

A Novel Mnemonic for the Rydberg Rule

Abstract – This tutorial presents a new mnemonic describing the filling order of atomic orbitals according to the Rydberg Rule. The mnemonic accounts for the reordering of atomic orbitals and the large orbital energy gaps responsible for the periodicity of elements. The mnemonic provides for future similarity and dissimilarity studies between elements of the periodic table based on the position of the s-, p-, d-, and f-blocks relative to these energy gaps.

Keywords: madelung rule, rydberg rule, mnemonic, energy gaps, atomic orbitals, electron configurations

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Introduction

A mnemonic is a memory aid device designed to improve recall. Mnemonics are popular tools in the classroom because help teachers and students to summarize large amounts of information without necessarily explaining facts. Conversely, mnemonics based on fallacies and blunders, or divorced from experimental results, can cause students more harm than good in their undergraduate studies.

For instance, mnemonics describing the Madelung Rule are frequently used by chemistry teachers to help students memorize the order in which electrons fill the atomic orbitals across the Periodic System of Elements (PSE). This is frequently done using the sloppy version of the *aufbau* principle (Scerri, 2013), intermingled with full/half-full orbital stability myths, and the “folklore-hilarious” Madelung version of, nearly, all textbooks:

“In the first-transition-row, the 4s atomic orbital is occupied first and then the 3d, but upon ionization the more bound 4s is ionized first”.

However, there is ample experimental evidence showing that the Madelung Rule applies to the first three periods of the PSE and the first two elements of the fourth period, K and Ca (Schwarz, 2010a). Furthermore, this rule fails to describe the filling order of atomic orbitals across the PSE. As stated by Schwarz and Rich (2010), it is misleading to consider the electron configurations of the ground states of free neutral atoms as the dominant configurations of bonded atoms in chemical substances.

The Madelung and Rydberg Rules: Conceptual Differences

There are conceptual differences between these rules. The Madelung Rule is good in neutral free-atomic vacuum physics, and the Rydberg Rule is good in compound chemistry of bonded atoms.

Misconceptions about the Madelung Rule can be traced back to the years after World War Two (WW2). Before WW2, Madelung and others discussed orbital occupations, not orbital energies. After WW2, his rule was somehow absorbed by chemistry textbook authors, suggesting then various graphic mnemonics. The chemists then, incorrectly, interpreted the 'Madelung graphic' as representing the orbital energy order in cations of a given element.

Nowadays it is recognized that the Madelung Rule applies to the ground states of free neutral atoms, and from which electron configuration the lowest spin-orbit coupled state of the respective LS-orbit-orbit-coupled term derives. The rule applies to the case where one increases the nuclear charge or element number by one, and increases the electron number by one.

Chemists are interested in something else, for instance in determining what is the filling order of the valence shell of a given element with fixed nuclear charge, beginning with the case of highest oxidation state.

In terms of usefulness, the Madelung Rule is useful for physicists, but only for neutral atomic spectroscopy in vacuum where it holds in about 70 % of the inner and outer d-block elements. By contrast, the Rydberg Rule is useful for chemists. It holds in general except in groups 1 & 2, and except in metallic anions, since the orbital energies depend on the attracting nuclear charge number and the number of the other repelling electrons.

The Rydberg Rule has been found theoretic and experimentally correct for most, though not all, chemically bonded atoms of the PSE. By contrast, the Madelung rule is acceptable for groups 1 and 2, but not for all other groups 3 through 18.

About this Tutorial

At the time of writing, one cannot find in the chemical literature a straightforward mnemonic for writing electron configurations according to the Rydberg Rule. The purpose of this tutorial is to present such a novel mnemonic and, in the process, help chemistry students to properly write electron configurations.

The tutorial is largely based on the research work of Schwarz (2013, 2010a, 2010b), Schwarz and Rich (2010), and Wang, Qiu, Fang, and Schwarz (2006), and Wang and Schwarz (2009).

The Madelung Rule Mnemonic

The Madelung Rule, also known as the Janet or Klechkowski Rule (after Erwin Madelung, Charles Janet, and Vsevolod Klechkovsky), can be summarized in two parts (Goudsmit & Richards, 1964):

- A. When considering neutral atoms of consecutive atomic number Z , the electron shells fill up in the order of quantum number sum $(n + l)$.
- B. For electrons in states of equal $(n + l)$, the order of filling goes with increasing n .

In A and B, $n = 1, 2, 3, 4, \dots$ is the principal quantum number and $l = 0, 1, 2, 3, \dots$ the azimuthal quantum number corresponding to the s, p, d, f... labels. Parts A and B are frequently called the $(n + l, n)$ Madelung rule, and given in textbooks and elsewhere using different energy level sequences, like this:

Wang, Qiu, Fang, & Schwarz (2006),

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p \quad (1)$$

Wang & Schwarz (2009),

$$1s \ll 2s \ll 2p < 3s \ll 3p < 4s \ll 3d < 4p < 5s \ll 4d < 5p < 6s \ll 4f < 5d < 6p < 7s \ll 5f < 6d \dots \quad (2)$$

where $<$ means a little higher and \ll significantly higher (Schwarz, 2010b). Sequences (1) and (2) then represent what is told to most chemistry students. Notice that sequence (2) incorrectly includes large orbital energy gaps (\ll) after the ns orbitals. However, empirical and theoretical evidences show that these energy gaps actually are above the 1s and 2p, 3p, etc. Therefore,

$$1s \ll 2s < 2p \ll 3s < 3p \ll 4s < 3d < 4p \ll 5s < 4d < 5p \ll 6s < 4f < 5d < 6p \ll 7s \dots \quad (3)$$

is the correct energy levels sequence, with the large orbital energy gaps determining the $1s^2$ and $2p^6$ to $6p^6$ noble gas core shells and the periodicity of elements (Kramida, Ralchenko, Reader, & NIST

ASD Team, 2014). It can be shown, with the procedure described in the Appendix section, that sequence (3) can be derived by evaluating

$$(n - 1)p \ll ns < (n - 2)f < (n - 1)d < np \quad (4)$$

Because the Madelung Rule is frequently represented by a mnemonic diagram similar to the one shown in Figure 1, it is also referred to as the *diagonal rule*.

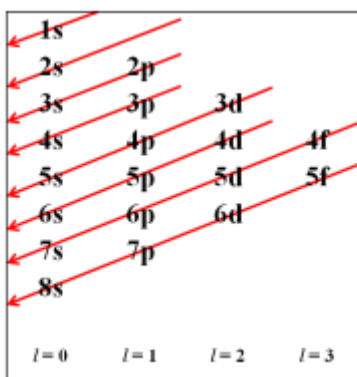


Figure 1. Mnemonic for the Madelung Rule.

In the figure, each diagonal arrow pointing to the left corresponds to the filling order of the atomic orbitals according to the Madelung Rule. Thus, each arrow represents a different constant value of $n + l$.

To account for the relative order of the large energy gaps given in sequence (3), one may redraw the mnemonic by properly using circles, vertical lines, etc. In Figure 2 we did so using broken arrows resembling a backbone which indicate the large orbital energy gaps (\ll), determining the $1s^2$ and $2p^6$ to $6p^6$ noble gas core shells; i.e., after the 1s there is an energy gap, then after the 2p, 3p, and so on.

We can use Figure 2 to understand the chemical significance of these gaps as the backbone of the PSE (Wang & Schwarz, 2009).

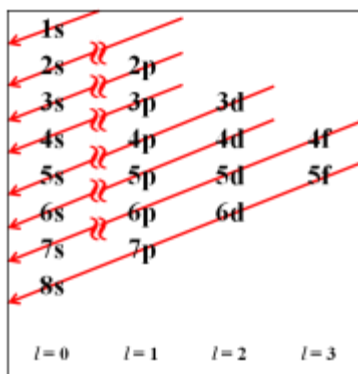


Figure 2. Modified Madelung Rule mnemonic. The broken arrows resembling a backbone indicate the large orbital energy gaps (\ll), determining the $1s^2$ and $2p^6$ to $6p^6$ noble gas core shells.

According to Figures 1 and 2, ns orbitals are filled before the $(n - 1)d$ orbitals; e.g., the 4s is filled before the 3d when going in physical vacuum from neutral atoms of noble gas (e.g., Ar) to alkali metal (K) to alkaline earth metal (Ca) to earth metal (Sc), etc.

However, the experimental chemical evidence shows that this is not the case for most, though not all, bonded atoms in compounds. As noted by Schwarz (2010a), for chemically bonded transition metals, the correct order is $(n - 1)d < ns$; i.e. the 3d subshell is filled before the 4s. To illustrate, consider the case of chromium, an element with fixed nuclear charge and different oxidation states. The filling order of the valence shell, beginning with the case of highest oxidation state is: $\text{Cr}^{\text{VI}}-3d^0$, $\text{Cr}^{\text{V}}-3d^1$, $\text{Cr}^{\text{IV}}-3d^2$, $\text{Cr}^{\text{III}}-3d^3$, $\text{Cr}^{\text{II}}-3d^4$, $\text{Cr}^{\text{I}}-3d^5$, and Cr^0-3d^6 (Vanquickenborne, Pierloot, & Devoghel, 1994).

As Schwarz asserted (2010a), there are about five different reasons responsible for the $(n - 1)d$ orbitals to be filled before the ns orbitals. These reasons can be used to understand why the Madelung Rule is not followed by, among others, the lanthanoids and actinoids, the so-called anomalous elements, and those traditionally considered non-anomalous like Ni, Fe, Co, Mo, Os, and Ir (Schwarz & Rich, 2010; Wang, Qiu, Fang, & Schwarz, 2006).

To sum up, the Madelung Rule and Figures 1 and 2 are not valid across atoms of the PSE for chemical purposes. Thus, to accommodate the predicted filling order of atomic orbitals with experiments, a better mnemonic is necessary. This is where the Rydberg Rule and our approach comes into play.

The Rydberg Rule Mnemonic

The Rydberg Rule can be summarized by the following energy levels sequence:

$$(n - 1)p \ll (n - 2)f < (n - 1)d < ns < np \quad (5)$$

where it can be shown that sequence (5) leads to

$$1s \ll 2s < 2p \ll 3s < 3p \ll 3d < 4s < 4p \ll 4d < 5s < 5p \ll 4f < 5d < 6s < 6p \ll 5f < 6d < 7s < 7p \dots \quad (6)$$

After the usual energy gap between the 1s and 2s orbitals, the Rydberg Rule predicts an energy gap after the np shells, with no longer a large gap above $n = 7$ (Wang & Schwarz, 2009). Again, these energy gaps are responsible for the periodicity of the PSE (Wang & Schwarz, 2009).

Notice from sequence (6) that the Rydberg Rule predicts that $(n - 2)f$ orbitals are filled before the $(n - 1)d$ and these before the ns . As a result, the following pairs of orbitals are reversed (4s, 3d), (5d, 4f), and (6d, 5f), as long predicted by Goudsmit and Richards (1964).

Exception are: in groups 1 and 2, $(n - 1)d$ is yet much above ns , and in group 3 $(n - 2)f$ is even above $(n - 1)d$. Then the d and f atomic orbitals "collapse" down according to sequence (6) for the subsequent d and f elements.

Sequence (6) is a goldmine of information. Comparing sequences (3) and (6), we can qualitatively derive one from the other by reordering the ns term. Also, by dropping the $(n - 2)f$ term, the Rydberg Rule gives the correct sequence of bound atomic valence orbitals above the $(n - 1)p^6$ rare-gas core shells for most atoms of the p and d blocks (Schwarz, 2010a).

Furthermore, by incrementing by 1 the terms of sequence (5) we obtain the Rydberg Rule representation of the atomic orbital sequences in the valence shells of most elements (Wang & Schwarz, 2010). All these derivations are depicted in Figure 3.

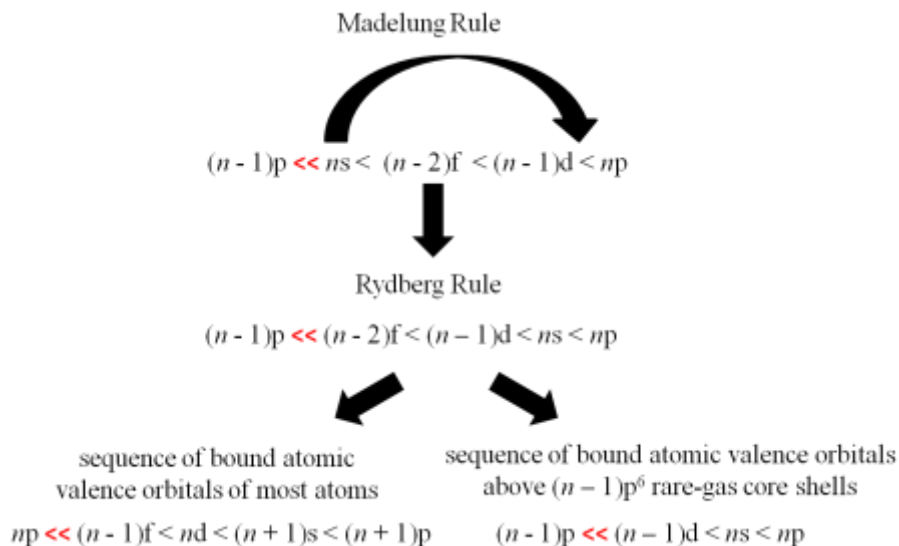


Figure 3. Qualitative derivation of the Rydberg Rule.

We can represent sequence (6) with a mnemonic where the reversal of atomic orbitals predicted by Goudsmit and Richards, namely the (4s, 3d), (5d, 4f), and (6d, 5f) are accounted for. We do this by explicitly swapping the 5d and 6d terms of Figure 1 with the 4f and 5f terms, respectively.

Producing the effect of swapping the ns and $(n-1)d$ terms, however, is indirectly done by aligning the content of all columns with respect to the eighth row. This also accounts for the lack of large orbital energy gaps above $n = 7$. All these operations are depicted in Figure 4.

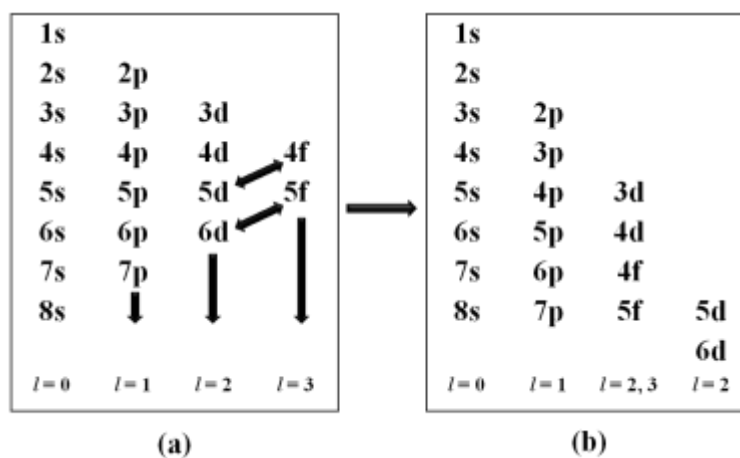


Figure 4. (a) Reordering of mnemonic. (b) New mnemonic.

For the grand finale, we redraw all diagonal arrows so these point now to the right, and maximizing $(n + l)$ values. The result is our proposed Rydberg Rule Mnemonic which we show in Figure 5 for the first time. The arrows now correspond to sequence (6).

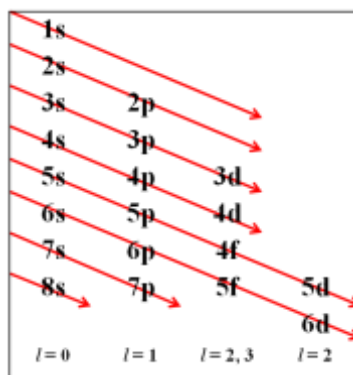


Figure 5. Mnemonic for the Rydberg Rule.

In Figure 6, we have modified Figure 5 to account for the energy gaps given in sequence (6). Again, the broken arrows indicate the large orbital energy gaps (\ll), determining the $1s^2$ and $2p^6$ to $6p^6$ noble gas core shells and the periodicity of elements. As in Figure 2, we can use Figure 6 to understand the chemical significance of these gaps as the backbone of the PSE (Wang & Schwarz, 2009).

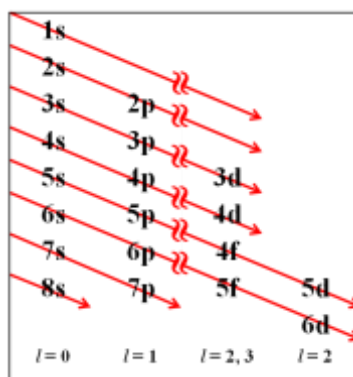


Figure 6. Modified Rydberg Rule mnemonic. Again, the broken arrows resembling a back bone indicate the large orbital energy gaps (\ll), determining the $1s^2$ and $2p^6$ to $6p^6$ noble gas core shells.

Comparing sequences (3) and (6) with that of a hydrogen-like atom,

$$ns \sim np \sim nd \sim nf \dots \quad (7)$$

it is clear that, for most atoms of the PSE, the filling order of atomic orbitals according to the Rydberg Rule can be rationalized as intermediate between the limiting cases described by sequences (3) and (7).

The mnemonics given in Figures 2 and 6 show that the **main group** of elements, those in groups 1 and 2 (s-block) and 13 to 18 (p-block) of the periodic table, are at the left of the large orbital energy gaps.

Final Thoughts and Future Work

In Figure 7, we modified even more Figure 6 to highlight the relative order of the s, p, d, and f blocks with respect to these energy gaps.

This time, we swapped the third and fourth columns of Figure 1, aligned their content with respect to its eight row, and stretched the corresponding diagonal arrows. None of these operations ultimately affect the filling order of atomic orbitals as given in Figure 6.

The modified Rydberg mnemonic given in Figure 7 illustrates that nf orbitals are deeply buried beneath the valence shell, rarely playing a role in chemical change or bonding (Senese, 2015). This chemical fact can hardly be grasped from Madelung's mnemonic where nf orbitals are at its far right column.

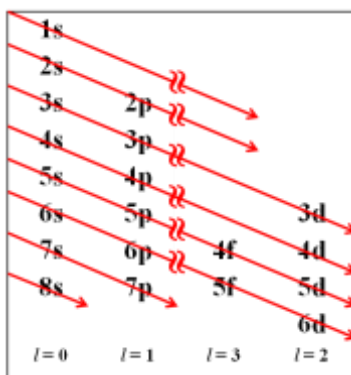


Figure 7. Block-level mnemonic for the Rydberg Rule.

We leave to future work the study of similarities and differences between elements located at both sides of these energy gaps, although relevant work have been documented (Restrepo & Pachón, 2007). As similarity (resemblance) and dissimilarity (distance) can be characterized in different ways, one may want to use different association measures and dimensionality reduction techniques while avoiding blunders like arithmetically adding/averaging similarities, or arbitrarily implementing similarity-distance transformations.

Over the years, we have developed several information retrieval and data mining resources along these lines. Some of these are available at the Tools and Tutorials sections of Minerazzi.com. An electron configurations tool based on this tutorial is also available (Garcia, 2016) along with tools for computing most of the similarity and distance measures found in the literature.

Conclusion

We have presented a new mnemonic for the Rydberg Rule which accounts for the large energy gaps responsible for the periodicity of the PSE.

The proposed mnemonic should not be taken for a silver-bullet approach, but as general outline for teaching the filling of atomic orbitals according to the Rydberg Rule. We recognize that said filling order and the proposed mnemonic is correct for most, though not all, cases.

While there is a correlation between electron configurations and chemical periodicity, the correlation is far from perfect. For instance, Wang et al. (2006) found that the ground configuration of Ni and Pt is d^9s^1 , not d^8s^2 .

Another example suffices: The electron configuration of lawrencium, $_{103}\text{Lr}$, should be $[\text{Rn}]7s^25f^{14}6d^1$, according to the Madelung Rule, and $[\text{Rn}]5f^{14}6d^17s^2$ according to the Rydberg Rule. However, Sato et al. (2015) have reported that the configuration of $_{103}\text{Lr}$ is, as long theorized, $[\text{Rn}]5f^{14}7s^27p^1$. Still, this element may behave in a similar fashion as d-block elements, being the true congeners of scandium ($_{21}\text{Sc}$) and yttrium ($_{39}\text{Y}$) which are in the d^1 group.

As mentioned early in this tutorial, mnemonics are devices for memorizing large amount of information, and as such can be manifested in different “forms and flavors”; for instance, in chemistry and to rationalize the PSE, as mental constructs in the form of short and long (left-step) periodic tables. Mnemonics are not necessarily devices for explaining facts.

It is when mnemonics are used without considering the experimental evidence that they must be avoided. In the case of the Madelung Rule, this is an idealized limiting rule applicable to free

neutral atoms. The Madelung Rule and its mnemonic can hardly be used to explain the chemistry of bonded atoms, though. As Wang and Schwarz asserted (2009),

“Indeed, the $n + l$ rule has little meaning in chemistry. However, since the rule occurs in all textbooks and is absorbed by all students and teachers, it will die out only very slowly. Only a few chemists need correct details about the electronic structure of the chemical transition elements; their re-education in graduate courses is not too difficult. Most other undergraduate students will not need the $n + l$ blunder in their future career.”

Very true. As new teaching tools that agree with theory and experiments are introduced in the chemistry classroom, we hope for similar blunders to die out sooner rather than later.

Appendix

One can derive the filling order of atomic orbitals using the following procedure, where ε_{nl} is a sequence of nl terms representing atomic orbitals.

Step 1 Write the ε_{nl} you are interested in.

Step 2 Evaluate ε_{nl} for a given n value.

Step 3 Deduplicate the results.

Let's go over these steps.

Step 1 needs no further explanation.

Step 2 is an iterative procedure, usually set from $n = 1$ to $n = 7$ where ns is defined for $n \geq 1$, $(n - 1)p$ for $n \geq 3$, $(n - 1)d$ for $n \geq 4$, and $(n - 2)f$ for $n \geq 6$.

Step 3 is a filtering process where repeated terms are removed from the n -specific sequences.

The final results are concatenated. Deduplication can be done before or after concatenation. Let's illustrate this procedure with the Madelung Rule.

The Madelung Rule (good for groups 1 and 2)

Step 1 Sequence, ϵ_{nl}

$$(n - 1)p \ll ns < (n - 2)f < (n - 1)d < np$$

Step 2 Evaluation

$$\epsilon_{nl} (n = 1): 1s$$

$$\epsilon_{nl} (n = 2): \ll 2s < 2p$$

$$\epsilon_{nl} (n = 3): 2p \ll 3s < 3p$$

$$\epsilon_{nl} (n = 4): 3p \ll 4s < 3d < 4p$$

$$\epsilon_{nl} (n = 5): 4p \ll 5s < 4d < 5p$$

$$\epsilon_{nl} (n = 6): 5p \ll 6s < 4f < 5d < 6p$$

$$\epsilon_{nl} (n = 7): 6p \ll 7s < 5f < 6d < 7p$$

Step 3 Deduplication

$$\epsilon_{nl} (n = 1): 1s$$

$$\epsilon_{nl} (n = 2): \ll 2s < 2p$$

$$\epsilon_{nl} (n = 3): \ll 3s < 3p$$

$$\epsilon_{nl} (n = 4): \ll 4s < 3d < 4p$$

$$\epsilon_{nl} (n = 5): \ll 5s < 4d < 5p$$

$$\epsilon_{nl} (n = 6): \ll 6s < 4f < 5d < 6p$$

$$\epsilon_{nl} (n = 7): \ll 7s < 5f < 6d < 7p$$

After concatenation, the result is sequence (3),

$$1s \ll 2s < 2p \ll 3s < 3p \ll 4s < 3d < 4p \ll 5s < 4d < 5p \ll 6s < 4f < 5d < 6p \ll 7s \dots$$

Let's now apply this procedure to derive the filling order of atomic orbitals according to the Rydberg Rule.

The Rydberg Rule (good for all groups 3 to 18)

Step 1 Sequence, ϵ_{nl}

$$(n - 1)p \ll (n - 2)f < (n - 1)d < ns < np$$

Step 2 Evaluation

$$\epsilon_{nl} (n = 1): 1s$$

$$\epsilon_{nl} (n = 2): \ll 2s < 2p$$

$$\epsilon_{nl} (n = 3): 2p \ll 3s < 3p$$

$$\epsilon_{nl} (n = 4): 3p \ll 3d < 4s < 4p$$

$$\epsilon_{nl} (n = 5): 4p \ll 4d < 5s < 5p$$

$$\epsilon_{nl} (n = 6): 5p \ll 4f < 5d < 6s < 6p$$

$$\epsilon_{nl} (n = 7): 6p \ll 5f < 6d < 7s < 7p$$

Step 3 Deduplication

$$\epsilon_{nl} (n = 1): 1s$$

$$\epsilon_{nl} (n = 2): \ll 2s < 2p$$

$$\epsilon_{nl} (n = 3): \ll 3s < 3p$$

$$\epsilon_{nl} (n = 4): \ll 3d < 4s < 4p$$

$$\epsilon_{nl} (n = 5): \ll 4d < 5s < 5p$$

$$\epsilon_{nl} (n = 6): \ll 4f < 5d < 6s < 6p$$

$$\epsilon_{nl} (n = 7): \ll 5f < 6d < 7s < 7p$$

After concatenation, the result is sequence (6),

$$1s \ll 2s < 2p \ll 3s < 3p \ll 3d < 4s < 4p \ll 4d < 5s < 5p \ll 4f < 5d < 6s < 6p \ll 5f < 6d < 7s < 7p \dots$$

We have written a tool that executes these steps. Students can use the tool to experiment with different sequences and then check the impact of these on specific electron configurations at the core or valence shell levels. Students can then do some critical thinking and classify the results as valid or invalid using basic quantum theory arguments and literature references.

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