as fol-lows:

A primary goal of the periodic table is to assist recognition of the ground-state valence electron configuration of each atom, the chief determinant of its chemical properties" ([21], p 5).

While it may be true that the periodic table is used in chemical education in order to arrive at the electronic configuration of any particular atom, this is surely not a primary goal of the periodic table for chemists in general. The main goal of the periodic table remains as the classification scheme for the properties of the elements, especially as they occur in chemical compounds.[9]

Of course, a more charitable interpretation of Bent and Weinhold's statement might be to empha-size that quantum mechanics provides an approxi-mate explanation for the periodic table, whereas the periodic table itself was merely a successful classi-fication awaiting a theoretical explanation. But one cannot help thinking that this interpretation is not what the authors had in mind. What they intended

[9]In other words, the element as a basic substance. The simi-larity between the elements occurring in the same group of the periodic table is not always obvious if one focuses on the ele-ments as simple substances. For example, consider the halogens. Who would think of grouping together such a diverse set of simple substances as two green-yellow gases, a brown liquid, and a violet-black solid? And yet the compounds of these four halogens with sodium, for example, are all very similar white crystalline solids.

was apparently the notion that all that really matters are the microscopic "goings on."

But the reductionist approach adopted by Bent and Weinhold is nevertheless consistent with their wanting to explain the periodic table through the properties of the neutral atoms of the elements rather than their macroscopic properties.

Bent and Weinhold on the $n + \ell$ rule

One of the main benefits of the paper by Bent and Weinhold is a plausible explanation for the $n + \ell$ rule which does not, at first sight, seem to suffer from the drawbacks of the explanations of Allen and Knight as well as Ostrovsky. However, the recent explanation by Bent and Weinhold comes at a certain cost as will be explained.

The authors begin by appealing to the Sturm-Liouville theory which applies to a wide class of differential equations. This theory essentially holds that the solutions to this class of differential equations can be placed in order of increasing energy according to the number of nodes that they possess. This notion appears to be rather promising given that orbitals with increasing values of n and ℓ are indeed known to have an increasing number of radial as well as angular nodes with a corresponding increase in orbital energy.

But the promise of simplicity is somewhat short-lived once one realizes that the total number of nodes in atomic orbitals, as normally defined, fail to predict the correct order of increasing energy. The 4s orbital has 3 radial nodes plus 0 angular nodes, making a total of 3 nodes altogether. Meanwhile, the 3d orbital has 0 radial nodes and 2 angular nodes and thus a total of only 2 nodes. And yet the 4s orbital with the higher total number of nodes is preferentially occupied or has a lower energy than the 3d orbital.

However, the authors soon inform the reader that that they are adopting a rather exotic sense of the term radial node, as well as treating the angular nodes in an unconventional manner. In addition to the radial nodes, given by the well-known equation of $n - \ell - 1$, the authors include an additional radial node because of the existence of a node at infinity. The result of this change is to produce a total of $n - \ell$ radial nodes.

Next, instead of counting the normal number of angular nodes, or ℓ, the authors consider twice the value of ℓ. The net result of both of these changes is to give $n - \ell + 2\ell$ or a total of $n + \ell$. Not

surprisingly they thereby obtain some consistency with the $n + \ell$ rule, and the number of nodes with increasing energy, by using this very specific way of counting the nodes in any particular atomic orbital. For example, the 4s orbital has 3 radial nodes plus 1, plus 0 angular nodes, making a total of 4 nodes if counted in this particular manner. Meanwhile, the 3d orbital has 0 radial nodes plus 1, plus 2 times 2, giving a total of 5 nodes when counted in the same manner.

As a result of this way of counting nodes the 4s orbital has a lower total number of nodes, that is, 4 when compared with 5 in the case of the 3d orbital. Moreover, this order agrees with the experimentally observed order whereby 4s has lower energy than 3d.[10] However, whether this is a satisfactory first principles explanation of the $n + \ell$ rule, which meets the Löwdin challenge, is something that seems rather unlikely given the ad hoc nature of the manner in which nodes have been counted.

It should also be said that the reason why Bent and Weinhold devote such attention to the $n + \ell$ rule is that, as mentioned earlier, the rule is clearly represented on the left-step table, the form of the periodic table that they favor. In addition, as was mentioned, the authors believe that the best representation of the periodic system should be based on the electronic structure of the neutral atoms of all the elements and not on their macroscopic properties.

The Concept of "Element" Revisited

But what does all this work have to do with the question of the interpretation of the concept of an "element"? This issue is not explicitly addressed in the paper by Bent and Weinhold but has been addressed by Bent in his recent book, which is entirely devoted to the left-step table [6].

Bent claims that the periodic system should be primarily based on the structure of neutral atoms rather than on macroscopic properties of the elements. In doing so he claims support from none other than Mendeleev. Bent also claims to garner support from the writings of Mendeleev in steering clear of the properties of the elements as simple substances in crucial matters of classification of the elements. In fact, the identification of elements as basic substances with the atoms of the elements is

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[10]This is the case for K and Ca but not for subsequent transition metal atoms [31].

indeed suggested by a number of passages in the writings of Mendeleev, which are duly cited by Bent.

For example, Bent cites what he calls Mendeleev's absolute distinction:

> The central idea that aided me in undertaking the study of the periodic law of the elements, consists primarily in the absolute distinction between an atom [of e.g. the element carbon] and a simple body [such as diamond or graphite] ([32, p 193]).

> All that I am going to say [about the Periodic Law] must be understood as relating to atoms... and not simple bodies ([32, p 193]).

But I would like to suggest that Mendeleev, and now Bent, are incorrect in drawing this identification. Nor do I claim any originality in pointing out Mendeleev's error because this was already clearly stated by Paneth in a couple of articles written in the 1930s.

> The reason why this distinction [two senses of "element"] has been so little noticed seems to be, on one hand, that the terms used by Mendeleeff are not very appropriate, and that, on the other hand, by coupling them to the pair of concepts, molecule and atom, he seems to have missed the essential point ([33], p 57).

> It is hardly possible in chemistry to introduce a contrast between elements and simple bodies, as the definition of element since Lavoisier is based on the simple body. It seems to me to be even less apt simply to equate the terms element/atom and simple body/molecule, respectively for apart from the fact that there are simple bodies whose molecules are single atoms, molecules and atoms belong indubitably to one and the same group of scientific concepts, while the essential difference between element and simple body in the Mendeleeffian sense of the words, lies in their belonging to quite different spheres in epistemology ([33], p 57).

To remedy this mistaken identification I propose a return to discussing elements as basic substances, without recourse to any microscopic account.

A Paper by Schwarz

I now proceed to an examination of a second recent paper by the German theoretical chemist Schwarz which was published in Foundations of Chemistry [7]. This paper I believe is more philosophically astute than the work of Bent and Weinhold or the book by Bent.

Schwarz addresses the question of the concept of an "element" directly and concludes that an element may be regarded not in just two, but three ways.

1. Basic chemical element: The original and still present meaning of element or principle in chemistry is the basic sub-stance behind chemical stuffs, only implicitly defined through a conservation law in chemical reactions.

2. Metallurgical element or simple material: The chemical stuff that contains only one CE. It is specified through the stationary physical properties of its different phases and modifications.

3. Astrophysical spectroscopic element or elemental atom: Physical atoms in vacuum specified by the nuclear charge.

The CEs, however, refer to the properties and reactions of macroscopic materials, made up of chemically *deformed* atoms ([7], p 142).

It immediately becomes clear from this list that Schwarz is not falling into the error of identifying elements as basic substances with the neutral atoms of the elements, given that he includes the neutral atoms as a third sense of element in addition to basic substances and simple substances.

Indeed the article by Schwarz is even more radical, in that he considers the attention that has been devoted to trying to derive the $n + \ell$ rule to be entirely misplaced.

> There are two basic differences of (sic) free atoms and chemically bound atoms. First, the more diffuse an AO, the stronger it is perturbed in molecular and condensed matter. The $(n + \ell)$s AOs of the transition metal atoms, especially of the earlier ones, are not of primary importance for chemical bonding. Their relevance is comparable to that of the diffuse orbitals of main group elements ([34], p 653).

> Second, metal atoms carry some positive charge in the majority of their compounds. Transition metal cations have pure d configurations, in contrast to the mixed d-s configurations of free neutral transition metal atoms. There is the chemical rule that "s electrons fall down into the d level

when chemical bonding occurs." The wide field of organic, inorganic and biochemical transition metal complexes is semi-quantitatively explained by pure d-bonding. This holds even for nonpolar complexes. For instance, while the ground configuration of the Ni atom in its neutral free state is d^9s^1, the valence configuration of Ni in the famous homopolar $Ni(CO)_4$ complex is d^{10} ([34], p 653).

There is no obvious logical or physical relation between the configurations of the neutral atomic ground states and the main chemical characteristics of the elements ([34], p 653).

During the endeavor to understand and explain the PT physically, a lot of effort has been spent on secondary problems. Even worse, an orbital ordering rule that has no general validity, has been assumed to be of central relevance. It has often been said that the structure of the neutral atoms is of primary importance for the periodic system. This is true, though in a modified sense ([34], p 653).

What is of primary importance chemically is not the ground state, nor the ground configuration, which is some average of valence states, of the free atom; but it is the atomic response properties to perturbations by other atoms. That is governed by the energies and spatial extensions and polarizabilities of the upper core and of the compact valence orbitals ([34], p 653).

What Schwarz appears to be implying, although this is nowhere stated explicitly, is the following parallel between the elements as basic and simple substances at both the macroscopic and microscopic levels.

Macroscopic	Microscopic
Elements as basic substances	Bonded atoms
Elements as simple substances	Neutral atoms

I believe this to be a step in the right direction, in that it avoids the identification of basic substances and neutral atoms, but still not a completely consistent picture. It is a step in the right direction since it focuses attention on bonded atoms rather than isolated neutral atoms and thus in keeping with the notion that the periodic system classifies the elements as they occur in compounds rather than in isolation.

Because Schwarz avoids the identification between elements as basic substances and neutral atoms, he is less willing to regard the derivation or otherwise of the $n + \ell$ rule as an important feature of the microscopic understanding of the periodic system. As Schwarz repeatedly stresses, the order of electron-shell filling in ions does not follow an $n + \ell$ rule but the simpler n rule.

Exceptions to the $n + \ell$ rule

In any case, as many authors have previously pointed out the $n + \ell$ rule is strictly speaking subject to about 20 exceptions, thus further hinting that it has no fundamental value.[11] The best known of these anomalies occur in the neutral atoms of chromium and copper which have the following expected and observed electronic configurations, which generations of general chemistry student have been obliged to learn:

	Expected configuration	Observed configuration
Chromium	[Ar] $4s^2\ 3d^4$	[Ar] $4s^1\ 3d^5$
Copper	[Ar] $4s^2\ 3d^9$	[Ar] $4s^1\ 3d^{10}$

The second transition series shows a total of six anomalous configurations:

	Expected configuration	Observed configuration
Niobium	[Kr] $5s^2\ 4d^3$	[Kr] $5s^1\ 4d^4$
Molybdenum	[Kr] $5s^2\ 4d^4$	[Kr] $5s^1\ 4d^5$
Ruthenium	[Kr] $5s^2\ 4d^6$	[Kr] $5s^1\ 4d^7$
Rhodium	[Kr] $5s^2\ 4d^7$	[Kr] $5s^1\ 4d^8$
Palladium	[Kr] $5s^2\ 4d^8$	[Kr] $5s^0\ 4d^{10}$
Silver	[Kr] $5s^2\ 4d^9$	[Kr] $5s^1\ 4d^{10}$

while there are two such anomalies in the third transition metal series:

	Expected configuration	Observed configuration
Platinum	[Xe] $6s^2\ 5d^8$	[Xe] $6s^1\ 5d^9$
Gold	[Xe] $6s^2\ 5d^9$	[Xe] $6s^1\ 5d^{10}$

The symbols for all these elements showing anomalous configurations are shown in boldface in Figure 3.

[11]These 20 cases do not represent anomalies to the order of orbital filling which is invariably governed by the $n + \ell$ rule but are anomalous in the sense that the s orbital is not completely filled before the corresponding d orbital begins to fill.

SCERRI

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	Co	Ni	**Cu**	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	**Nb**	**Mo**	Tc	**Ru**	**Rh**	**Pd**	**Ag**	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	**Pt**	**Au**	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	T	Yb
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

FIGURE 3. Medium-long form table highlighting elements with 10 anomalous configurations (in bold face) among 30 the d-bock elements.

What would happen if we were to take up Schwarz's suggestion on concentrating on bonded atoms rather than neutral atoms, which do not occur in bonded transition metal atoms? What kind of periodic table would one be led to?[12] For example, one might examine the electronic configurations of the highest and most common oxidation states for each of these metals. This is carried out in Figure 4, below, in which we find that of the 10 anomalous neutral atom configurations, only two remain anomalous in the sense of differing from the configurations of other metal ions in their respective groups. Whereas the Cu^{+2} ion has configuration [Ar] $3d^9$, those of the Ag^+ and Au^{3+} ions are [Kr] $4d^{10}$ and [Xe] $5d^8$.

However, Schwarz's suggestion to focus on bonded atoms rather than neutral atoms also runs into a major problem because the atoms of any element typically show a large variety of oxidation states. For example, atoms of chlorine occur in the zero oxidation state in the chlorine molecule, the −1 state in NaCl, +1 in HOCl, +3 in $HClO_2$, +5 in $HClO_3$, and +7 in $HClO_4$.

To devise a periodic table of configurations of bonded atoms we would be obliged to focus on perhaps the highest oxidation state or the lowest oxidation state. Such decisions would not appear to be sufficiently categorical. Unfortunately one must abandon the notion that the problem may be solved by merely switching attention from neutral atoms to bonded atoms of the elements, as Schwarz seems to be recommending. A more satisfactory solution to such questions must surely be sought elsewhere.

A Possible Solution

It was suggested earlier that Schwarz's identification of bonded atoms with elements as basic substances represents a step in the right direction. This notion will now be examined more carefully, since it too will be found lacking in a rather fundamental way, which was hinted at in some earlier quotations from Paneth. The concern voiced by Paneth regarding associating elements as basic substances with neutral atoms was due to the fact that these concepts inhabit different epistemological levels. This is equally true of the identification of elements as basic substances with bonded atoms, which is the identification that Schwarz supports.

Instead of identifying elements as basic substances with neutral atoms (Bent and Weinhold and almost everybody else) or elements as basic substances with bonded atoms (Schwarz), I would like to propose just focusing on elements as basic substances in Paneth's macroscopic sense. The one ma-

[12]This question has not been pursued by Schwarz.

CONCEPT OF "ELEMENT," MADELUNG RULE, AND OPTIMAL PERIODIC TABLE

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc +3	Ti +4	V +5	Cr +6	Mn +7	Fe +3	Co +3	Ni +3	Cu +2	Zn +2	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y +3	Zr +4	Nb +5	Mo +6	Tc +7	Ru +3	Rh +3	Pd +3	**Ag +1**	Cd +2	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu +3	Hf +4	Ta +5	W +6	Re +7	Os +3	Ir +3	Pt +3	**Au +3**	Hg +2	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	112						

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

FIGURE 4. Medium-long form table showing highest and most common oxidation states of the d-block elements. Only two of these 30 ions, Ag^{+1} and Au^{+3}, (shown in bold-face) show anomalous electronic configurations with respect to other ions in the same groups.

jor characteristic of such a sense of the term "element," as we have discussed earlier, is simply its atomic number. It is something of a paradox that even in modern chemistry where we have learned that electrons are responsible for all manner of reactivity, be it electron transfer, sharing, or exchange of various kinds, one is nevertheless forced into conceding that the identity of any element resides in the unchanging nuclear charge and not in the electrons.

Seen from a somewhat different perspective this fact should not seem at all paradoxical, because in seeking identity one needs to focus precisely on what does not change. But how can the mere value of Z, or some function of it, be used in the classification of the elements into groups? Of course, the use of atomic number in arranging the elements into a sequence (primary classification) has been appreciated in the pioneering work of van der Broek and Moseley (see Chapter 6 in [18]).

What will now be proposed is that in addition to its role in ordering the elements, the quantity Z may be used to also affect a secondary classification of the elements, that is, their placement into vertical groups in the sense of the conventional periodic table. In proposing this idea, I make use of what was historically the earliest hint of chemical periodicity, namely, the existence of triads of elements [35].

The realization that the better ordering criterion is atomic number rather than atomic weight invites us to consider triads of atomic numbers. This reveals a most remarkable fact, namely that ~50% of all conceivable triads on a conventional periodic table are in fact exact. For example, the elements sulfur, selenium, and tellurium have atomic numbers of 16, 34, and 52, respectively, thus showing that the atomic number of the middle of these three
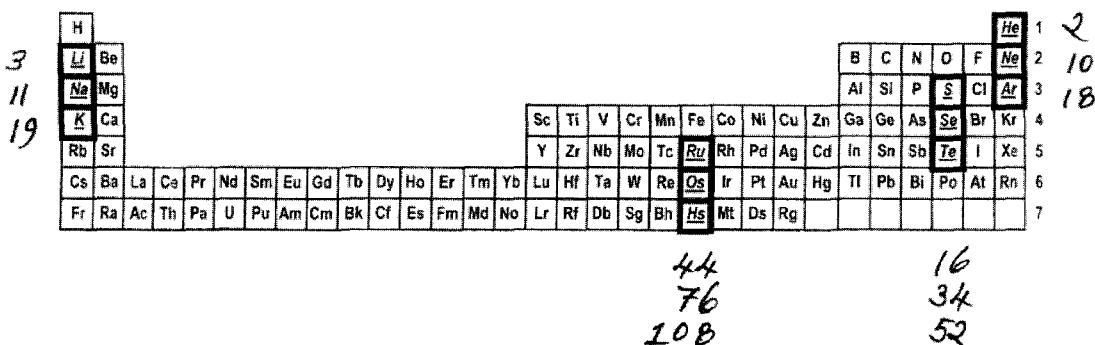
Summary of How the Elements as Basic Substances are Regarded by Various Authors.

Bent and Weinhold	Neutral atoms
Schwarz	Bonded atoms
Mendeleev, Paneth, Scerri	Macroscopic elements, characterized by Z

FIGURE 5. Long-form periodic table highlighting several atomic number triads.

elements has an atomic number that is exactly intermediate between those of the two flanking elements. Moreover, the reason why such atomic number triads are exact is well understood. It results quite simply from the fact that the length of the periods containing selenium and tellurium are of identical lengths, being eighteen elements. Figure 5 shows selected instances of such perfect atomic number triads as they occur on a long-form periodic table.

What is being suggested is that given the fundamental importance of concentrating on elements as basic substances, and given the fact that such elements are characterized by their atomic numbers, one should aim to maximize the number of perfect triads in displaying the periodic table. This proposal has an immediate consequence on the question of where the element helium, as well as other troublesome elements such as hydrogen, should be placed.[13]

Instead of moving helium into the alkaline earths and thereby losing a perfect atomic number triad, we suggest that helium should remain in its usual position. It is rather the element hydrogen that should be relocated to the top of the halogen group in order to obtain a new perfect atomic number triad. Needless to say, the relocation of hydrogen to the halogen group has a long history based on chemical and physical grounds [38–40].

[13]The element hydrogen has been placed by different authors in the alkali metals, in group 14 on top of carbon, among the halogens and sometimes simply allowed to float in an apparently unconnected manner above the main body of the periodic table. Citations for the first placement are unnecessary because this is a frequent choice. For the second, third, and fourth placements, see [36–40].

Conclusions

Schwarz has suggested that the $n + \ell$ rule is relatively unimportant. He believes that it is because attention should be directed to the configurations of bonded atoms rather than neutral atoms. As he points out, the configurations of bonded atoms do not follow the $n + \ell$ rule but rather the simpler rule of increasing values of n.

The suggestion of the present author is more radical. It is suggested that both of these rules, $n + \ell$ for neutral atoms and the rule of increasing n for bonded atoms, are somewhat irrelevant in the question of the foundations of the periodic system. This is because chemical identity resides at the level of the nucleus and therefore with atomic number, and not at the ever-changing level of electrons whose configuration is summarized by the aforementioned rules.[14]

Schwarz has taken the significant step of denying the identification of gas phase with elements as basic substances as well as denying the importance of the configurations of gas phase atoms. Consequently he also denies the importance of the Madelung rule for the filling of orbitals in gas phase neutral atoms. However, by merely focusing the attention on bonded atoms Schwarz is still not referring to elements as "basic substances" as he seems to believe that he is doing. According to the present author, and in keeping with the views of Paneth, elements as basic substances should be characterized by just their atomic numbers. Furthermore, as I have recently suggested,

[14]A few studies are starting to claim correlations between nuclear structure and electronic configurations such as the occurrence of anomalous configurations in atoms [41–43].

the use of atomic numbers, and more specifically atomic number triads, may cast new light on the question of the placement of hydrogen in the periodic table [44]. This element is traditionally placed at the head of the alkali metals, with the result that it does not form part of an atomic number triad. If it is moved to the top of the halogen group, one thereby obtains a new atomic number triad consisting of H (1), F (9), and Cl (17).

Similarly, the desire to maximize the number of atomic number triads would suggest that helium should not be moved away from its traditional place at the top of the noble gases as has been suggested by proponents of the left-step periodic table such as Bent and Weinhold.

Finally, if there is any validity in the use of the triad principle in resolving such issues, it would suggest that just one criterion, Z, can be used for both primary and secondary classification. This Z can be used for primary classification, or to provide an ordering of the elements, which is of course completely uncontroversial. The new idea lies in using a relationship among values of Z (atomic number triads), to classify elements into groups or secondary classification as we are calling it here. In addition, such an approach lends further support to the notion that group 3 of the periodic table should consist of the elements Sc, Y, Lu, Lr, rather than Sc, Y, La, Ac, as one finds in many modern periodic tables. Whereas the elements Y, Lu, Lr form an atomic number triad, Y, La, and Ac do not.[15]

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[15]Many textbooks and even IUPAC place La and Ac in the latter positions, whereas there are good physical arguments for placing Lu and Lr in these places as argued sometime ago by Jensen [45].

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