

## CHAPTER 6 | The Changing Views of a Philosopher of Chemistry on the Question of Reduction

ERIC R. SCERRI

### 1 *The Question of Reduction*

The question of the reduction of chemistry to quantum mechanics has been inextricably linked with the development of the philosophy of chemistry since the field began to develop in the early 1990s. In the present chapter I would like to describe how my own views on the subject have developed over a period of roughly 30 years.

A good place to begin might be the frequently cited reductionist dictum that was penned in 1929 by Paul Dirac, one of the founders of quantum mechanics.

The underlying laws necessary for the mathematical theory of a larger part of physics and the whole of chemistry are thus completely known, and the difficulty is only that exact applications of these laws lead to equations, which are too complicated to be soluble.

(DIRAC 1929)

These days most chemists would probably comment that Dirac had things backward. It is clear that nothing like “the whole of chemistry” has been mathematically understood. At the same time most would argue that the approximate solutions that are afforded by modern computers are so good as to overcome the fact that one cannot obtain exact or analytical solutions to the Schrödinger equation for many-electron systems. Be that as it may, Dirac’s famous quotation, coming from one of the creators of quantum mechanics, has convinced many people that chemistry has been more or less completely reduced to quantum mechanics. Another quotation of this sort (and one using more metaphorical language) comes from Walter Heitler who together with Fritz London was the first to give a quantum mechanical description of the chemical bond.

Let us assume for the moment that the two atomic systems  $\uparrow\uparrow\uparrow\dots$  and  $\downarrow\downarrow\downarrow\dots$  are always attracted in a homopolar manner. We can, then, eat Chemistry with a spoon.

(HEITLER 1927)<sup>1</sup>

Philosophers of science eventually caught up with this climate of reductionism and chose to illustrate their views with the relationship with chemistry and quantum mechanics. It must also be said that such a view agreed entirely with the prevailing notion of the unity of science as developed by the Logical Positivist school of philosophy. Here are some examples of what these philosophers wrote on the subject:

the possibility that science may one day be reduced to microphysics (in the sense in which chemistry seems today to be reduced to it...).

(OPPENHEIM, PUTNAM 1958)

Certain parts of 19th century chemistry (and perhaps the whole of this science) is reducible to post-1925 physics.

(NAGEL 1961)

Today it is possible to say that chemistry is a part of physics, just as much as thermodynamics or the theory of electricity.

(REICHENBACH 1978)

Then in the 1960s and '70s logical positivism came under increasing criticism by the likes of Popper, Kuhn, Lakatos, and Feyerabend, many of whom appealed to the history of science to challenge the prevailing view that the various special sciences could be reduced to physics. It became almost politically incorrect to hold reductionist views about any of the special sciences such as chemistry. Not surprisingly, therefore, as a graduate student beginning a PhD thesis on the reduction of chemistry, I duly climbed onto the bandwagon of anti-reductionism and produced a number of articles in which I gave specific instances of what I took to be the failure of reductionism.<sup>2</sup>

Moreover this position seemed to coincide with the fact that the philosophy of chemistry had been almost completely neglected up to that point. If chemistry were indeed reduced to quantum mechanics it would justify the belief that chemistry was very much an applied field with no particularly deep questions or big ideas. One might therefore say that in the early 1990s there were “political reasons” for claiming that chemistry had not been reduced, especially among people like myself who were campaigning for the growth of a philosophy of chemistry. In this chapter I want to take stock of the situation some 20 or more years later.

<sup>1</sup> Heitler's program to explain all of chemistry got him in trouble more than once. Wigner used to tease him. He would ask: “what chemical compounds would you predict between nitrogen and hydrogen? And of course, since he did not know any chemistry he couldn't tell me.” Heitler confessed as much. I am indebted to Gavroglu and Simoes for this episode.

<sup>2</sup> At a recent workshop on reduction and emergence at the Sorbonne University, Paul Humphreys jokingly suggested that part of the attraction for the concept of emergence comes from New Age thinking. I think the same can be said about anti-reductionism. As much as academics think they look down of such cultural movements I think they still pervade the Zeitgeist of any particular era. The popularity of New Age thinking contributes to the attraction that philosophers have for such notions as emergence and anti-reductionism.

First of all it has to be said that the field has not developed in the way that some of us believed that it might. I find it remarkable that even after 20 years there are still fewer than 10 books devoted specifically to the philosophy of chemistry. In addition, as I will be arguing, I think that our anti-reductionist claims may have been over exaggerated, due perhaps to a form of pioneering zeal on our part.<sup>3</sup>

To take another example from a recent meeting on reduction and emergence in the sciences held in Paris, only 2 of the 15 speakers were people who would describe themselves as philosophers of chemistry. The vast majority of philosophers of science still prefer to consider the philosophy of physics or of biology while conveniently skipping the field of chemistry, which lies between physics and biology in many obvious respects.

I hardly think that the unpleasant reputation that chemistry enjoys because of its messy, smelly, and often dangerous nature can be entirely to blame for the continued neglect among philosophers of science for the field of chemistry. I rather believe that it is because of a popular misconception that there are no “big ideas” in chemistry. In this chapter I will be discussing one undeniably big chemical idea, namely the existence of the periodic system.

Before moving on to the more specific part of this chapter let me also pause to mention the fact that in terms of numbers of practitioners, chemistry outnumbers all other scientific disciplines. In fact according to some measures the number of chemistry practitioners may even outnumber the sum total of combined practitioners from all other scientific fields, with the possible exception of computer science (Schummer 1997).

In very broad terms, the complexity found in the biological world ensures that the non-reducibility of biology is generally upheld. At the same time physics is physics and as such is the supreme reducing discipline while chemistry, which is a closer neighbor than biology is popularly believed to be reducible, and indeed to have been reduced. Let me quickly say that I now believe that this view is essentially correct and that chemistry is more or less a reduced science. There is no denying that chemistry has been living somewhat in the shadow of physics since the beginning of the ~~nineteenth~~ twentieth century. In this chapter I will be looking at more specific aspects, and especially at parts of chemistry which I personally claimed as examples of the breakdown of reduction but on which I have now changed my opinion as a result of more recent research.

In any case I have always tried to stress that much of the philosophical discussion is far too general to be of much use. To simply ask whether chemistry has been reduced to physics without qualification is rather meaningless.

<sup>3</sup>In spite of the lack of monographs on the subject there are two international journals devoted to the philosophy of chemistry. They are *Foundations of Chemistry* (published by Springer) and *Hyle* (published independently of any major publishing house). The parent association for *Foundations of Chemistry* is the International Society for the Philosophy of Chemistry that has held regular meetings in different locations around the world for the past consecutive 18 years. There have also been frequent sessions devoted to the philosophy of chemistry at the biennial meetings of the Philosophy of Science Association. However, as I have suggested in some earlier articles these sessions have tended to be somewhat inward looking and arranged by speakers who have agreed in advance to advance a similar agenda rather than opposing each other's work where this might be a more appropriate course of action.

Similarly, to expect there to be a yes or no answer to such a complex question is, I believe, a gross oversimplification. On this theme I think I have been fairly consistent (Scerri 1994a, Scerri 1994b).

In addition I have rejected the use of the classical criteria for reduction that have been proposed by Logical Positivist philosophers of science in favor of more naturalistic criteria. In examining the extent to which a specific area of chemistry has been reduced to quantum mechanics I have used the criteria that chemists and physicists themselves would regard as constitutive of a reduction. In simple terms this means the extent to which the contents of the secondary science can be calculated in a completely *ab initio* manner from the principles of quantum mechanics, in very much the same spirit as the quotes from Dirac and London mentioned at the outset.

Let me make one final preliminary remark before presenting my more specific arguments concerning reduction. As in most of my work I will be discussing what is generally described as the epistemological reduction of chemistry to quantum mechanics. This is sometimes also termed theoretical reduction as it concerns the reduction of theories of a special science to the theory or theories of physics. I have not devoted much attention to the more general question of the ontological reduction of chemistry to quantum mechanics since I see no way in which this task can genuinely be conducted without smuggling back epistemological aspects of both the two sciences in question. In saying this I take epistemological reduction to mean whether chemistry for example is nothing but quantum physics irrespective of our laws and theories about the two domains. I disagree with the philosophers that seem to believe that merely switching to talk of entities or laws of the various sciences rather than their theories entitles them to suddenly enter the realm of ontology.

Returning to my own contributions in the area of so-called ontological reduction, as I will call it, my work has consisted of criticizing the views of other authors rather than putting up positive arguments either for or against the ontological reduction of chemistry (Scerri 2007, 2012).

## *2 The Periodic System—Easily the Biggest Idea in Modern Chemistry*

Much has been written on the periodic system of the elements (Van Spronsen 1969, Gordin 2004, Scerri 2007). It is beyond any doubt one of the major discoveries in all of modern science and certainly the most influential discovery in the field of chemistry. The existence of the periodic system serves to unify the whole of inorganic chemistry and upholds the essential unity of all chemical substances, in spite of the tremendous variety possessed by individual elements and their compounds. In addition to being of theoretical value it serves an extremely useful didactic purpose and has permeated the teaching of chemistry since very soon after it was initially discovered in the 1860s (Kaji, Kragh, and Pallo 2015).

To most observers this seems like an obvious case of the reduction of chemistry to quantum mechanics, if not the supreme example of this kind of relationship. As we all learn in high school and college chemistry the wonderful edifice of the periodic table (see figure 6.1) that was gradually discovered on purely chemical grounds became fully understood and explained following the development of quantum mechanics and its talk of electron shells and orbitals. What may originally have seemed like a mysterious system of classification at the turn of the twentieth century scientists became regarded as a simple outcome of the underlying physics of the atom. In order to discuss this subject in greater depth I will begin with a very brief historical tour of the discovery of chemical periodicity and will take as my somewhat arbitrary starting point the publication of a set of atomic weights by John Dalton in 1808.

One can gain a simple understanding of the periodic system by considering what has been called the element line, as shown in figure 6.2. Here the elements have been ordered according to their atomic numbers, meaning the number of protons in the nuclei of their atoms. At the time of the discovery of the periodic system in the late 1860s the quantity used to bring about this ordering was that of atomic weight, such as the values published by Dalton. In any case the

Part of an early table of atomic and molecular weights published by Dalton

<i>Element</i>	<i>Weight</i>
Hydrogen	1
Azot	4.2
Carbon (charcoal)	4.3
Ammonia	5.2
Oxygen	5.5
Water	6.5
Phosphorus	7.2
Nitrous gas	9.3
Ether	9.6
Nitrous oxide	13.7
Sulphur	14.4
Nitric acid	15.2

Adapted from J. Dalton, *Memoirs of the Literary and Philosophical Society of Manchester*, 2(1), 207, 1805, table on p. 287.



FIGURE 6.1 Dalton's atomic weights list of 1808.

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
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25

FIGURE 6.2 The element line.

differences in the ordering depending on whether one used atomic weight or atomic number are minimal and this issue need not detain us here (Scerri 2014).

Once the number line is established one then looks for chemical analogies among the listed elements. The next step is to cut the number line in order to obtain certain sequences of elements such that they reflect the chemical analogies when they are stacked on top of one another. In other words chemically analogous elements should fall together into vertical columns or groups as shown in figure 6.3.

We now turn to the reason why the sequence of elements has been terminated in figure 6.2 at the 25th element, manganese. This has been done because a complication occurs with the very next element, iron. Whereas the previous few elements such as potassium, calcium, scandium, titanium, vanadium, chromium, and manganese show increasing maximum oxidations states or combining powers of 1 to 7 inclusive, the element iron shows a value of +3, therefore breaking the previous sequence. What Mendeleev and other early discoverers of the periodic system did was to expel iron and the next few elements from the main body of the periodic table, placing them instead into an additional column on the right-hand side of the table. The sequence of increasing oxidation numbers resumes again with the element rubidium, which displays a maximum oxidation state of +1, and is therefore placed in the first column of the table (figure 6.4).<sup>4</sup>

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	

FIGURE 6.3 A short-form periodic table obtained by cutting the element line 3 times and stacking the shorter sequences on top of each other to reflect chemical analogies.

Tabelle II.

Reihen	Gruppe I. R <sup>0</sup>	Gruppe II. R <sup>0</sup>	Gruppe III. R <sup>0</sup>	Gruppe IV. R <sup>1</sup> R <sup>2</sup>	Gruppe V. R <sup>2</sup> R <sup>3</sup>	Gruppe VI. R <sup>3</sup> R <sup>3</sup>	Gruppe VII. R <sup>4</sup> R <sup>5</sup>	Gruppe VIII. R <sup>6</sup>
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Co=140	—	—	—	—
9	(—)	—	—	—	—	—	—	—
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	—
12	—	—	—	Th=231	—	U=240	—	—

FIGURE 6.4 Mendeleev's short form periodic table including all known elements from hydrogen to uranium.

<sup>4</sup>One rather odd feature is that the element copper and a few others appear in two places at once. This was corrected in later versions of Mendeleev's periodic tables.

Although this short form of the periodic table is perfectly adequate in many respects it was eventually replaced by an 18-column or medium-long form table. In this representation the transition elements beginning with scandium, or element 21, are removed from the main body of the short form table and are placed as a central block between the first two and subsequent six columns of the short-form table. The advantage of this format is that it reflects chemical periodicities more accurately than the short form does. For example there is a greater similarity among titanium, zirconium, and hafnium than there is between these elements and carbon, silicon, tin, and lead—all of which find themselves classified together in the short-form table. The modern 18-column or medium-long format table is shown below in figure 6.5.

One final adjustment can be made in order to improve the periodic table further. As the medium-long form table stands it features the elements called the lanthanides and actinides rather awkwardly as a disconnected footnote. In

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	Cn		Fl		Lv		

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 6.5 18-column, medium-long form periodic table. The lanthanide and actinide series appear as a disconnected footnote below the main body of the table.

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	Cn	113	Fl	115	Lv	117	118

FIGURE 6.6 32-column or long-form periodic system.

reality these elements are as much a part of the periodic system as are all the others. In order to encapsulate this fact the periodic system can be expanded further to produce the 32-column or long-form periodic table as displayed in figure 6.6.

### 3 A Little More History

Returning to the historical sequence of events, let me mention just a few of many momentous discoveries that occurred in physics at the turn of the twentieth century and which contributed to the physical explanation of the periodic system. In a period of three consecutive years starting in 1895, Wilhelm Röntgen discovered X-rays, Becquerel discovered radioactivity, and J. J. Thomson discovered the electron. Each of these achievements was to open up new vistas in the

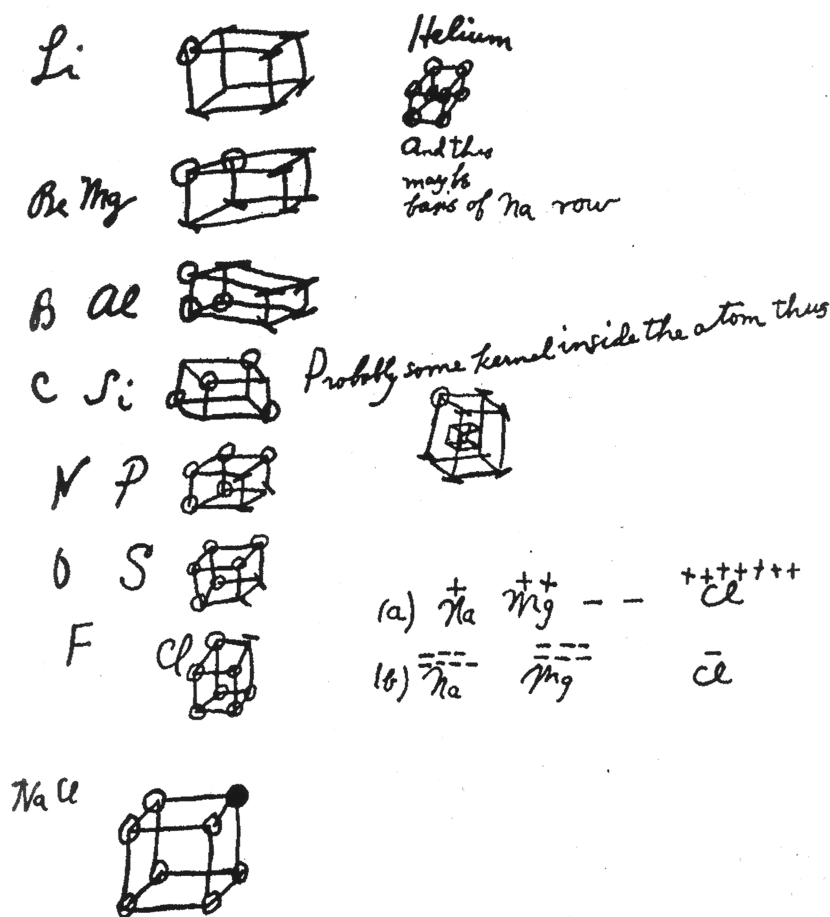


FIGURE 6.7 Lewis' 1902 sketch of the electron configurations of atoms from hydrogen to chlorine to explain chemical periodicity.



study of radiation and matter. Soon afterward Ernest Rutherford and many others pioneered the study of the structure of the atom.

A mere six years after the discovery of the electron, the chemist G. N. Lewis began to suggest how this particle could be used to explain the periodic system.

Lewis's idea is simple and ingenious. The number eight governs chemical periodicity in the short-form table that was prevalent at the time. In other words the properties of elements recur approximately every eight elements. Meanwhile each cube has eight corners. Lewis therefore suggested that on moving through the elements one adds an additional electron onto a corner of a cube until an octet is reached, whereupon the next cube begins to fill its corners with electrons. Elements that fall in the same group of the periodic table share the same number of outer cube electrons—for example, beryllium and magnesium, which each have two outer cube electrons, or boron and phosphorus that each have three outer cube electrons as shown in his sketch (see figure 6.7).

The notion of static electrons was soon demolished by the work of Ernest Rutherford. But Ernest Rutherford's model had little to say about the distribution of electrons around the nucleus, a task that was taken up by Bohr in his famous trilogy paper of 1913. Bohr's model located electrons in successive circular orbits, each specified by just one quantum number. By working backward from chemical behavior and spectral data Bohr succeeded in accommodating chemical periodicity and produced the table of configurations shown in figure 6.8.

We can stop to ask whether this represents a reduction of the periodic system. The answer would have to be very crudely yes, but the fact that Bohr accommodated already known experimental data and used that data to fix the configurations somewhat weakens the claim to any serious form of reduction of chemistry to quantum mechanics.

Subsequent developments over a period of about 10 years saw the introduction of three further quantum numbers to describe further degrees of freedom for each electron in an atom. The fourth quantum number, usually referred to as electron spin, was introduced by Pauli in 1924. By this point the reductive case became considerably stronger. The derivation of the quantization of various properties of the electron—such as its angular momentum and the possible values of the quantum numbers, as well as the manner in which the quantum numbers are all related to each other—were all derived from first principles of quantum mechanics, unlike what Bohr had carried out in the first incarnation of the theory in 1913. At this point it became possible to explain the sequence of numbers that governs the lengths of periods even in the most sophisticated representation of the periodic system, that is to say the long-form table.

The sequence of numbers to be explained is 2, 8, 18, 32, 50—or in general  $2n^2$ . These numbers drop out of quantum mechanics quite simply and represent periods involving the filling of s orbitals only for number 2; the filling of s and p orbitals for the number 8; filling of s, p, and d orbitals for the number 18; and the filling of s, p, d, and f orbitals for the number 32. Looked at from this perspective the reduction of the periodic system to quantum mechanics represents a tremendously successful enterprise.

1	H	1				
2	He	2				
3	Li	2	1			
4	Be	2	2			
5	B	2	3			
6	C	2	4			
7	N	4	3			
8	O	4	2	2		
9	F	4	4	1		
10	Ne	8	2			
11	Na	8	2	1		
12	Mg	8	2	2		
13	Al	8	2	3		
14	Si	8	2	4		
15	P	8	4	3		
16	S	8	4	2	2	
17	Cl	8	4	4	1	
18	Ar	8	8	2		
19	K	8	8	2	1	
20	Ca	8	8	2	2	
21	Sc	8	8	2	3	
22	Ti	8	8	2	4	
23	V	8	8	4	3	
24	Cr	8	8	2	2	2

FIGURE 6.8 Bohr’s electronic configurations of the first 24 atoms.  
 N. Bohr, On the Constitution of Atoms and Molecules *Philosophical Magazine*, 26, 476–502, 1913, 497

#### 4 *But Not Everything Is Derived from Quantum Mechanics*

In spite of the apparent success offered by the reduction of the periodic system that has just been described, there is a remaining problem that caused authors such as myself to claim that the periodic system had not in fact been fully reduced. This concerns the simple fact that the lengths of all periods, apart from the first short period of two elements, repeat in terms of their length. The correct sequence of successive periods of elements in the medium, or as better displayed in the long-form, table, is 2, 8, 8, 18, 18, 32, 32, . . .

Nobody has yet succeeded in deducing this sequence from quantum mechanics although there are certain claims to having done so (Löwdin 1969, Allen and Knight 2002, Ostrovsky 2001). In terms of reduction I would now interpret the situation as an example of the fact that each successful step toward reduction raises further questions and new aspects that have yet to be reduced fully. But let me return to the facts of the periodic table and the above sequences of

elements. The sequence of elements that denotes successive period lengths can be summarized by the following relatively simple mathematical expression,

$$L_n = \frac{1}{8} [2n + 3 + (-1)^n]^2$$

where  $L_n$  is the number of elements in any period with period number  $n$  (Kryachko 2007). However this is merely a mathematical trick, since there is no underlying physical theory that leads us to why this particular equation is required. More specifically the expression has not been derived from quantum mechanics, which is of course the putative reducing theory in this context.

The correct sequence is also generated by the Madelung, or  $n + l$ , rule, which states that the order of filling of atomic orbitals proceeds with increasing values of the  $n + l$  quantum numbers for any particular atomic orbital (Scerri, 2009). Stated in other words, it predicts the following order of orbital filling:

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < \dots \quad (1)$$

The reductive claim on behalf of quantum mechanics therefore appeared to hinge on whether or not this expression had been derived from quantum mechanics. Some authors claim that indeed it had but I believe I showed that this was not in fact the case. This finding strengthened my former anti-reductionist stance regarding the periodic system. And this is where matters stood until 2012 at which time I began to read and understand the work of the theoretical chemist Eugen Schwarz, who coincidentally has been a frequent participant at our summer conferences of the International Society for the Philosophy of Chemistry.

### 5 *The Current Situation: Anti-reductionism No Longer Seems So Clear-Cut*

A simple way to express the gist of Schwarz's contribution to the debate would be to say that contrary to what is stated in 99 percent of all chemistry and physics textbooks, the sequence of orbitals shown above in expression (1) does *not* in fact represent the correct order of filling of atomic orbitals, except in the case of metals in the s-block of the periodic table, meaning the two columns on the far left of the periodic table (figure 6.9).

Although the above Madelung rule succeeds in giving the overall configuration of the transition metals beginning with scandium, or element 21, the order of filling is not provided by this rule. There is clear-cut experimental evidence to support this view, a fact that makes the persistence of the incorrectly used Madelung rule somewhat intriguing.<sup>5</sup>

<sup>5</sup>This is not something that I will pursue here but I have done so in other publications, such as in Scerri (2013).

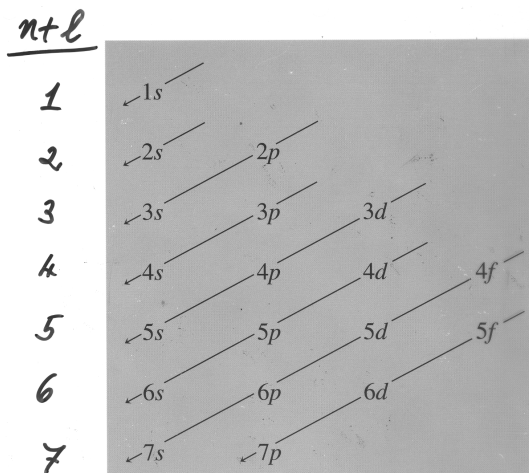


FIGURE 6.9 A graphical representation of the Madelung or  $n + l$  rule. The order of filling of atomic orbitals is generally supposed to be provided by following the diagonal arrows starting at the top of the diagram with the  $1s$  orbital and then moving downwards to give  $2s$ , followed by  $2p$ , then  $3s$  etc.

Returning to the question of the reduction of the periodic system we must now ask a new question. Given the lack of fundamental status of the Madelung rule, is it still essential for this rule to be derived from quantum mechanics in order to consider that chemical periodicity has been fully reduced? The situation would appear to have changed. Admittedly, the use of the rule is still valid in trying to obtain the expected configuration of any atom but the fact that it fails to predict the precise order of filling of orbitals in any particular atom is a rather serious issue. For example, in the case of the atom of scandium, which has atomic number 21, the order of orbital filling is such that  $3d$  orbital fills before a  $4s$  orbital. This subsequently explains the fact that ionization of a scandium atom to form a  $Sc^+$  ion invariably involves the removal of a  $4s$  orbital electron. According to the usual (and incorrect) account whereby the  $4s$  orbital fills preferentially in scandium, the preferential ionization of a  $4s$  electron appears to be a complete mystery, which most books attempt to cover over with all manner of ad hoc maneuvers.

My previous ardent claims that the periodic system has not been fully reduced to quantum mechanics because of a lack of a derivation of the  $n + l$  rule has therefore fallen by the wayside. Mea culpa. I was wrong.

### 6 Another Twist: Those Anomalous Configurations— The Good Side of Reduction

There is another issue concerning reduction and electronic configurations, apart from the question of whether the  $n + l$  rule has been deduced from first principles. The anti-reductionist can appeal to the fact that even if the Madelung

H																				He
Li	Be													B	C	N	O	F	Ne	
Na	Mg													Al	Si	P	S	Cl	Ar	
K	Ca	Sc	Ti	V	<i>Cr</i>	Mn	Fe	Co	Ni	<i>Cu</i>	Zn	Ga	Ge	As	Se	Br	Kr			
Rb	Sr	Y	Zr	Nb	<i>Mo</i>	Tc	<i>Ru</i>	<i>Rh</i>	<i>Pd</i>	<i>Ag</i>	Cd	In	Sn	Sb	Te	I	Xe			
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	<i>Pt</i>	<i>Au</i>	Hg	Tl	Pb	Bi	Po	At	Rn			
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	<sub>113</sub>	Fl	<sub>115</sub>	Lv	<sub>117</sub>	<sub>118</sub>			

FIGURE 6.10 Periodic Table showing gas phase anomalous configurations among d-block elements shown in smaller symbols. These seem to occur almost randomly throughout the d-block. The f-block is not displayed.

rule were derived in a fully convincing fashion there remains one important aspect that suggests that not everything has been reduced. There are approximately 20 elements whose atoms do not follow the Madelung rule in that their configurations are anomalous. For example, the atom of chromium would be expected to have a configuration of  $[\text{Ar}] 3d^4 4s^2$  according to the Madelung rule; yet experimental evidence points to its being  $[\text{Ar}] 3d^5 4s^1$ . Figure 6.10 shows all the atoms, which behave in this anomalous manner in the sense that their outermost s orbital does not possess an  $s^2$  configuration. The anti-reductionist can appeal to this behavior in order to maintain an anti-reductionist position. Until recently I would also have supported this view as a further argument against those who would claim that the periodic table has been reduced to quantum mechanics.

More recently I have become persuaded otherwise. It now appears that there is an intriguing explanation for these anomalous configurations, which is provided by quantum mechanics as well as an appeal to experimental data on the spectra of atoms.

## 7 How Is an Electronic Configuration Obtained from Experimental Data?

In this section we will examine the way in which the electronic configuration of any atom is obtained from spectral data and we will also examine an alternative way of obtaining electronic configurations.

First there is the traditional approach. This consists of examining the spectrum of the gas phase atoms of any particular element and looking for the spectroscopic term of lowest energy. One then tries to identify the electronic configuration which gives rise to this spectroscopic term and one takes this configuration to represent the ground state configuration of the atom in question. Consider for example the spectrum of neutral scandium. Figure 6.11 is a

Sc I					Sc I					
Config.	Design.	J	Level	Interval	Obs. g	Config.	Design.	J	Level	Interval
3d 4s <sup>2</sup>	a <sup>1</sup> D	3/2	0.00		0.79	3d <sup>2</sup> (a <sup>1</sup> F)4p	y <sup>1</sup> D°	1/2	38637.40	21.81
		2/2	168.34	168.34	1.20			1/2	38656.81	37.63
3d <sup>2</sup> (a <sup>1</sup> F)4s	a <sup>1</sup> F	1/2	11520.15	37.49				2/2	38696.84	54.70
		2/2	11637.64	52.60		3d <sup>2</sup> (a <sup>1</sup> F)4p	z <sup>1</sup> G°	3/2	38751.54	95.21
		3/2	11610.24	67.07				4/2	38058.19	
		4/2	11677.31					3/2	35161.40	
3d <sup>2</sup> (a <sup>1</sup> F)4s	a <sup>1</sup> F	2/2	14928.24	115.74		3d <sup>2</sup> (a <sup>1</sup> F)4p	z <sup>1</sup> F°	2/2	33154.01	124.63
		3/2	15041.98					3/2	33878.64	
3d 4s(a <sup>1</sup> D)4p	z <sup>1</sup> P°	1/2	15672.55	83.96		3d <sup>2</sup> (a <sup>1</sup> F)4p	z <sup>1</sup> D°	1/2	33616.09	92.19
		2/2	15756.51	125.25				2/2	33707.25	
		3/2	15831.78	144.78		3d <sup>2</sup>	e <sup>1</sup> F	1/2	33763.57	35.11
		4/2	16086.62					2/2	33798.68	47.94
3d 4s(a <sup>1</sup> D)4p	z <sup>1</sup> D°	1/2	16009.71	12.07				3/2	33845.02	59.78
		1/2	16021.72	119.26				4/2	33906.40	
		2/2	16141.04	69.78		3d 4s(a <sup>1</sup> D)5s	e <sup>1</sup> D	1/2	34390.25	32.60
		3/2	16810.30					1/2	34422.85	57.20
3d 4s(a <sup>1</sup> D)4p	z <sup>1</sup> D°	2/2	16022.78	-74.14				2/2	34480.05	87.05
		1/2	16096.86					3/2	34567.10	
3d <sup>2</sup> (b <sup>1</sup> D)4s	b <sup>1</sup> D	2/2	17012.98	-12.38		3d 4s(a <sup>1</sup> D)5s	e <sup>1</sup> D	1/2	35671.00	74.57
		1/2	17025.36					2/2	35745.57	
3d <sup>2</sup> (a <sup>1</sup> P)4s	a <sup>1</sup> P	1/2	17918.85	29.13		3d <sup>2</sup>	f <sup>1</sup> D	1/2	36278.76	53.73
		1/2	17947.98	52.27				2/2	36330.49	
		2/2	18000.25			3d <sup>2</sup>	e <sup>1</sup> P	1/2	36492.82	22.94
3d 4s(a <sup>1</sup> D)4p	z <sup>1</sup> P°	1/2	18504.05	11.72				1/2	36515.76	57.04
		1/2	18515.77	55.63		3d <sup>2</sup> (b <sup>1</sup> D)4p	w <sup>1</sup> D°	1/2	36884.15	105.62
		2/2	18671.40					2/2	37036.77	
3d 4s(a <sup>1</sup> D)4p	z <sup>1</sup> P°	1/2	18711.03	144.73		3d 4s(a <sup>1</sup> D)4d	e <sup>1</sup> P	1/2	37088.72	62.53
		1/2	18855.76					1/2	37148.25	
3d <sup>2</sup> (a <sup>1</sup> G)4s	a <sup>1</sup> G	4/2	20237.10	-2.82		3d <sup>2</sup> (b <sup>1</sup> D)4p	w <sup>1</sup> P°	1/2	37086.31	-39.41
		3/2	20239.92					1/2	37125.72	
3d 4s(a <sup>1</sup> D)4p	z <sup>1</sup> P°	2/2	21032.78	53.06		3d <sup>2</sup> (a <sup>1</sup> P)4p	z <sup>1</sup> D°	1/2		
		3/2	21035.84					1/2	37186.48	66.86
3d <sup>2</sup> (a <sup>1</sup> P)4s	a <sup>1</sup> P	1/2	21400	80.40				2/2	37553.34	163.77
		1/2	21450					3/2	37717.11	
3d 4s(a <sup>1</sup> D)4p	y <sup>1</sup> P°	1/2	24656.80			3d 4s(a <sup>1</sup> D)4d	g <sup>1</sup> D	1/2	37780.88	74.67
		1/2						2/2	37855.50	
3d 4s(a <sup>1</sup> D)4p	y <sup>1</sup> D°	1/2	24896.18	147.97	0.82	3d <sup>2</sup> (a <sup>1</sup> P)4p	z <sup>1</sup> S°	1/2	38179.92	
		2/2	25014.15		1.17					

FIGURE 6.II An extract from Charlotte Moore's tables of atomic energy levels for the neutral scandium atom. The electronic configuration is generally taken to be whichever configuration gives rise to the spectroscopic term with lowest energy. In this case it is the 3d<sup>1</sup> 4s<sup>2</sup> configuration (Moore, 1970).

copy of part of the spectrum of neutral scandium for which the spectroscopic term of lowest energy, shown as .00 in the fourth column, originates from the configuration 3d<sup>1</sup> 4s<sup>2</sup> as shown in the first column. In most treatments of electronic configurations this is the end of the story.

However in more accurate work one seeks the average configuration which is obtained by taking an average of the energies of all the spectroscopic terms arising from each of the lowest lying electronic configurations of any atom (Wang et al. 2006).

In the spectrum shown in figure 6.II this involves taking an average of all the terms originating from the 3d<sup>1</sup> 4s<sup>2</sup> configuration and comparing this energy with the average value for all the spectroscopic terms arising from the 3d<sup>2</sup> 4s<sup>1</sup> configuration—of which there are 15 terms in this case. Moreover the manner in which this averaging is carried out requires making use of the J, or overall quantum, number that is the result of coupling the total orbital angular momentum of the atom L with its total spin angular momentum or S.

In physical terms this represents a move from considering gas phase atoms to atoms in condensed phases, meaning in the liquid or solid states. It also represents a move away from isolated atoms to atoms that are in chemical combination. Broadly speaking both of these changes mean that one is dealing

## Configuration averages in scandium

 $d^1s^2$ 

Term	J	E / cm <sup>-1</sup>	2J+1	E <sub>weighted</sub>	Degeneracy	E <sub>average</sub> / cm <sup>-1</sup>	E <sub>average</sub> / eV
<sup>2</sup> D	1.5	0.00	4	0.00	10	101.00	0.012523
	2.5	168.34	6	1010.04			E <sub>average</sub> rel. s <sup>2</sup> / eV -1.99

 $d^2s^1$ 

Term	J	E / cm <sup>-1</sup>	2J+1	E <sub>weighted</sub>	Degeneracy	E <sub>average</sub> / cm <sup>-1</sup>	E <sub>average</sub> / eV
4F	1.5	11519.99	4	46079.96	90	16165.20	2.00
	2.5	11557.69	6	69346.14			E <sub>average</sub> rel. s <sup>1</sup> / eV 0.00
	3.5	11610.28	8	92882.24			
	4.5	11677.38	10	116773.80			
2F	2.5	14926.07	6	89556.42			
2D	3.5	15041.92	8	120335.36			
	2.5	17012.76	6	102076.56			
4P	1.5	17025.14	4	68100.56			
	0.5	17226.04	2	34452.08			
	1.5	17255.07	4	69020.28			
2G	2.5	17307.08	6	103842.48			
	4.5	20236.86	10	202368.60			
2P	3.5	20239.66	8	161917.28			
	0.5	20681.43	2	41362.86			
2S	1.5	20719.86	4	82879.44			
	0.5	26936.98	2	53873.96			



FIGURE 6.12 Calculation of average configuration energies arising from various possible configurations in scandium atom.

with more physically and chemically relevant species than gas phase atoms of isolated atoms, thus providing further motivation for taking these alternative configurations more seriously.

Figure 6.12 presents the results of calculating the lowest lying configuration of the scandium atom, when carried out via this averaging procedure. In the case of this atom the ground state configuration is the same, namely  $3d^1 4s^2$ , regardless of whether it is obtained in the traditional manner or by this averaging procedure. In fact the  $3d^1 4s^2$  configuration is found to be almost exactly 2 eV more stable than the next configuration of  $3d^2 4s^1$ .

But this is not true in all cases. Figure 6.13 shows the variation in the energies of the  $s^2$ ,  $s^1$  and  $s^0$  configurations for each atom beginning with calcium and ending with copper. Clearly, as atomic number increases the energy of the  $s^2$  configuration shows an increase relative to that of the  $s^1$  configuration. Whereas the  $s^2$  configuration is considerably more stable for elements such as scandium, the energies of these configurations cross over each other once the atom of iron has been reached. In the case of the nickel atom the  $s^1$  configuration is found to be approximately 1 eV lower than the  $s^2$  configuration. These results imply that the ground state configurations for several atoms are different from what they are generally regarded as according to the traditional approach (Figure 6.14).



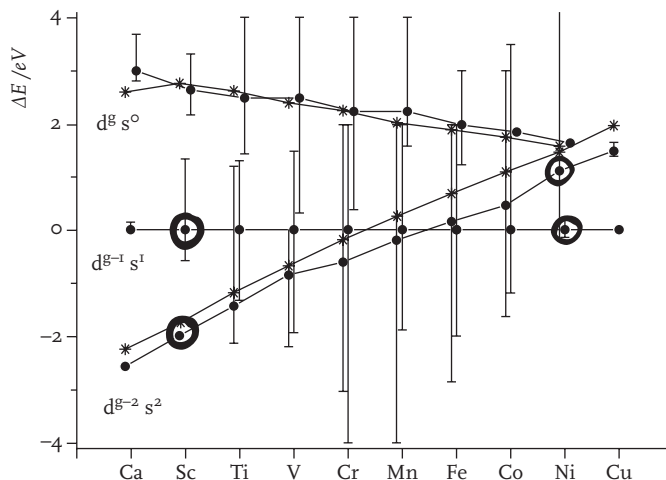


FIGURE 6.13 Variation in energies of  $s^2$ ,  $s^1$  and  $s^0$  configurations across the first transition series. For iron and elements beyond, the  $s^1$  configuration is more stable than  $s^2$ . The atoms of scandium and nickel have been highlighted with circles. In the case of scandium the average  $s^2$  configuration lies lower than the  $s^1$  configuration. In the case of the nickel atom the situation is the other way round. Bold circles represent configurations obtained experimentally from spectral evidence. The crosses represent configuration energies obtained theoretically via the Hartree-Fock method. (Wang et al, 2006).

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	<i>Fe</i>	<i>Co</i>	<i>Ni</i>	<i>Cu</i>	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	<i>Mo</i>	<i>Tc</i>	<i>Ru</i>	<i>Rh</i>	<i>Pd</i>	<i>Ag</i>	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	<i>Os</i>	<i>Ir</i>	<i>Pt</i>	<i>Au</i>	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Lr	Rf	Db	<i>Sg</i>	<i>Bh</i>	<i>Hs</i>	<i>Mt</i>	<i>Ds</i>	<i>Rg</i>	Cn	113	114	115	116	117	118



FIGURE 6.14 Periodic Table showing anomalous configurations for condensed phase atoms (smaller symbols). Again the f-block is not displayed.

Returning to the theme of this chapter, this alternative method for calculating electronic configurations of atoms provides a perfectly natural explanation for the so-called anomalous configurations. It could be argued that there are in fact no anomalies since one is merely observing the result of the variation of two energies, those of the  $s^2$  and  $s^1$  configurations, which happen to cross at a certain point along the first transition series. Moreover, and perhaps



more pertinent to the present project, the energies of these configurations can be computed from first principles via the Hartree-Fock method and they too show very similar trends, including a crossing of energies at more or less the same point along the transition series.<sup>6</sup>

## Conclusions

This study illustrates the fact that the philosophers of chemistry, especially those influenced by the prevailing anti-reductionist zeitgeist, can too easily conclude from episodes in the history of chemistry and physics that reductionism fails. This is in fact how my own work until recently can be characterized, although I like to think I have been consistent in adopting a cautious approach and have stayed close to the scientific facts.

In the case under discussion one can only conclude that the periodic table has not been reduced to quantum mechanics if one restricts oneself to gas phase atoms rather than atoms in condensed phases. But this represents a serious omission since the condensed phases are overwhelmingly more relevant to most of chemistry and physics. Second, there is the related fact that by restricting oneself to gas phase atoms one is only considering isolated atoms of the elements rather than atoms that are bonded and present in compounds.

Third, let me make a general comment about philosophy of science which has been made many times before but which is especially pertinent in the present case. There is a tendency for philosophers of science to obtain their knowledge of science from textbooks, which inevitably present impoverished accounts of the particular fields that they are describing. Of course it is not difficult to understand this tendency, which stems from the fact that philosophers are generally not sufficiently technically proficient to cope with the latest research on the subject and prefer to fall back on the version of the science that they themselves learned during their earlier scientific education.

In the case under discussion in this chapter, experts in chemistry and physics are well aware of the limitations of focusing on the configurations of gas phase atoms. Meanwhile philosophers of science build their anti-reductionist cases on idealist textbook accounts of what electronic configurations really consist of. Neither the  $n + l$  rule nor the so-called anomalous configurations of atoms apply in general. The  $n + l$  rule applies strictly to just the s-block elements which constitute about 10 percent of all the known elements.<sup>7</sup>

<sup>6</sup>The only disagreement would seem to be over the atom of manganese. According to spectral data the s configuration has a lower average energy than the s configuration while according to the theoretical prediction the energy order is reversed.

<sup>7</sup>The precise value depends on how one performs such a calculation. I have calculated the proportion by considering the 13 s-block elements as a percentage of the 118 currently known elements. Others might want to exclude the super-heavy elements in which case the percentage of s-block elements will be a little higher.

The electronic configurations that are generally believed to be anomalous because they feature an incomplete outer s-orbital are seen in a completely new light when one turns to considering the average configuration of atoms taken over all spectroscopic terms that emerge from any particular configuration (figure 6.14). Any claims to the failure of reductionism that are based on the  $n + l$  rule or the anomalous configurations are thus rendered invalid. The reduction of the periodic table to quantum mechanics is far more successful than contemporary philosophers of chemistry have been willing to admit.

Perhaps the best way to think of reduction might be as a “direction” rather than as a goal. Each attempt to explain chemical and physical phenomena such as the anomalous electronic configurations generally results in a deeper understanding of the phenomena. The goal of complete reduction may never be reached but scientific knowledge continues to advance, whatever some uninformed philosophers might believe.

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