

[Letters to the editors](#)

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On the Madelung Rule

[Eric Scerri](#),

reply by [Marc Henry](#)

In response to "[Super-Saturated Chemistry](#)"

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*To the editors:*

As a chemist, and somebody who has tried to promote the philosophy of chemistry, I was delighted to see Marc Henry's article.<sup>1</sup> As numerous authors have emphasized, chemistry, the central science, seems to have been largely neglected by philosophers of science until about the mid 1990s.<sup>2</sup> But even in the twenty or so subsequent years the field remains rather small and little appreciated. Physics is rightly regarded as the most fundamental of the natural sciences, and so receives the most attention from philosophers. About fifty years ago a philosophy of biology began to take shape and it has now become a well-established sub-discipline. This feat was not so difficult to achieve since life itself is clearly not reducible to physics. On the other hand, the question of the extent to which chemistry is reduced is more ambiguous.

At first glance, it would seem that chemistry *does* reduce to physics. One only needs to think of the periodic table, that paradigm of chemistry, and the idea that its very existence can be explained by appealing to electron shells and orbitals in the atoms of the various elements which it houses. The fact that elements within the same vertical column such as lithium, sodium, and potassium, for example, behave in a similar fashion is explained by recognizing that the atoms of these elements all have one outer-shell electron. In fact, many classic texts in the philosophy of science refer to this example as the archetypal case of a successful reduction of one science (chemistry) to another (physics).<sup>3</sup>

## **The Periodic Table and Electronic Configurations**

Henry begins his article with a detailed analysis of the reduction claim, and this is the part of his article that I will concentrate upon because of my own interests and because of my own limitations when it comes to the more exotic physics and mathematics that he later turns to.

As I think Henry correctly points out, chemistry remains a singular science, which has not been reduced to physics when matters are examined more closely. As he writes, the possible period lengths in the periodic table, namely 2, 8, 18, or 32 can be predicted in a completely rigorous manner by solving the time-independent Schrödinger equation for the hydrogen atom and augmenting the three quantum numbers that are thereby obtained with yet a fourth quantum number.<sup>4</sup>

This much is already a highly impressive feat on the part of theoretical physics and it is surely what fuels the claims for a complete reduction that one generally encounters. However, a deeper problem, also mentioned by Henry, is that the closing of periods, as opposed to the closing of sequential shells, occurs after the following sequences: 2, 8, 8, 18, 18, 32, and 32. This doubling in successive period lengths, with the exception of the very first period, is usually summarized by appealing to Madelung's rule of  $n + l$  whereby electron occupation proceeds according to increasing numerical values of this quantity representing the sum of the first and second quantum numbers for any given atomic orbital.<sup>5</sup>

But I wish to take issue with Henry's next claim, although it is a commonly held view and one that I have also regrettably reinforced in previously published articles, several of which the author is generous enough to cite.<sup>6</sup> In quoting from Löwdin, Henry says that the Madelung rule cannot be derived from quantum mechanics. For many years, I think it is fair to say, I was one of the main torchbearers for Löwdin's statement. More recently I have somewhat changed my mind as I will now try to explain.

Briefly put, whether or not the Madelung rule can be derived from quantum mechanics may be irrelevant to the fundamental question of whether the periodic table, and consequently an important part of chemistry, can be reduced to physics.

When one examines the electronic configurations of atoms more closely, it emerges that the build-up of electronic orbitals does not always follow the Madelung rule. Contrary to 99% of textbook accounts, the configuration of the atom of element 21, or scandium, is  $[\text{Ar}]3d^14s^2$  and not  $[\text{Ar}]4s^23d^1$  as commonly stated.<sup>7</sup> This innocent looking inversion in the final two orbitals harbors a great deal of information, which I need to explain briefly. The reason why the erroneous version continues to be propagated by textbook authors and chemistry instructors is that it seems to make a good deal of common sense. In a recent article, addressed mainly to chemical educators, I have called this state of affairs the "sloppy aufbau" to distinguish it from the more careful aufbau principle.<sup>8</sup>

The sloppy version assumes that in moving from the atom of element number 20, or calcium, to element 21, or scandium, the twenty-first electron is added to the configuration that already exists in calcium. Since calcium possesses a configuration of  $[\text{Ar}]4s^2$  it is very reasonable to suppose that the next element should show a configuration of  $[\text{Ar}]4s^23d^1$ . However, experimental evidence clearly points against such a simplistic view.

First, spectroscopic evidence indicates the preferential occupation of a 3d orbital rather than 4s in scandium. The reason is that even though 4s possesses a lower energy than 3d for the atoms of potassium (19) and calcium (20), the opposite is the case for scandium and for all nine subsequent transition elements. Moreover, when a single electron is removed from a scandium atom, it is a 4s electron that is preferentially ionized and not one from a 3d orbital.<sup>9</sup> This fact cannot be rationalized according to the popular notion that the configuration of scandium should be  $[\text{Ar}]4s^23d^1$ .<sup>10</sup>

But let me resume the question of the Madelung rule. According to what I have been saying, the building-up of atoms with electrons does not in fact follow this time-honored rule and so whether or not the rule can be derived from quantum mechanics is neither here nor there when it comes to the question of reduction of the periodic table.<sup>11</sup> Nevertheless there is no need to jettison the Madelung rule altogether since it does provide the correct overall configuration in the majority of atoms. What I have been focusing on is that it does not provide the order of occupation of atomic orbitals within the independent electron approximation.

Henry piles on the anti-reductionism further when he continues that some elements belonging to the same group, such as nickel, palladium and platinum show different outer-shell configurations. Now admittedly this fact points against the simple high-school account that holds that elements in the same group share the same outer-shell configuration. However, it fails to address the point at issue, namely the question of whether the periodic table can be reduced to quantum mechanics. If quantum mechanics were capable of predicting the experimentally-observed configurations for all three of these atoms, then reduction would have been achieved for all intents and purposes.<sup>12</sup>

## Anomalous Configurations

This talk of the configurations of nickel, palladium and platinum raises another interesting and related question. There are about twenty elements in the periodic table whose atoms do not have the electronic configuration that one would expect. These elements are anomalous in the sense of having one electron instead of two in their outermost shells.<sup>13</sup> That is to say, the outermost shell has configuration  $s^1$  rather than the more usual  $s^2$ .

This issue is well known in chemical education and again there exist many ad hoc attempts to try to explain the facts, the most common of which is an appeal to the presence of a half-filled subshell in the case of atoms such as chromium and molybdenum. The only problem with this ploy is that the possession of a half-filled sub-shell is neither necessary nor sufficient for an atom to display an anomalous configuration of the type that I am discussing here.<sup>14</sup> The only rigorous explanation that I am aware of that does not pull the proverbial wool over the reader's eyes lies in an article that was published by the theoretical chemist Eugen Schwarz and his co-authors.<sup>15</sup>

What Schwarz has suggested is that one should not simply consider the lowest energy state of any particular atom but that one should take an average of the various spectroscopic contributions arising from any particular configuration.

The traditional approach to determining the configuration of an atom from observed data consists of examining the spectra of gas phase atoms of any particular element and then simply 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 of the atom in question. However, in more accurate work one seeks the average for each configuration, taken over the energies of all the spectroscopic terms arising from that particular configuration, with the aim of identifying the one with the lowest energy. This is then regarded as the ground state configuration of the atom in question.

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 more physical terms, this approach also represents a move away from considering gas phase atoms to considering those in condensed phases and atoms that are in chemical combination. Broadly speaking, these features mean that one is dealing with more physically and chemically relevant species than gas phase atoms of isolated atoms, thus providing a further motivation for taking these alternative configurations more seriously.

What emerges from this approach is that, as the atomic number increases, the energy of the  $s^2$  configuration shows a steady 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  $s^2$ . These results imply that the ground state configurations for several atoms are different from what is generally stated in the traditional textbook approach.

The 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  $s^1$  and  $s^2$  configurations, which happen to cross at a certain point along each transition series. Moreover, and perhaps more pertinent to the question of reduction to quantum mechanics, the energies of these configurations can be computed from first principles via the Hartree-Fock method and they too show very similar trends, including the crossing of energies at more or less the same point along the transition series.

Since condensed phases and bonded atoms are overwhelmingly more relevant to most of chemistry and physics, this represents a triumph rather than a failure of reduction.

Experts in atomic physics and related areas in chemistry and physics are well aware of the limitations of focusing on the configurations of gas phase atoms. 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.

The reduction of the periodic table to quantum mechanics is far more successful than some chemists and contemporary philosophers of chemistry have been willing to admit. It is

regrettable that a chemist like Henry should have been misled by such philosophical accounts. Could it be that the philosophy of chemistry is having more of an impact than I implied at the outset? Although we certainly do not need this kind of negative impact.

## The Born-Oppenheimer Approximation

Another topic that has exercised a minority of chemists as well as the philosophy of chemistry community has been the question of the Born-Oppenheimer approximation.

Because of the difficulties of solving the many-particle Schrödinger equation it helps to make whatever approximations one can safely get away with. It so happens that in molecules the relative motion of the nuclei is far, far smaller than that of the electrons. Consequently, it is customary to apply the clamped nuclei approximation and to omit any terms having to do with the motion of nuclei from the equations of motion.

A few chemists that Henry cites have made careers of examining the consequences of making such an assumption. They have argued that molecular structure is therefore something of an epiphenomenon that is incompatible with a full quantum mechanical treatment. The structure of the molecule, largely defined by the relative positions of the nuclei, appears to be imposed by a mathematical approximation, they argue, and does not sit well with quantum mechanics, the putative underlying theory for all of chemistry.

Some declare that this signals another failure of reductionism since molecular structure is so obviously real and undeniable, especially to the chemist. Henry buys into all of this and is once again ready to declare the failure of attempts to reduce chemistry.

But, there is a possible escape, which actually involves a more recent development in quantum mechanics, namely the subject of quantum decoherence. Once upon a time it was thought that the collapse of the wavefunction occurred instantaneously. Today we understand that this is not the case. Similarly, it was once thought that the collapse of the wavefunction only occurred as a result of an observation, be it human or through mechanical devices. Today it is realized that interaction with the environment of a system can equally bring about the collapse of the wavefunction.

Typical decoherence times for molecules like ethanol and dimethyl ether are on the order of picoseconds, or less. Consequently, even if we grant that the pure quantum mechanical formalism may be devoid of structural information in the absence of Born-Oppenheimer, a newly formed molecule will only lack structure, if we can put it in such terms, for something like a picosecond. This suggests that, for all intents and purposes, molecular structure, so meaningful to chemists, is indeed a real phenomenon, which does not conflict with quantum mechanics.<sup>16</sup>

As in the case of the periodic table and electronic configurations, I do not believe that appealing to the Born-Oppenheimer approximation and the putative mismatch between quantum mechanics and the existence of molecular structure gives any solace to the anti-reductionist. If chemistry is not dissolved by physics, there are surely better ways of upholding this claim than by focusing on what lurks behind the Born-Oppenheimer style clamping of nuclei.

## Conclusion

Having said all this, I hasten to mention that I am not turning my back on my own anti-reductionist position concerning the status of chemistry. It is just that I am increasingly appreciative of what physics has achieved. I may have been a little too hasty in the way that I attacked the reduction claims at earlier stages of my career. These days, if I am asked point-blank if chemistry has been reduced to physics my response tends to either be “It depends what you mean by reduction,” or, on other occasions, “Yes, almost but not quite.”<sup>17</sup>

One of the failings of philosophy of science, which unfortunately does a great disservice to the discipline, is that practitioners seldom have technical skill in the science that they claim to be philosophizing about. In this respect I am rather lucky to be a philosopher of chemistry who is hiding out in a chemistry department at a first rate research university where my colleagues do their best to keep me on the straight and narrow.

It would have been interesting to see some kind of a conclusion to Henry’s article and a resumption of the question of reduction rather than a relentless pedagogical romp through a dazzling array of advanced topics in physics and mathematics followed by a rather abrupt ending.

I also worry a little that Henry’s focus on these more mathematical topics seems to suggest that he has not entirely given up on the idea of reducing chemistry to physics. This is a little puzzling given the earlier parts of his article in which he confidently proclaims the impossibility of any such reduction.

I must also mention the distinction between reduction in practice and reduction in principle. All that we can really say is whether reduction has been achieved in practice. In principle we have to admit that anything is possible. It would therefore be claiming far too much to say that chemistry will never be reduced to physics.

Nevertheless, this is a small criticism that does not detract too much from the immense value of Henry’s stimulating and super-saturated article. I have learned a great many new facts from his interdisciplinary tour de force and will enjoy pursuing many of the references that he provides to the emerging areas that we humble chemists are seldom exposed to.

I would have preferred it if the article had been saturated with more inherently chemical arguments aimed at warding off the reductive claims. Instead Henry has super-saturated his article with all manner of mathematics and physics, thus inadvertently seeming to arm the reductionists further in their quest to dissolve chemistry. But in saying this I am once again betraying my own philosophical prejudice, and, I suspect, that of many chemists, in support of the non-reducibility of our field.

Perhaps the best way to think of reduction might be as a direction rather than as a goal. Attempts to explain chemical and physical phenomena generally result in deeper understanding. The goal of complete reduction may never be reached, but scientific knowledge continues to advance precisely because we adopt the general direction and program of reductionism.

## Eric Scerri

### Marc Henry *replies*:

First, I would like to thank Eric Scerri for his interesting comments that give me the opportunity to dot the i's and cross the t's on some points that need further comments and/or development.

Contrary to 99% of textbook accounts, the configuration of the atom of element 21, or scandium, is  $[\text{Ar}]3d^14s^2$  and not  $[\text{Ar}]4s^23d^1$  as commonly stated.

I would simply add that, nowadays, students do not refer to textbooks, but rather learn science from the internet. As can be checked, the electronic configuration of scandium is correctly stated by the Royal Society of Chemistry website on the periodic table.<sup>18</sup>

Henry fails to mention that there have been various claims to the effect that the Madelung rule has been derived from first principles.

Eric Scerri then gives in endnote eleven a reference to a paper published in 2001 by Valentin Ostrovsky. In fact, this paper is cited in my essay in endnote thirteen. So, the problem has been addressed, but not in great detail, in order to keep the essay at a reasonable length.

I would add that, in France, the problem of Madelung's rule is further complicated by the fact that this rule is not attributed to Madelung himself, but to a Russian chemist named Klechkowski. So, from a historical viewpoint, one may wonder what the relative contributions of Madelung and Klechkowski were to this problem. In fact, as correctly pointed by Scerri, it should be obvious that Madelung's rule or Klechkowski's rules are empirical findings and it should be very surprising to find a quantum-mechanical derivation from first principles of such a rule.

My main message to the wide audience of this review was that deriving the correct electronic configuration from first principles for all the elements of the periodic table was, beyond any doubt, a mathematical experiment rather than a mathematical deduction. I would like to stress that Scerri was a true pioneer in delivering such a message for chemists, even if he seems now to regret having written so much on this crucial subject. It was brilliant work and will continue to stimulate open-minded chemists in the recognition of the fact that chemistry is definitively not soluble in physics.

Concerning the problem of anomalous configurations, I thank Scerri for having stressed the importance of the paper published in 2009 by Wang and Schwartz. As I am a chemist synthesizing molecules made of bonded atoms, I am not very interested in atomic electronic configurations in the gaseous phase that are of little help in explaining observed chemical facts. Bonded atoms do not display the same properties as gaseous ones; bonded molecules in a crystal do not display the same shapes as gaseous molecules.

The key point is that theoretical computations are always done in the gaseous phase, whereas most experiments in chemistry deal with liquids, solutions or solids. It is thus quite amazing that

Hartree-Fock or density functional calculations in the gas phase are perfectly able to explain experimental facts observed in condensed states. For me, this does not represent a triumph at all, but merely points to the fact that some kind of experimental data not included in first principles are implicitly used.

Accordingly, the choice of a good basis set that must be used to get reliable results is not driven by theory alone, but rather selected by its ability to reproduce experimental results in very simple systems. The only way to have computations truly disconnected from experience would be to rely on an infinite basis set, and this is just not possible.

The essay was written in this spirit of not confusing mathematical deductions from first principles with mathematical experiments involving very clever algorithms of computation. The idea that the reduction of the periodic table to quantum mechanics is becoming more and more successful as computational power increases cannot be a demonstration that chemistry is a sub-branch of physics. In fact, this is just the opposite.

The more sophisticated the computations become, the better the agreement with experience, but also the greater the gap between theoreticians and synthetic chemists. It follows that I am not really misled by philosophical accounts, as suggested by Scerri, but rather quite pleased to find that some philosophers were smart enough to predict the widening gap that we observe nowadays in chemistry between those who are mastering computers and algorithms and those who are mastering beakers and real chemical substances.

The essay was not written for physicists nor philosophers, but rather for synthetic chemists in order to convince them that their way of thinking and practicing chemistry cannot be captured by a single mathematical equation, as suggested by Paul Dirac.

Another important point addressed by Scerri concerns the case of quantum decoherence. In fact, the problem of coherence in condensed matter was exposed in another essay published in this review.<sup>19</sup>

One of the big problems with coherence is that the conceptual frame of thinking is not quantum mechanics, but rather quantum field theory. With this enlarged viewpoint, it becomes completely useless to solve Schrödinger's or Dirac's equations, because the coupling between atoms and the physical vacuum is ignored in both cases. I thus completely agree with Scerri that focusing on what lurks behind the Born-Oppenheimer approximation is not the best way of tackling the problem of what is a molecular structure.

In his conclusion, Scerri argues about the apparent lack of conclusion of my essay and suggests that my focus on advanced topics in physics and mathematics is puzzling given my message that chemistry is not reducible to physics.

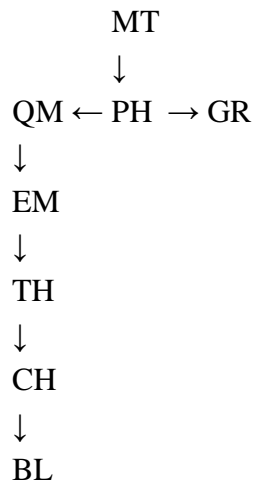
First, the principal aim of the essay was to provide readers with important facts that are usually not discussed, or even ignored by mainstream science.



The inescapable conclusion then is that scientific research tries to find answers to six basic questions:

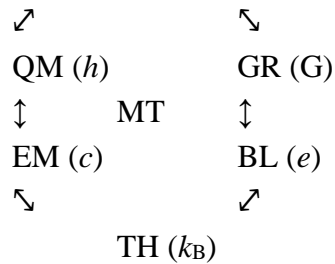
1. Q: What is a universe?  
A: refer to general relativity (GR).
2. Q: What is a vacuum?  
A: refer to quantum mechanics (QM).
3. Q: What is light?  
A: refer to electromagnetism (EM).
4. Q: What is matter?  
A: refer to chemistry (CH).
5. Q: What is information?  
A: refer to thermodynamics (TH).
6. Q: What is life?  
A: refer to biology (BL).

Consequently, neither physics (PH), nor mathematics (MT) have to respond to any particular question. Concerning physics, the main reason is the faith in its ability to give answers to any kind of question concerning Nature, a hegemonic position called reductionism. Concerning mathematics, the reason seems to be that it appears as a purely immaterial science, a purely speculative activity of the human brain. In fact, there is a strong tendency in the minds of physicists towards a pyramidal viewpoint, such as this one:



In this diagram, GR has been set apart owing to the considerable difficulties in merging QM with GR within a single theoretical frame. If one sticks to such a pyramidal structure, making extensive use of mathematics may appear a reductionist attitude. I want to stress here that this is definitively not the viewpoint which has been defended in this essay. The proposed structure is, rather, based on a circle, with mathematics at the center and appearing as the natural link among the six basic sciences:

CH (N<sub>A</sub>)



In short, there is no place for physics.

To add support to this viewpoint, I have also associated to each basic science a natural constant encapsulating the quintessence of each domain: Avogadro's constant  $N_A$  for chemistry, Planck's constant  $h$  for quantum mechanics, Einstein's constant  $c$  for electromagnetism, Boltzmann's constant  $k_B$  for thermodynamics, Coulomb's constant  $e$  for biology and Newton's constant  $G$  for astronomy. Of course, one may add other constants such as Hubble's constant (GR), or Sommerfeld's constant  $\alpha$  (QM) for instance.

The circular placement of the double arrows stresses the fact that each pole is interdependent with the other poles. It follows that the claim that one science is reducible to another is not only short-sighted, but also useless.

It also follows that the privileged position of mathematics is not due to its immaterial character, but rather to its ability to facilitate exchanges of information among the six poles that may occur not only at the periphery (double arrows), but also by passing through the center, the only point allowing to go directly from one pole to any other pole.

With such a circle in hand, do we really need to add a seventh pole named physics?

My answer in the essay is simply, "No." To justify this answer, I was obliged to go right to the center, mathematics in its more powerful expression: group theory, in order to retrieve this beautiful circular structure. Knowing that the symmetry of the vacuum was described by the  $SO(4,2)$  symmetry group having six independent parameters (1 for time, 3 for space and 2 for dilations in space or in time), the idea that there could exist such a thing as a GUT is doomed to fail.

Accordingly, the mere fact that mass scales as  $L^{-1}$  in QM and as  $L$  in GR, precludes any kind of marriage between both approaches. I would thus say to Scerri that immersion in mathematics does not necessarily mean that we are further arming reductionists in their quest to dissolve chemistry.

Instead we must learn to use the same arms in order to convince them of the vanity of this kind of quest. It should also be realized that what applies to chemistry, applies as well to thermodynamics and biology. Each pivotal science has its own way of thinking that is definitively not reducible to another way of thinking. Both philosophers and scientists should acknowledge this fundamental irreducibility.

Using the universal group theoretical language, my conclusion could thus have been: GR, QM, EM, TH, CH and BL are irreducible representations of Nature's  $SO(4,2)$  symmetry group.

Everything is said concisely, leaving no room for any kind of reductionist assault.

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1. I am the founder and editor of the Springer journal *Foundations of Chemistry*, now in its nineteenth year of publication. [↵](#)
2. J. Van Brakel, "On the Neglect of the Philosophy of Chemistry," *Foundations of Chemistry* 1 (1999): 111–74. [↵](#)
3. E. Nagel, *The Structure of Science: Problems in The Logic of Explanation* (New York: Harcourt, Brace and World, 1961). H. Reichenbach, *Selected Writings, 1909–1953*, M. Reichenbach, R.S. Cohen, eds. (Dordrecht: Reidel, 1978). [↵](#)
4. The latter feat was first achieved by Wolfgang Pauli, even before the identification of his fourth quantum number with a classically non-describable property which became somewhat misleadingly termed "spin." [↵](#)
5. Henry's article contains a persistent typo in that L is used several times instead of  $\ell$ . The usual meaning of L is the vector sum of the individual quantum numbers for the electrons in an atom that is an altogether different property. [↵](#)
6. Another article in which I examined this issue was E. R. Scerri, "The Changing Views of a Philosopher of Chemistry on the Question of Reduction," in E. R. Scerri, G. Fisher, eds. *Essays in the Philosophy of Chemistry* (New York: Oxford University Press, 2016). [↵](#)
7. I know of literally only two textbooks that give a correct account. They are, S. Glasstone, *Textbook of Physical Chemistry* (1946) and D. W. Oxtoby, H. P. Gillis, and A. Campion, *Principles of Modern Chemistry* (2007). [↵](#)
8. E. R. Scerri, "The Trouble with the Aufbau Principle," *Education in Chemistry* 50 (2013). [↵](#)
9. Strictly speaking, electrons are completely indistinguishable. When labeling electrons as belonging to particular orbitals I am operating within the independent electron approximation. [↵](#)
10. Textbooks, at least those that even recognize the problem, tend to appeal to all manner of ad hoc maneuvers in order to try to "have their cake and eat it." What I mean is that they attempt to claim that 4s is preferentially occupied and yet also preferentially ionized in transition metal atoms. This is quite simply illogical and yet it is precisely what is maintained by the vast majority of chemistry, and physics textbooks, for that matter.

Henry fails to mention that there have been various claims to the effect that the Madelung rule has been derived from first principles. L. C. Allen and E. T. Knight, *International Journal of Quantum Chemistry* 90 (2000); H. A. Bent and F. Weinhold, *Journal of Chemical Education* 85 (2007); V. N. Ostrovsky, *Foundations of Chemistry* 3 (2001). [↵](#)

11. The Madelung rule not only fails to describe the true situation in scandium, but also in the following nine transition elements, not to mention the remaining 30 transition elements that occur in the second, third, and fourth transition series. One might say that

these elements rather follow an  $n$  rule rather than an  $n + l$  rule. Even more shockingly to the traditionalists, the Madelung rule is only really valid for the elements in the s-block of the periodic table, which accounts for only about 10% of all elements. In the case of the f-block elements, the situation is more complicated and here we encounter some genuine cases in which these inner transition elements do indeed follow the Madelung rule. [↵](#)

12. I do not have the space here to discuss this question further. The reader is referred to E. R. Scerri, "What is an Element? What is the Periodic Table? And What Does Quantum Mechanics Contribute to the Question," *Foundations of Chemistry* 14 (2012): 69–81. [↵](#)
13. In just one particular case of the palladium atom, the configuration may be said to be doubly anomalous in that there are no electrons whatsoever in the outermost shell in which they are generally found in other transition elements in the same period. [↵](#)
14. E. R. Scerri, "The Changing Views of a Philosopher of Chemistry on the Question of Reduction," in E. R. Scerri, G. Fisher, eds., *Essays in the Philosophy of Chemistry* (New York: Oxford University Press, 2016). [↵](#)
15. S-G Wang and W. H. E. Schwarz, *Angewandte Chemie International Edition* 48, no. 3,404 (2009). [↵](#)
16. Opposing views on this question are presented in R. F. Hendry, "Ontological Reduction and Molecular Structure," *Studies in History and Philosophy of Modern Physics* 41 (2010): 183–91, and E. R. Scerri, "Top Down Causation Regarding the Chemistry – Physics Interface – A Skeptical View," *Interface Focus: Royal Society Publications* 2 (2012): 20–25. [↵](#)
17. E. R. Scerri, "It All Depends What You Mean By Reduction," in *From Simplicity to Complexity, Information, Interaction, Emergence*, Proceedings of the 1994 ZiF Meeting in Bielefeld, 77-93, K. Mainzer, A. Müller, and W. Saltzer, eds. (Wiesbaden: Vieweg-Verlag, 1994). [↵](#)
18. *Royal Society of Chemistry*, "[Periodic Table: Scandium](#)." [↵](#)
19. Marc Henry, "[The Hydrogen Bond](#)," *Inference: International Review of Science* 1, no. 2 (2015). [↵](#)

[Eric Scerri](#) is a historian and philosopher of chemistry in the Department of Chemistry & Biochemistry at UCLA.

[Marc Henry](#) is a Professor of Chemistry, Materials Science, and Quantum Physics at the University of Strasbourg.

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reply by Marc Henry

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