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Shannon Entropy of Chemical Elements

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Abstract: Hund rule of maximum spin multiplicity is a powerful empirical tool to determine the electron population of electronic shells. It was recently discovered that electron populations within an orbital minimize Shannon entropy and maximize spin multiplicity, which seems to be the physical basis for the Hund rule. This study extends these findings to the Aufbau rule, strengthening its meaning. We observed that only about half of the elements with ground state configurations that violate the Aufbau rule have Shannon entropies lower for the actual element's configurations; the remaining ones have the same entropies in actual and Aufbau configurations. Furthermore, for the two nonsingleton sets of consecutive elements that violate the Aufbau rule, the first set ($44 \leq Z \leq 47$) contains elements having lower entropies and the same spin multiplicities in actual and Aufbau configurations, except palladium, the only element that violates the higher or equal multiplicity rule. The second set ($89 \leq Z \leq 93$) contains elements having the same entropies and spin multiplicities.

Keywords: Hund's rule; Aufbau rule; second law of infodynamics; emergent dimensionality; mathematical physics

1. Introduction

Hund's rule of maximum multiplicity is a powerful empirical tool for determining the electron population of electronic shells. It was recently reported [1] that the real driving force behind Hund's rule appears to be the second law of infodynamics [2]

$$\frac{dS_{info}}{dt} \leq 0, \tag{1}$$

where S_{info} in this time derivative is the information entropy proportional to Shannon entropy

$$H = \sum_{k=1}^{n} p_k \log_b \left(\frac{1}{p_k} \right), \quad b \in \mathbb{R}_+ \setminus \{1\}, \tag{2}$$

of a discrete random variable that attains maximum $\log_b(n)$ if the events are equiprobable (i.e., if the probabilities $p_k = 1/n$) and vanishes for certain and impossible events[1] In other words, electron populations within an orbital minimize Shannon entropy (2).

It is now generally accepted [1–13] that information in the universe evolves, decreasing the information entropy S_{info}. Assuming that the total entropy of the universe S is constant and is the sum of the information entropy and the physical entropy S_{phys}, we obtain [1]

$$\frac{dS_{info}}{dt} + \frac{dS_{phys}}{dt} = 0. \tag{3}$$

This study extends the findings of [1] to the Aufbau rule and discusses them from the perspective of emergent dimensionality [7–14].

[1] In the latter case $0 \ln(1/0)$ is not defined. It is, by convention, taken as 0.

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2. Hund's rule and Shannon entropy

A simple but inventive procedure for calculating Shannon entropies of electron populations was disclosed in [1]. Any set of N electrons satisfies $N = N_\uparrow + N_\downarrow$, where $N_\uparrow$ and $N_\downarrow$ denote, respectively, the number of up- and down-spin electrons. Thus, the probabilities of finding $\uparrow$ and $\downarrow$ electrons within the set of N electrons are $p_\uparrow = N_\uparrow/N$ and $p_\downarrow = N_\downarrow/N$.

Definition 1 (Electron set entropy)**.** *An electron set entropy is*

$$\begin{aligned} H &= -p_\uparrow \log_b(p_\uparrow) - p_\downarrow \log_b(p_\downarrow) = \\ &= \log_b(N) - \frac{N_\uparrow}{N}\log_b(N_\uparrow) - \frac{N_\downarrow}{N}\log_b(N_\downarrow). \end{aligned} \tag{4}$$

This definition was disclosed in [1] but is given here for clarity. Electrons are fermions, so electron sets populating chemical elements' orbitals must satisfy the Pauli exclusion principle. For the s orbital, for example, which can accommodate a maximum of $N = 2$ electrons, the corresponding probabilities are $p_\uparrow = 1 \cup p_\downarrow = 1$ if the orbital accommodates one electron and $p_\uparrow = p_\downarrow = 1/2$ if the orbital accommodates two electrons. Thus, possible electron set entropies (4) are $H = \{0, \log_b(2)\}$.

We do not assume any particular logarithm base b, noting that nature uses natural logarithm in Landauer's principle [15] and Boltzmann/Gibbs physical entropy S_{phys}. Furthermore, the author of [1] assumes that the electron set entropies of states s^1 and s^2 are the same, but this assumption is unjustified, as we shall discuss later.

The situation becomes more diverse for orbitals with a larger angular momentum quantum number ℓ as multiple sets with different electron set entropies and spin multiplicities are possible, as shown in Figures 1–4 for orbitals p-g.

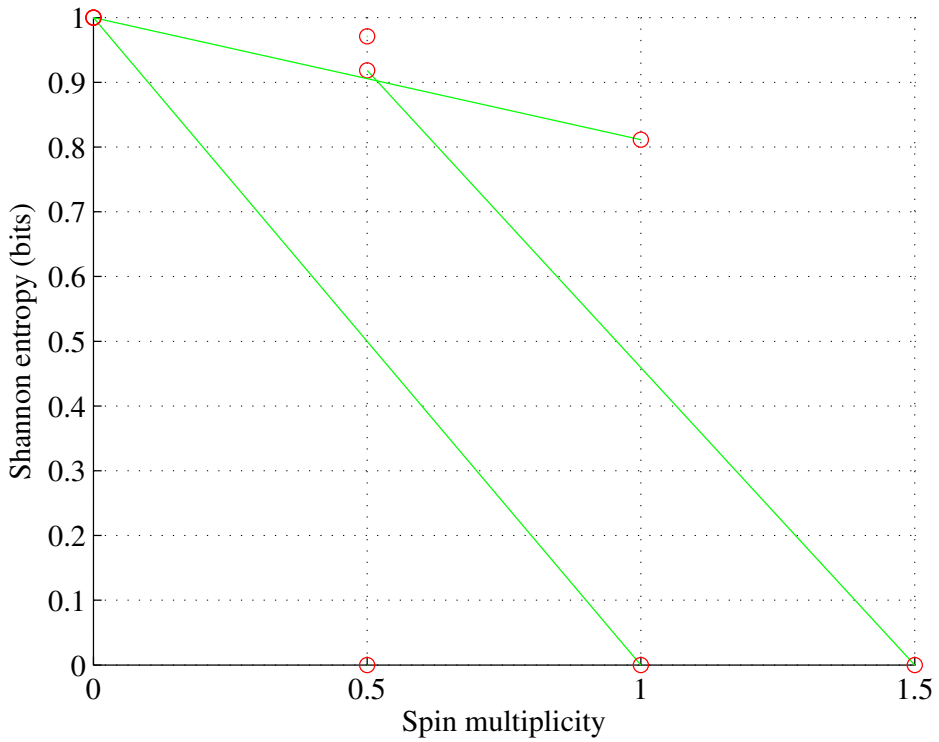

Figure 1. Orbital p. $p^k \leftrightarrow \{k/2, 0\}$, for $1 < k < 3$, $p^4 \leftrightarrow \{1, \log_b(4) - 3\log_b(3)/4\}$, $p^5 \leftrightarrow \{0.5, \log_b(5) - 3\log_b(3)/5 - 2\log_b(2)/5\}$, $p^6 \leftrightarrow \{0, \log_b(2)\}$.

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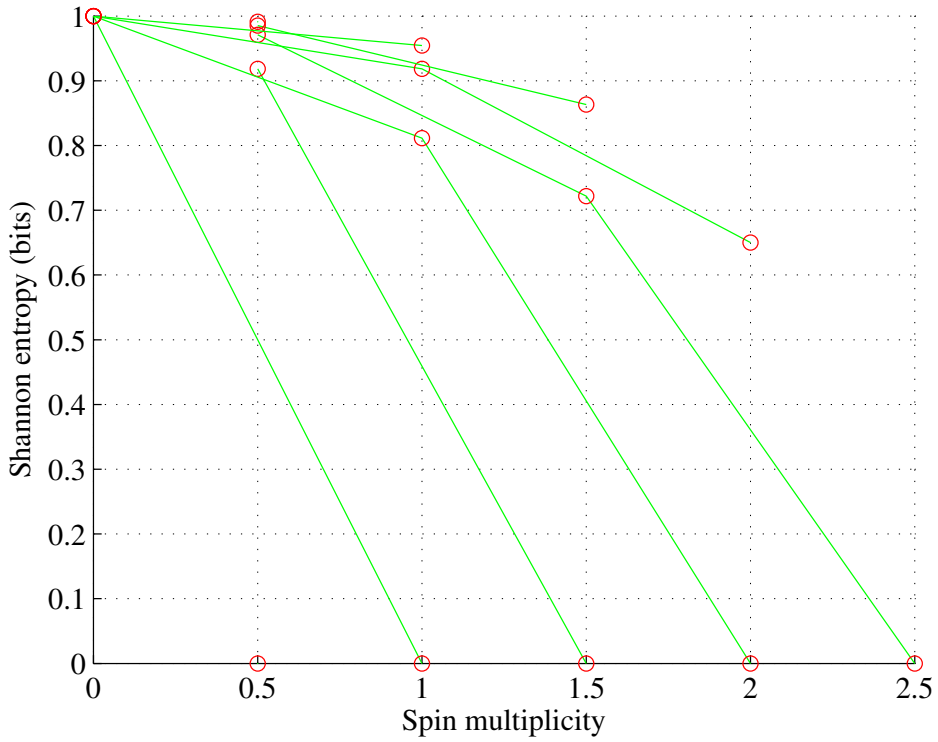

Figure 2. Orbital d. $d^k \leftrightarrow \{k/2, 0\}$, for $1 < k < 5$, $d^{10} \leftrightarrow \{0, \log_b(2)\}$.

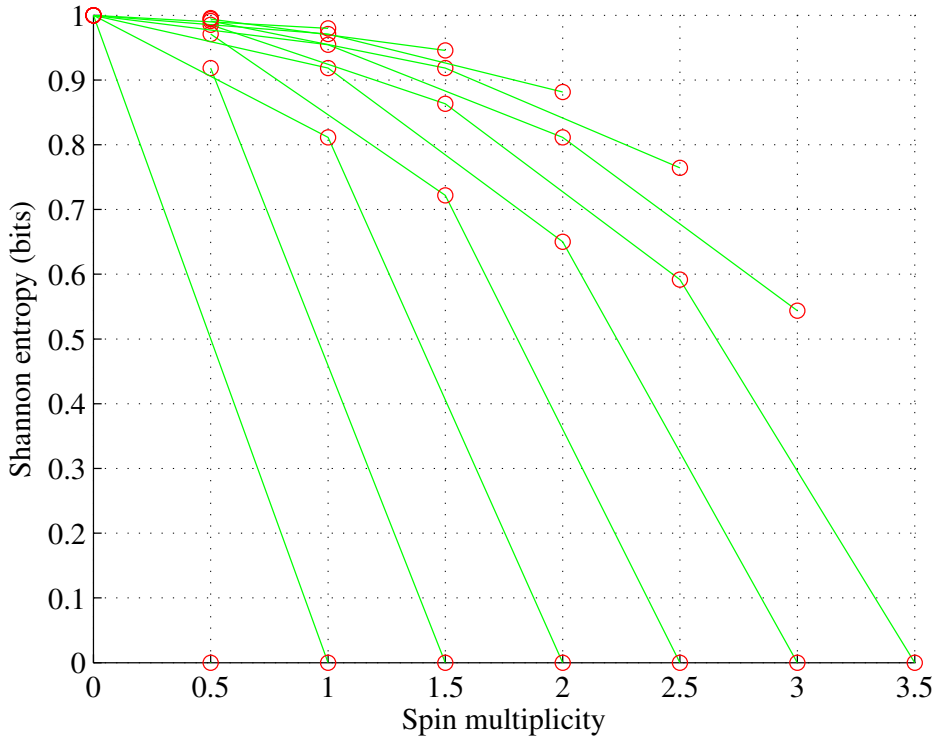

Figure 3. Orbital f. $f^k \leftrightarrow \{k/2, 0\}$, for $1 < k < 7$, $f^{14} \leftrightarrow \{0, \log_b(2)\}$.

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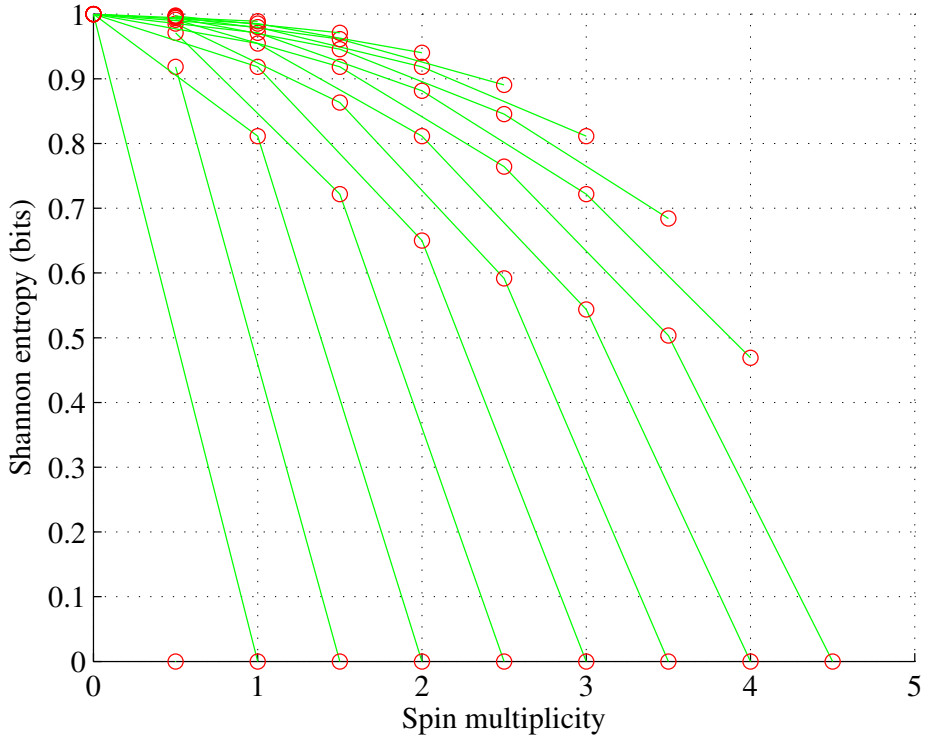

Figure 4. Orbital g. $g^k \leftrightarrow \{k/2, 0\}$, for $1 < k < 9$, $g^{18} \leftrightarrow \{0, \log_b(2)\}$.

However:

- for $1 \leq N \leq N_{max}/2$, $H = 0$;
- for $N = \{1, N_{max} - 1, N_{max}\}$, only one electron set is possible; and
- for $N_{max}/2 + 1 \leq N \leq N_{max}\}$, $H \neq 0$;

wherein nature selects this electron set among the ones allowed by the Pauli exclusion principle that maximizes spin multiplicity. However, as shown in [1], for $N_{max}/2 + 1 \leq N \leq N_{max} - 2\}$, nature also selects this electron population among the allowed ones, which minimizes the orbital Shannon entropy. This rule of populating the sublevels can be stated in the simple theorem illustrated in Figure 5.

Theorem 1 (Orbital entropy). *For any orbital capable of storing $N_{max} = 4n + 2$, $n \in \mathbb{N}_0$ electrons and storing N electrons and populated to maximize spin multiplicity (i.e. according to Hund's rule), the orbital Shannon entropy vanishes iff $N \leq N_{max}/2$ and amounts*

$$\begin{aligned} H = \log_b(N) - \frac{N_{max}/2}{N} \log_b\left(\frac{N_{max}}{2}\right) \\ - \left(\frac{N - N_{max}/2}{N}\right) \log_b\left(N - \frac{N_{max}}{2}\right) \end{aligned} \tag{5}$$

otherwise.

Proof. According to Hund's rule, for $N \leq N_{max}/2$ the spin multiplicity is equal to $S = \pm N/2$, while for $N > N_{max}/2$ is equal to $S = \pm(N_{max} - N)/2$. For $N \leq N_{max}/2$ electrons can freely populate available $N_{max}/2$ sublevels to maximize the spin multiplicity and therefore $H = \frac{N_\uparrow}{N} \log_b\left(\frac{N_\uparrow}{N}\right) = \log_b(1) = 0$ (the same for $\downarrow$). For $N > N_{max}/2$ the electrons will begin to repopulate the available $N_{max}/2$ sublevels following the Pauli exclusion principle up to $N = N_{max}$, where $H = \log_b(N) - \log_b\left(\frac{N}{2}\right) = \log_b(2)$, which completes the proof. □

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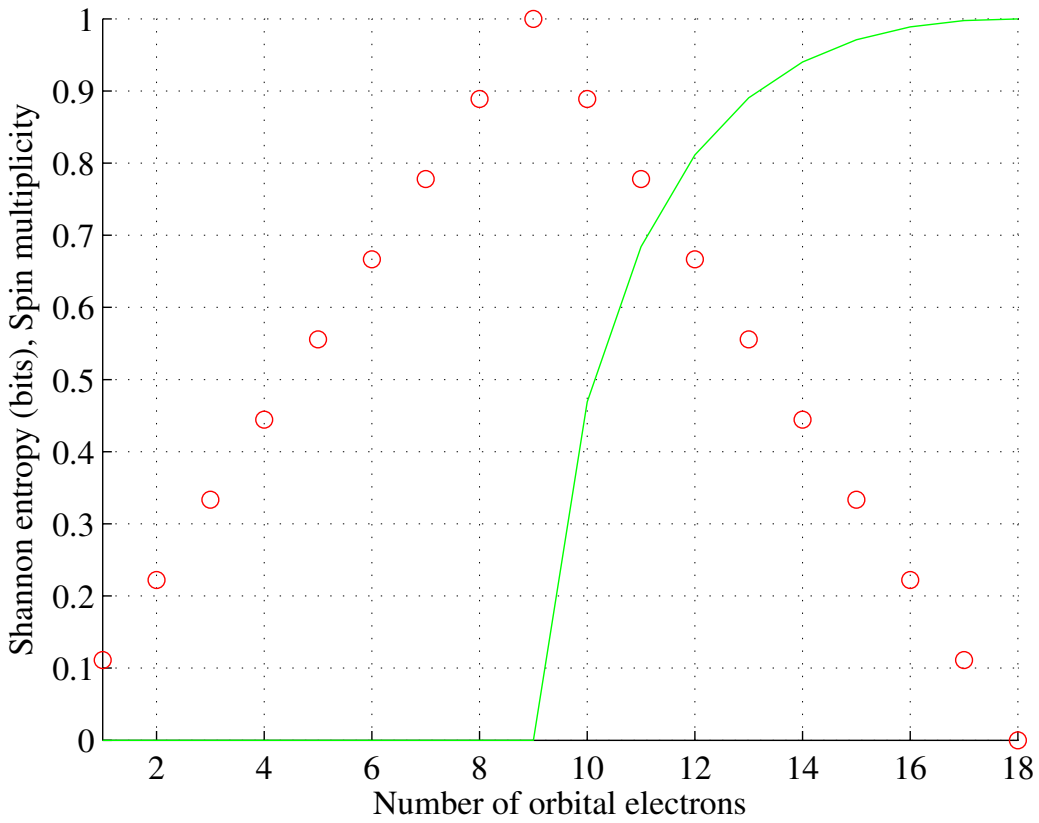

Figure 5. Orbital f. Spin multiplicity (red, rescaled) and associated orbital entropy (green).

Some researchers postulate that certain elements are exceptions to Hund's rule. Chromium, for example, having the atomic number $Z = 24$ is between vanadium ($Z = 23$, electron configuration $[Ar]3d^34s^2$) and manganese ($Z = 25$, $[Ar]3d^54s^2$) within the periodic table of elements. Thus, it should have electron configuration $[Ar]3d^44s^2$, following Hund's rule, but instead, it has $[Ar]3d^54s^1$, as one electron from 4s *moves* to 3d to make it more stable. But it is not Hund's rule that is violated. It is the Aufbau rule. Hund's rule governs the electron population of a solitary orbital only.

3. Aufbau rule and Shannon entropy

The Aufbau or Madelung energy ordering rule is another powerful empirical tool for predicting the electron configurations of chemical elements corresponding to the ground state. It correctly predicts the electron configurations of most of the elements. However, about twenty chemical elements violate the Aufbau rule, leading to intriguing exceptions and anomalies. Chromium and copper violations are attributed to a delicate balance of electron-electron repulsion and the energy gap between the 3d and 4s orbitals [16]. Palladium, often called a "double anomaly" [17], exhibits a rare electron configuration, $[Kr]4d^{10}5$, where all ten electrons fill the 4d orbital. This exceptional behavior is attributed to the compactness of 3d orbitals and complex electron interactions [17]. In addition, there are no chemical elements that have orbital f^8 in their electron configurations, although the Aufbau rule predicts f8 for gadolinium ($Z = 64$) as $[Xe]+6s^2+4f^8$ and for curium ($Z = 96$) as $[Rn]+7s^2+5f^8$. Furthermore, there are only two nonsingleton sets of consecutive elements violating the Aufbau rule (Nickel has a disputed configuration). We note that for $Z \geq 105$, actual ground states are predicted. Thus, perhaps other elements, such as darmstadtium ($Z = 110$) and roentgenium ($Z = 111$) also violate the Aufbau rule.

The elements that violate the Aufbau rule are listed in Table 1, showing their actual electron configurations, and the configurations predicted by the Aufbau rule. Furthermore, Table 1 shows the

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spin multiplicities of the elements, i.e., $S = |N_\uparrow - N_\downarrow|/2$. $S \in \mathbb{N}$ if Z is even and $S \in \frac{1}{2}\mathbb{N}$ otherwise. Furthermore, all but one of the violating elements satisfy a higher or equal multiplicity rule; i.e., actual spin multiplicity is mostly greater or equal to the spin multiplicity predicted using the Aufbau and Hund rules. The only exception is palladium ($Z = 46$).

Table 1. Chemical elements violating Aufbau rule.

		Ground state electron configuration		Spin multiplicity		Shannon entropy ($H_{act}(Z) \leq H_{A/H}(Z) \quad \forall Z$)	
	Z	actual	Aufbau	$S_{act}(Z)$	$S_{A/H}(Z)$	$H_{act}(Z)$	$H_{A/H}(Z)$
Cr	24	$[Ar]3d^5 4s^1$	$[Ar]3d^4 4s^2$	3	2	$5\log_b(2)$	$6\log_b(2)$
Ni	28	$[Ar]3d^8 4s^2$ (or $[Ar]3d^9 4s^1$)	$[Ar]3d^8 4s^2$	1	1	$\log_b(2^{37/9}3^2 5^{-5/9})$	$\log_b(2^9 3^{-3/8} 5^{-5/8})$
Cu	29	$[Ar]3d^{10} 4s^1$	$[Ar]3d^9 4s^2$	1/2	1/2	$6\log_b(2)$	$\log_b(2^{46/9}3^2 5^{-5/9})$
Nb	*41*	$[Kr]4d^4 5s^1$	$[Kr]4d^3 5s^2$	5/2	3/2	$9\log_b(2)$	$9\log_b(2)$
Mo	*42*	$[Kr]4d^5 5s^1$	$[Kr]4d^4 5s^2$	3	2	$9\log_b(2)$	$9\log_b(2)$
Ru	44	$[Kr]4d^7 5s^1$	$[Kr]4d^6 5s^2$	2	2	$\log_b(2^{54/7}5^{-5/7}7)$	$\log_b(2^{10}35^{-5/6})$
Rh	45	$[Kr]4d^8 5s^1$	$[Kr]4d^7 5s^2$	3/2	3/2	$\log_b(2^{11}3^{-3/8}5^{-5/8})$	$\log_b(2^{61/7}5^{-5/7}7)$
Pd	**46**	$[Kr]4d^{10}$	$[Kr]4d^8 5s^2$	0	1	$9\log_b(2)$	$\log_b(2^{12}3^{-3/8}5^{-5/8})$
Ag	47	$[Kr]4d^{10} 5s^1$	$[Kr]4d^9 5s^2$	1/2	1/2	$9\log_b(2)$	$\log_b(2^{73/9}3^2 5^{-5/9})$
La	*57*	$[Xe]5d^1 6s^2$	$[Xe]4f^1 6s^2$	1/2	1/2	$12\log_b(2)$	$12\log_b(2)$
Ce	*58*	$[Xe]4f^1 5d^1 6s^2$	$[Xe]4f^2 6s^2$	1	1	$12\log_b(2)$	$12\log_b(2)$
Gd	*64*	$[Xe]4f^7 5d^1 6s^2$	$[Xe]4f^8 6s^2$	4	3	$12\log_b(2)$	$\log_b(2^{15}7^{-7/8})$
Pt	*78*	$[Xe]4f^{14} 5d^9 6s^1$	$[Xe]4f^{14} 5d^8 6s^2$	1	1	$\log_b(2^{16}3^{-3/8}5^{-5/8})$	$\log_b(2^{16}3^{-3/8}5^{-5/8})$
Au	79	$[Xe]4f^{14} 5d^{10} 6s^1$	$[Xe]4f^{14} 5d^9 6s^2$	1/2	1/2	$13\log_b(2)$	$\log_b(2^{109/9}3^2 5^{-5/9})$
Ac	*89*	$[Rn]6d^1 7s^2$	$[Rn]5f^1 7s^2$	1/2	1/2	$16\log_b(2)$	$16\log_b(2)$
Th	*90*	$[Rn]6d^2 7s^2$	$[Rn]5f^2 7s^2$	1	1	$16\log_b(2)$	$16\log_b(2)$
Pa	*91*	$[Rn]5f^2 6d^1 7s^2$	$[Rn]5f^3 7s^2$	3/2	3/2	$16\log_b(2)$	$16\log_b(2)$
U	*92*	$[Rn]5f^3 6d^1 7s^2$	$[Rn]5f^4 7s^2$	2	2	$16\log_b(2)$	$16\log_b(2)$
Np	*93*	$[Rn]5f^4 6d^1 7s^2$	$[Rn]5f^5 7s^2$	5/2	5/2	$16\log_b(2)$	$16\log_b(2)$
Cm	*96*	$[Rn]5f^7 6d^1 7s^2$	$[Rn]5f^8 7s^2$	4	3	$16\log_b(2)$	$\log_b(2^{142/9}3^2 7^{-7/9})$
Lf	*103*	$[Rn]5f^{14} 7s^2 7p^1$	$[Rn]5f^{14} 6d^1 7s^2$	1/2	1/2	$17\log_b(2)$	$17\log_b(2)$

Italic Z - the same entropy; underlined $\underline{Z}$ - higher multiplicity; bold **Z** - the exception to the higher or equal multiplicity rule.

As the entropies of independent systems are additive quantities, we can calculate the Shannon entropies of chemical elements by summing the orbital entropies of electron configurations using the relation (5).

Definition 2. *An element's ground-state Shannon entropy is the sum of the orbital entropies in the electron configuration of this element, neglecting the principal quantum number.*

For example, the electron configuration of oxygen is $[He]2s^2 2p^4 \to s^2 s^2 p^4$, where $H(s^2) = \log_b(2)$ and $H(p^4)$ is given by the relation (5). Thus, the Shannon entropy for oxygen is equal to

$$\begin{aligned} H_O &= \\ &= \log_b(2) + \log_b(2) + \log_b(4) - \frac{3}{4}\log_b(3) - \frac{4-3}{4}\log_b(4-3) = \\ &= 4\log_b(2) - \frac{3}{4}\log_b(3). \end{aligned} \tag{6}$$

Similarly, for chromium $[Ar]3d^5 4s^1 \to 3 \times s^2 + 2 \times p^6 + d^5 + s^1 \to H_{Cr} = 3\log_b(2) + 2\log_b(2) + 0 + 0 = 5\log_b(2)$, and so on.

Shannon entropies H_{act} and $H_{H/A}$ for $0 \leq Z \leq 118$ are shown in Figure 6 based on actual ground state configurations and configurations obtained using the Aufbau rule.

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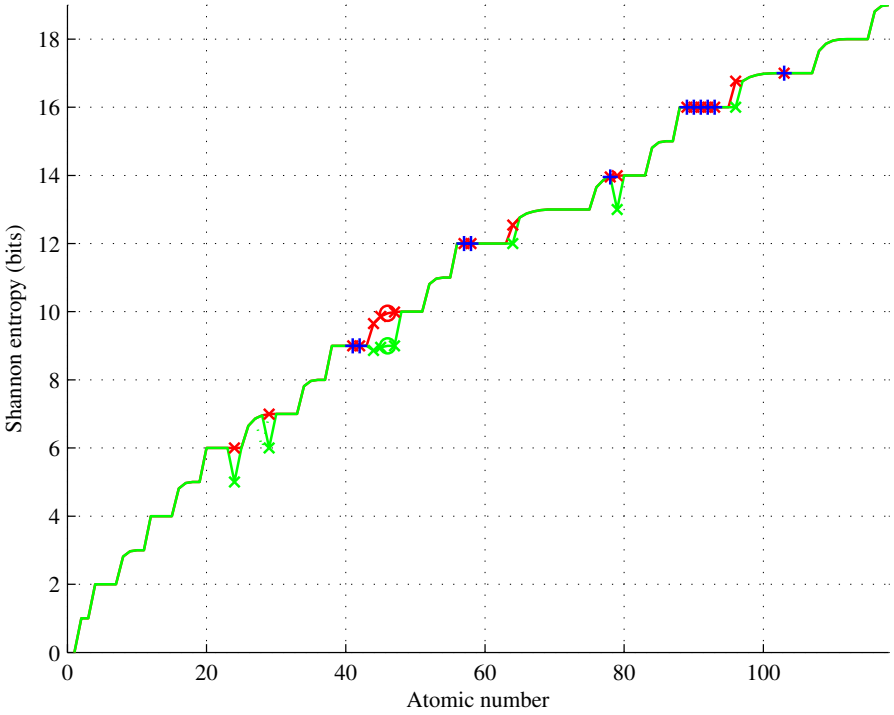

Figure 6. Shannon entropy of chemical elements (green) showing Aufbau rule violations (red) and elements of the same entropy (blue).

4. Conclusions

We observed that the following holds for the elements violating the Aufbau rule:

- for less than half (10/21) of them, the element's entropy is lower for the actual and Aufbau configurations, the remaining ones have the same entropies in actual and Aufbau configurations;
- the first nonsingleton set $44 \leq Z \leq 47$ contains four elements having lower entropies and the same spin multiplicities, with the exception of $Z = 46$, the only element that violates the higher or equal multiplicity rule;
- the second nonsingleton set $89 \leq Z \leq 93$ contains five elements having the same entropies and spin multiplicities.

Overall, these results significantly strengthen the meaning of the Aufbau rule.

We finally note that the Shannon entropy H_{H} of hydrogen is zero, not $\log_b(2)$. In emergent dimensionality [7–14], neither one nor two electrons *exist*. Therefore, s^1 is populated before s^2 not because one electron is *less than* two electrons, but because the Shannon entropy for one electron $H = 0$ is lower than the Shannon entropy $H = \log_b(2)$ for two electrons.

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