From permutation patterns to the periodic table

Lara Pudwell
Department of Mathematics and Statistics
Valparaiso University
Valparaiso, Indiana, USA

April 11, 2020

Permutation patterns is a burgeoning area of research with roots in enumerative combinatorics and theoretical computer science. Although much current work in this area still relates to its computer science origins, its rapid expansion over the past two decades has led to some surprising connections with other areas of mathematics. This article first presents a brief overview of pattern avoidance and a survey of enumeration results that are standard knowledge within the field. Then, we turn our attention to a newer optimization problem of pattern packing. We survey pattern packing results in the general case before we consider packing in a specific type of permutation that leads to a new and surprising connection with physical chemistry.

Let $\mathcal{S}_k$ be the set of all permutations on $[k] = \{1, 2, \ldots, k\}$. Given $\pi \in \mathcal{S}_k$ and $\rho \in \mathcal{S}_\ell$ we say that π *contains* ρ as a pattern if there exist $1 \leq i_1 < i_2 < \cdots < i_\ell \leq k$ such that $\pi_{i_a} \leq \pi_{i_b}$ if and only if $\rho_a \leq \rho_b$. In this case we say that $\pi_{i_1} \cdots \pi_{i_\ell}$ is *order-isomorphic* to ρ, and that $\pi_{i_1} \cdots \pi_{i_\ell}$ is an *occurrence* or a *copy* of ρ in π. If π does not contain ρ, then we say that π *avoids* ρ. For example $\pi = 43512$ contains the pattern $\rho = 231$ because the digits of $\pi_2\pi_3\pi_5 = 352$ have the same relative order as the digits of ρ; this is one of four instances of 231 in π.

The definition of pattern containment may be made more visual by considering the *plot* of π. In particular, for $\pi = \pi_1\pi_2 \cdots \pi_k \in \mathcal{S}_k$, the plot of π is the graph of the points (i, π_i) in the Cartesian plane. The plots of $\pi = 43512$ and $\rho = 231$ are given in Figure 1. An alternate way to see that π contains

ρ is to notice that if we remove the rows and columns with red points from the plot of π, the remaining (black) points form a plot of ρ.

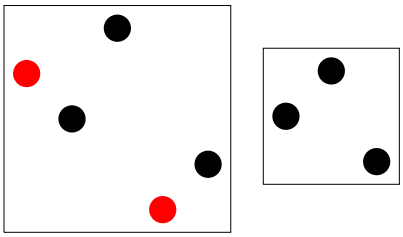


Figure 1: The plots of $\pi = 43512$ and $\rho = 231$

Of particular interest are the sets $\mathcal{S}_k(\rho) = \{\pi \in \mathcal{S}_k \mid \pi \text{ avoids } \rho\}$. For example,

$$\begin{aligned}\mathcal{S}_4(123) = \{&1432, 2143, 2413, 2431, 3142, 3214, 3241,\\ &3412, 3421, 4132, 4213, 4231, 4312, 4321\},\end{aligned}$$

and $\pi = 43512 \in \mathcal{S}_5(123)$ since there is no increasing subsequence of length 3 in π.

One early occurrence of pattern avoidance is the Erdős-Szekeres Theorem [9], which can be rephrased as follows: Let $I_a = 12\cdots a$ be the *increasing permutation* of length a and let $J_b = b(b-1)\cdots 1$ be the *decreasing permutation* of length b. Then $\mathcal{S}_k(I_a) \cap \mathcal{S}_k(J_b) = \emptyset$ if $k > (a-1)(b-1)$. The study of pattern-avoiding permutations in their own right was instigated by Knuth's work in *The Art of Computer Programming* [12] when he showed that a permutation $\pi \in \mathcal{S}_k$ is sortable after one pass through a stack if and only if $\pi \in \mathcal{S}_k(231)$. Pattern avoidance has also proven to be a useful language to describe inputs sortable through a variety of other machines. Generalizations of pattern avoidance have been used to characterize geometric properties of Schubert varieties. More recently, researchers have connected permutation patterns with results in genomics, statistical mechanics, and more.

Counting

Much of the existing literature in permutation patterns studies the quantity $s_k(\rho) = |\mathcal{S}_k(\rho)|$ for various patterns ρ. While the results in this section are

central ideas in permutation patterns research, they are not closely related to the final result of this paper. The reader interested in a connection to chemistry may wish to skip ahead to the section on pattern packing.

Starting with the simplest case, it is immediate that $s_k(1) = 0$ if $k \geq 1$ since each digit of a non-empty permutation is a copy of the pattern 1. We also have that $s_k(12) = s_k(21) = 1$ for $k \geq 0$, since the unique permutation of length k avoiding 12 (resp. 21) is J_k (resp. I_k).

The fact that $s_k(12) = s_k(21)$ is a special case of a more general phenomenon. If $s_k(\rho) = s_k(\rho^*)$ for all k, we say that ρ and ρ^* are *Wilf-equivalent*. A number of Wilf-equivalences are made clear by considering the plot of a permutation as in Figures 1 and 2. All points in the plot of π lie in the square $[1, k] \times [1, k]$, and thus we may apply various symmetries of the square to obtain involutions on the set $\mathcal{S}_k$. For $\pi \in \mathcal{S}_k$, we define $\pi^r = \pi_k \cdots \pi_1$ and $\pi^c = (k + 1 - \pi_1) \cdots (k + 1 - \pi_k)$, which are called the *reverse* and *complement* of π, respectively. Notice that the plot of π^r is obtained by reflecting the plot of π across the vertical line at $\frac{k+1}{2}$ and π^c is obtained by reflecting the plot of π across the horizontal line at $\frac{k+1}{2}$. We obtain one additional important equivalence by considering π^{-1} which reflects the plot of π over the line $y = x$. For example, the graphs of $\pi = 1342$, $\pi^r = 2431$, $\pi^c = 4213$, and $\pi^{-1} = 1423$ are shown in Figure 2. Notice that if π contains ρ, then π^r contains ρ^r, π^c contains ρ^c, and π^{-1} contains ρ^{-1}. Thus, these involutions on $\mathcal{S}_k$ also provide bijections between $\mathcal{S}_k(\rho)$, $\mathcal{S}_k(\rho^r)$, $\mathcal{S}_k(\rho^c)$, and $\mathcal{S}_k(\rho^{-1})$. As a consequence, for any pattern ρ, ρ is Wilf-equivalent to ρ^r, ρ^c, and ρ^{-1}. These Wilf-equivalences that follow from the action of the dihedral group on the plot of π are known as *trivial Wilf-equivalences*.

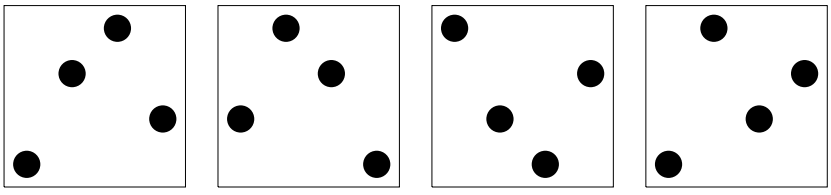


Figure 2: The plots of $\pi = 1342$, $\pi^r = 2431$, $\pi^c = 4213$, and $\pi^{-1} = 1423$

By trivial Wilf-equivalence, we have that $s_k(132) = s_k(213) = s_k(231) = s_k(312)$ and that $s_k(123) = s_k(321)$. In fact, it turns out that $s_k(\rho) = \frac{\binom{2k}{k}}{k+1}$

for $\rho \in \mathcal{S}_3$. Consider the case of $\mathrm{s}_k(132)$. We have $\mathrm{s}_0(132) = \mathrm{s}_1(132) = 1$. Now, consider $\pi \in \mathcal{S}_k(132)$ and suppose that $\pi_i = k$. For any π_a and π_b with $a < i < b$, it must be that $\pi_a > \pi_b$ otherwise $\pi_a k \pi_b$ would form a 132 pattern. Since $\pi_1 \cdots \pi_{i-1}$ and $\pi_{i+1} \cdots \pi_k$ must also avoid 132, this implies

$$\mathrm{s}_k(132) = \sum_{i=1}^{k} \mathrm{s}_{i-1}(132) \cdot \mathrm{s}_{k-i}(132).$$

It is easily checked that $\mathrm{s}_k(\rho) = \frac{\binom{2k}{k}}{k+1}$ satisfies this recurrence and matches the required initial values. Notice that $\mathrm{s}_k(\rho)$ is the kth Catalan number. Pattern-avoiding permutations are just one of many enumerative combinatorics contexts where the Catalan numbers appear; Stanley [16] has collected more than 200 occurrences of this celebrated sequence. There are also a number of bijections between $\mathcal{S}_k(123)$ and $\mathcal{S}_k(132)$ that preserve various statistics; see, for example, Bóna's text [7].

Although $\mathrm{s}_k(\rho)$ only depends on k and $|\rho|$ for patterns of length at most 3, the general case is more complicated. It is known that if $\rho \in \mathcal{S}_4$, then ρ is Wilf-equivalent to 1342, 1234, or 1324, but $\mathrm{s}_k(1342)$, $\mathrm{s}_k(1234)$, and $\mathrm{s}_k(1324)$ are three distinct values for sufficiently large k. Bóna [6] showed the sequence $\mathrm{s}_k(1342)$ has a nonrational algebraic generating function. Gessel [10] showed the sequence $\mathrm{s}_k(1234)$ has a nonalgebraic holonomic generating function. However, there is no known general formula for $\mathrm{s}_k(1324)$, and better understanding the structure of $\mathcal{S}_k(1324)$ for large k is an ongoing active area of research.

The patterns we have discussed thus far are known as *classical* permutation patterns. A number of variations have been considered including consecutive patterns (where digits of ρ must appear in adjacent positions of π), vincular patterns (a hybrid between classical and consecutive patterns), and bivincular patterns (which also place restrictions on the relative sizes of the digits forming a copy of ρ, not just on their positions). Barred patterns, where π avoids ρ unless ρ is part of a larger specified pattern in π, have proved useful in characterizing permutations sortable after repeated passes through a stack and in describing geometric properties of Schubert varieties. Other types of enumeration questions are also of interest. Researchers have enumerated pattern-avoiding words, set partitions, integer partitions, lattice paths, and other combinatorial objects with appropriate definitions of patterns. Pattern avoidance itself is really a special case of the more general

question of studying

$$\mathcal{S}_{k,c}(\rho) = \{\pi \in \mathcal{S}_k \mid \pi \text{ contains } c \text{ copies of } \rho\}.$$

Thus far, we have focused on the situation when $c = 0$. For some specific patterns ρ, $|\mathcal{S}_{k,c}(\rho)|$ is known for $c \geq 1$, but in general, the pattern containment question is hard. The literature on pattern-avoiding permutations is vast, but in the remainder of this paper we focus on pattern packing. In other words, given a pattern ρ, we consider the maximum value of c (given as a function of k) for which $\mathcal{S}_{k,c}(\rho)$ is non-empty.

Packing

In this section, we consider the maximum number of copies of ρ that can occur in a permutation of length k. Let $\nu(\rho, \pi)$ be the *number of occurrences* of ρ in π. If we wish to determine $\max_{\pi \in \mathcal{S}_k} \nu(\rho, \pi)$, it is advantageous to report the percentage of copies of ρ out of all subsequences of length $|\rho|$ in π rather than just the number of copies.

Definition. *The* packing density *of ρ, denoted $d(\rho)$, is given by*

$$d(\rho) = \lim_{k \to \infty} \frac{\max_{\pi \in \mathcal{S}_k} \nu(\rho, \pi)}{\binom{k}{|\rho|}}.$$

In this rest of this section, we survey the packing literature. However, for our final connection to physical chemistry, we care about packing into a specific kind of permutation that is addressed in the next section. The reader interested more in this chemistry connection than in pattern packing in general may read the definition of *sum* below and then skip ahead to the section on alternating permutations.

The most straightforward pattern of length a to pack is the monotone increasing pattern. We have that $d(I_a) = 1$ since every subsequence of I_k of length a is a copy of I_a. For more general patterns, it may not initially be clear that $d(\rho)$ exists, but an unpublished argument of Fred Galvin (described by Price in [15]) shows that $\frac{\max_{\pi \in \mathcal{S}_k} \nu(\rho, \pi)}{\binom{k}{|\rho|}}$ is nonincreasing for $k \geq |\rho|$. Since this sequence is also clearly bounded below by 0, it converges.

The main other type of permutation pattern for which we can say something about $d(\rho)$ is that of *layered* patterns.

Definition. *The* sum *of permutations* $\alpha = \alpha_1 \cdots \alpha_a$ *and* $\beta = \beta_1 \cdots \beta_b$*, denoted* $\alpha \oplus \beta$*, is given by*

$$\alpha \oplus \beta = \begin{cases} \alpha_i & 1 \leq i \leq a, \\ a + \beta_{i-a} & a+1 \leq i \leq a+b. \end{cases}$$

Definition. *A permutation is* layered *if it can be written in the form* $J_{a_1} \oplus J_{a_2} \oplus \cdots \oplus J_{a_p}$ *for positive integers* $a_1, \ldots, a_p$*.*

The permutation shown in Figure 3 is an example of a layered permutation since it is of the form $J_1 \oplus J_2 \oplus J_2 \oplus J_2 \oplus J_1$. However, the simplest non-trivial layered permutation pattern is $132 = J_1 \oplus J_2$. Stromquist [17] showed that if ρ is layered, then $\frac{\max_{\pi \in \mathcal{S}_k} \nu(\rho,\pi)}{\binom{l}{|\rho|}}$ is achieved by a layered π. Stromquist and later Barton [4] showed that $d(132) = 2\sqrt{3} - 3 \approx 0.464$ by focusing on layered $\pi \in \mathcal{S}_k$ and showing that $\frac{\max_{\pi \in \mathcal{S}_k} \nu(\rho,\pi)}{\binom{k}{|\rho|}}$ is achieved when the top layer is of size $a \approx \left(\frac{3-\sqrt{3}}{2}\right) k$ and the remaining entries are filled in recursively with an optimal 132-packing layered permutation of length $k-a$.

For patterns of length 4, Price [15] showed that $d(1432)$ is given by the real root of $x^3 - 12x^2 + 156x - 64$ and that $d(2143) = \frac{3}{8}$. Later, Albert et. al. [1] showed that $d(1243) = \frac{3}{8}$. Bounds on $d(1324)$, $d(1342)$, and $d(2413)$ are known but have not yet been proved to be sharp. In the case of 1324, this illustrates that even if a pattern is layered, that does not imply the packing density is straightforward to determine. A variety of additional packing literature exists, both packing patterns into permutations and into words (i.e. permutations with repeated digits) [5, 8, 11, 18, 19, 20], but in general packing problems have seen slower progress than pattern avoidance problems.

Packing in Alternating Permutations

Rather than focusing on packing in all permutations, in the rest of this paper we will focus on packing patterns into permutations with extra restrictions. This family of packing problems will provide a new link between permutations and physical chemistry.

Definition. *Permutation* π *is an* alternating *permutation if*

$$\pi_1 < \pi_2 > \pi_3 < \pi_4 \cdots .$$

Alternating permutations are also known as zig-zag permutations or up-down permutations. They were first studied by André [2, 3] in the nineteenth century. Let $\mathcal{A}_k$ be the set of alternating permutations of length k. André proved the surprising result that

$$\sum_{k=0}^{\infty} \frac{|\mathcal{A}_k|\, x^k}{k!} = \sec(x) + \tan(x),$$

giving a natural combinatorial interpretation to a series expansion of trigonometric functions.

Now, instead of the classical definition of packing density above, we consider the following modification.

Definition. *The* alternating packing density *of ρ, denoted $d_A(\rho)$, is*

$$d_A(\rho) = \lim_{k\to\infty} \frac{\max_{\pi\in\mathcal{A}_k} \nu(\rho,\pi)}{\binom{k}{|\rho|}}.$$

Although it is not necessary for the upcoming chemistry result, the interested reader may wish to compare $d_A(\rho)$ to the classical packing density $d(\rho)$ introduced in the previous section. We know $d(\rho)$ exists because $\frac{\max_{\pi\in\mathcal{S}_k} \nu(\rho,\pi)}{\binom{k}{|\rho|}}$ is nonincreasing in k. However, this is no longer the case for $\frac{\max_{\pi\in\mathcal{A}_k} \nu(\rho,\pi)}{\binom{k}{|\rho|}}$ when we restrict our attention to alternating permutations. If $d_A(\rho)$ exists, we immediately have that $d_A(\rho) \leq d(\rho)$ for any pattern ρ since $\mathcal{A}_k \subseteq \mathcal{S}_k$. Strikingly, it turns out that $d_A(\rho) = d(\rho)$ for any pattern ρ. Since $d(\rho)$ exists, we may construct a sequence of permutations with $\tau_k \in \mathcal{S}_k$ such that $\lim_{k\to\infty} \frac{\nu(\rho,\tau_k)}{\binom{k}{|\rho|}} = d(\rho)$. The proof that $d_A(\rho) = d(\rho)$ relies on a construction that replaces each point in the plot of τ_k with an alternating permutation to produce a sequence of alternating permutations σ_k with $\lim_{k\to\infty} \frac{\nu(\rho,\sigma_k)}{\binom{k}{|\rho|}} = d(\rho)$ as well.

To see the connection with physical chemistry, the last problem we will consider is packing I_a into an alternating permutation of length k. We already know the optimal way to pack I_a into an arbitrary permutation of length k is to pack it into I_k, where every subsequence of length a is a copy of I_a.

However, $I_k \notin \mathcal{A}_k$. To address this, we construct the alternating permutation $\widehat{I_k}$ defined as

$$\widehat{I_n} = \begin{cases} J_1 \oplus \underbrace{J_2 \oplus \cdots \oplus J_2}_{\frac{k}{2}-1 \text{ times}} \oplus J_1 & k \text{ even}, \\ J_1 \oplus \underbrace{J_2 \oplus \cdots \oplus J_2}_{\frac{k-1}{2} \text{ times}} & k \text{ odd}. \end{cases}$$

As an example, the plot of $\widehat{I_8}$ is given in Figure 3.

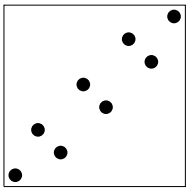


Figure 3: The plot of $\widehat{I_8}$

Although $\dfrac{\nu(I_a, \widehat{I_k})}{\binom{k}{a}} < 1$ for specific values of k, we claim that $\widehat{I_k}$ is the construction that proves $d_A(I_a) = 1$. For the case where we pack $I_3 = 123$ into $\pi = \widehat{I_k}$ notice that every subsequence of length three still forms a 123 pattern unless two digits of the subsequence come from the same layer of $\widehat{I_k}$. While there are $\binom{k}{3}$ total subsequences of length 3 in $\widehat{I_k}$, there are less than $2\binom{k}{2}$ subsequences with two digits from the same layer of $\widehat{I_k}$. Therefore $\nu(I_3, \widehat{I_k}) \geq \binom{k}{3} - 2\binom{k}{2}$ and in the limit,

$$1 \geq d_A(123) \geq \lim_{k\to\infty} \frac{\binom{k}{3} - 2\binom{k}{2}}{\binom{k}{3}} = \lim_{k\to\infty} \frac{k-8}{k-2} = 1.$$

Since a length 3 subsequence of $\widehat{I_k}$ only fails to be a 123 pattern when it uses adjacent digits that were required to be in decreasing order by the definition of alternating permutation, $\widehat{I_k}$ is, in fact, the alternating permutation of length k with the maximum number of copies of 123. Finding the exact value of $\nu(123, \widehat{I_k})$ is a straightforward exercise in cases. We have:

Theorem. *The maximum number of copies of 123 in an alternating permu-*

tation of length k is given by

$$\nu(123, \widehat{I_k}) = \begin{cases} \frac{(k-2)(k^2-4k+6)}{6} & k \text{ even}, \\ \frac{(k-1)(k-2)(k-3)}{6} & k \text{ odd}. \end{cases}$$

Proof. In the case when k is even, there are $\frac{k}{2} - 1$ layers of size 2 and two layers of size 1 in $\widehat{I_k}$. A copy of 123 can be formed by using both, one, or neither layer of size 1. If we use both layers of size 1, it remains to choose a layer of size 2 and then choose one point from the layer to complete the 123 pattern. If we use one layer of size 1, we must first choose the layer of size 1, then choose two of the layers of size 2 and choose one point from each of those layers. If we use no layers of size 1, then we need to choose three distinct layers of size 2 and then choose one point from each of those layers. Therefore, there are

$$2\left(\frac{k}{2} - 1\right) + 8\binom{\frac{k}{2} - 1}{2} + 8\binom{\frac{k}{2} - 1}{3} = \frac{(k-2)(k^2-4k+6)}{6}$$

copies of 123 in $\widehat{I_k}$ when k is even.

The odd case is similar, with the adjustment that there are now $\frac{k-1}{2}$ layers of size 2 and one layer of size 1 in $\widehat{I_k}$. There are $4\binom{\frac{k-1}{2}}{2}$ ways to construct a 123 pattern using the initial layer of size 1 and two layers of size 2. Otherwise, we must pick three distinct layers of size 2 and then choose one point from each of those layers. Therefore, there are

$$4\binom{\frac{k-1}{2}}{2} + 8\binom{\frac{k-1}{2}}{3} = \frac{(k-1)(k-2)(k-3)}{6}$$

copies of 123 in $\widehat{I_k}$ when k is odd. □

k	4	5	6	7	8	9	10
$\nu(123, \widehat{I_k})$	2	4	12	20	38	56	88

Table 1: Values of $\nu(123, \widehat{I_k})$ for $4 \leq k \leq 10$

While this argument is not complicated, the numbers themselves are interesting. Table 1 gives the values of $\nu(123, \widehat{I_k})$ for $4 \leq k \leq 10$. This is

sequence A168380 in the On-Line Encyclopedia of Integer Sequences [14]. However, the primary description is perhaps surprising: this is the sequence of atomic numbers of the alkaline earth metals of the periodic table. For emphasis, see Figure 4. The values of $\nu(123, \widehat{I_k})$ correspond to the atomic numbers in the second column, labeled as Group "2 - IIA". In other words, the quasi-polynomial sequence $2, 4, 12, 20, 38, 56, 88, \ldots$ not only gives values of $\nu(123, \widehat{I_k})$; it also gives the atomic numbers of helium, beryllium, magnesium, calcium, and more. This is unexpected! Although permutation patterns appear in a wide variety of contexts, a connection to physical chemistry is novel and quite different from other more abstract appearances of patterns. In the rest of this paper we give a bijective proof connecting our pattern packing problem to the language of physical chemistry.

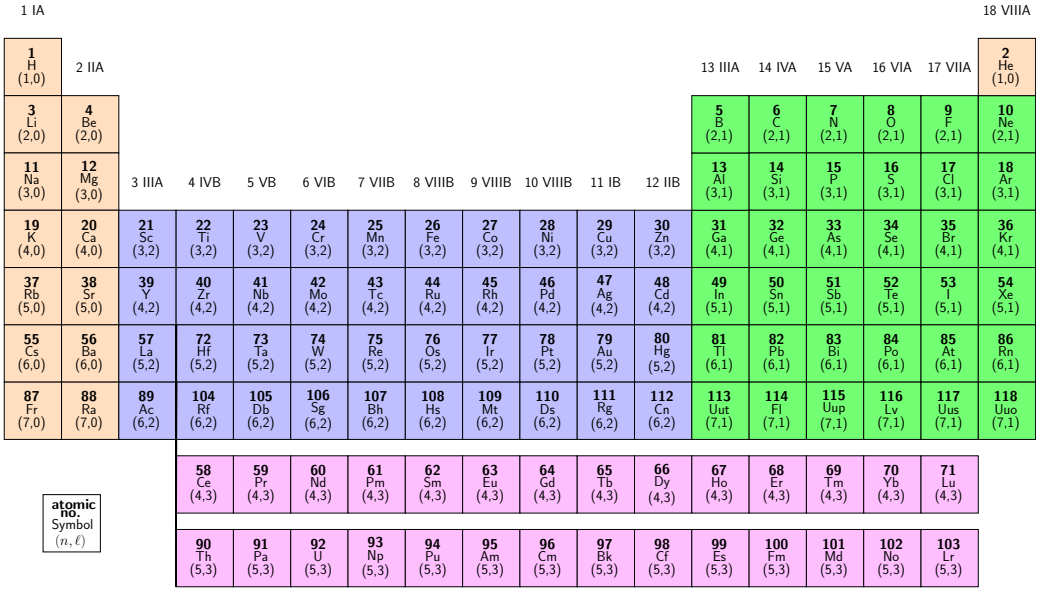


Figure 4: The periodic table of chemical elements

Physical Chemistry

In the periodic table, the atomic number of an element is the number of protons in an atom of that element. While various ions exist, the atomic

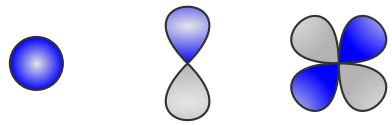
number also gives the number of electrons in a neutral atom. In Schrödinger's model, electrons move in space about the atom's nucleus, and Schrödinger's wave equation is used to predict possible electron orbitals, that is, the regions where electrons are most likely to be found. In three dimensional space, three variables are required to describe the size, shape, and orientation of an orbital. These are the principal quantum number (n), the angular quantum number (ℓ), and the magnetic quantum number (m). More details can be found in any standard chemistry book such as [13].

The principal quantum number n corresponds to the size of an electron orbital. n is given as a positive integer, and larger values of n correspond to larger orbitals. All orbitals that have the same principal quantum number are said to be in the same shell of the atom.

The angular quantum number ℓ gives the shape of an orbital. While multiple electrons may be in the same shell, the angular quantum number partitions the orbitals of a shell into subshells. Larger values of n allow more room for different shapes of subshells. Given n, ℓ is an integer with $0 \leq \ell \leq n-1$. The shapes of orbitals for small values of ℓ are shown in Figure 5. To determine the (n, ℓ) pairs that describe subshells in a particular atom, consider the coloring of the periodic table given in Figure 4. Each color corresponds to an ℓ value. Since $\ell \leq n-1$, the first elements with a particular ℓ value have principle number $n = \ell + 1$. Subsequent rows of elements with a particular ℓ value increment n by 1. This gives a straightforward mapping from an element to one (n, ℓ) pair. Any (n, ℓ) pair that corresponds to an element with a smaller atomic number is also possible in the original element. For example, calcium (atomic number 20) is shaded as $\ell = 0$. This is the fourth row of $\ell = 0$ orbitals. Therefore, calcium has orbitals with $(n, \ell) = (4, 0)$. However, looking at the elements with smaller atomic numbers, we see calcium also has orbitals with $(n, \ell) \in \{(1, 0), (2, 0), (2, 1), (3, 0), (3, 1)\}$. Notice that $(n, \ell) = (3, 2)$ first occurs in scandium (atomic number 21), so calcium has no $(n, \ell) = (3, 2)$ subshell.

Although there is only one way to orient an $\ell = 0$ (spherical) orbital around an atom's nucleus, subshells with $\ell \geq 1$ can be oriented in multiple ways. The magnetic quantum number m describes an orbital's orientation in space. Given n and ℓ, m is reported as an integer such that $-\ell \leq m \leq \ell$. For example, a polar ($\ell = 1$) orbital has three possible orientations, i.e. $m = -1$, $m = 0$, and $m = 1$, which could be thought of orienting this orbital shape along the x-axis, y-axis, or z-axis in space.

Finally, there is a fourth quantum number that is independent of the



$\ell = 0$ $\ell = 1$ $\ell = 2$

Figure 5: Simple electron orbital shapes

other three called the spin quantum number (s). For any valid combination of (n, ℓ, m), there are two possible spins for an electron.

In summary, in Schrödinger's model of the atom, pairs of electrons are in bijection with tuples of integers (n, ℓ, m) such that $n \geq 1$, $0 \leq \ell \leq n - 1$ and $|m| \leq \ell$. However, knowing the highest n-value that appears in a particular atom does not mean that all (n, ℓ, m) tuples following these inequalities appear. Observe that in the periodic table there are always two shells with orbitals of shape ℓ before orbitals with shape $\ell + 1$ are introduced.

The Bijection

Consider $\widehat{I_k} = J_1 \oplus J_2 \oplus \cdots$. We wish to connect copies of 123 in $\widehat{I_k}$ to valid tuples (n, ℓ, m, s) of quantum numbers for electrons in alkaline earth metals.

First, we address the spin number, s. Just as there are two spin numbers for any valid (n, ℓ, m) tuple, observe that copies of 123 in $\widehat{I_k}$ come in pairs. In particular if $\pi_a \pi_b \pi_c$ form a 123 pattern in $\pi = \widehat{I_k}$, then π_a, π_b, and π_c must come from different layers of π. Let π_b' be the other digit in the same layer as π_b. Then $\pi_a \pi_b' \pi_c$ is a second 123 pattern in $\widehat{I_k}$. Two copies of 123 that use the same layer of $\widehat{I_k}$ for the second digit correspond to pairs of electrons that have the same principal (n), angular (ℓ), and magnetic (m) quantum numbers but different spin numbers.

Now, for the remaining quantum numbers, m encodes the value of the "1" in a 123 pattern, ℓ encodes the layer of the "2", and n encodes the value of the "3". To be more precise, call the initial J_1 layer of $\widehat{I_k}$ layer 0, and enumerate the remaining layers starting with layer 1. A copy $\pi_a \pi_b \pi_c$ of 123 in $\pi = \widehat{I_k}$ maps to a tuple of integers in the following way: $\widehat{m}$ is the layer of

$\widehat{I}_k$ where π_a is found. Then

$$m = \begin{cases} -\widehat{m} & \pi_a \text{ is the smaller entry of layer } m, \\ \widehat{m} & \pi_a \text{ is the larger entry of layer } m. \end{cases}$$

$\ell+1$ is the layer of $\widehat{I}_k$ where π_b is found. Finally, given ℓ and π_c, we compute $n = \pi_c - \ell - 3$; intuitively, larger values of n correspond to a larger gap between the location of π_b and π_c in $\widehat{I}_k$, but with an appropriate offset to ensure n is positive.

As an example, consider copies of 123 in $\widehat{I}_7 = J_1 \oplus J_2 \oplus J_2 \oplus J_2 = 1325476$. There are 20 copies of 123 in $\widehat{I}_7$, and these 20 copies correspond to the 20 electrons in an atom of calcium. Just as copies of 123 come in pairs, electrons in calcium come in 10 pairs that correspond to 10 different tuples of quantum numbers (n, ℓ, m). The 20 copies of 123 in $\widehat{I}_7$ are given in pairs with their corresponding (n, ℓ, m) tuples in Table 2. For instance, both 246 and 256 are copies of 123 in $\widehat{I}_7$. Both have their initial element in layer 1, so both correspond to $\widehat{m} = 1$. Since 2 is the smaller digit in this layer, we have $m = -1$. We see that in both copies π_j comes from layer 2, so $\ell + 1 = 2$, i.e., $\ell = 1$. Finally, $n = 6 - 1 - 3 = 2$. So these two copies correspond to the tuple $(2, 1, -1)$. The tuples corresponding to other (pairs of) copies of 123 may be verified similarly. Layers of $\widehat{I}_7$ are highlighted in different colors for easy reference throughout Table 2.

copies	tuple	copies	tuple	copies	tuple
124,134	(1,0,0)	146,156	(2,1,0)	147,157	(3,1,0)
125,135	(2,0,0)	246,256	(2,1,-1)	247,257	(3,1,-1)
126,136	(3,0,0)	346,356	(2,1,1)	347,357	(3,1,1)
127,137	(4,0,0)				

Table 2: Copies of 123 in $\widehat{I}_7 = 1325476$, which correspond to tuples (n, ℓ, m) of quantum numbers for the 20 electrons in an atom of calcium

We still must show that this mapping of pairs of occurrences of 123 in $\widehat{I}_k$ to integer tuples obeys the inequalities that determine valid quantum numbers.

First, by construction, layer 0 of $\widehat{I}_k$ contains the digit 1, while for $L \leq \frac{k-1}{2}$, layer L contains the digits $2L$ and $2L+1$. When k is even, layer $\frac{k}{2}$ contains the digit k.

Consider the occurrence $\pi_a\pi_b\pi_c$ of 123 in $\widehat{I_k}$. Since π_b comes from layer $\ell+1$, we know $\ell \geq 0$ and π_c comes from layer $\ell+2$ or higher. This implies $\pi_c \geq 2(\ell+2)$. Together with the fact that $n = \pi_c - \ell - 3$, we have $n \geq 2(\ell+2)-\ell-3 = \ell+1 \geq 1$. $n \geq \ell+1$ also implies $\ell \leq n-1$. Finally, since $|m|$ denotes the layer of π_a and $\ell+1$ denotes the layer of π_b, we have $|m|+1 \leq \ell+1$, or $|m| \leq \ell$, as desired. These are exactly the restrictions on quantum numbers discussed earlier! Notice that a new ℓ value is introduced for each even value of k since $\widehat{I_{2i}}$ has one more layer than $\widehat{I_{2i-1}}$. This corresponds exactly to the frequency with which new subshell shapes are introduced in the periodic table.

Conclusion

This connection between pattern packing and physical chemistry is striking even to long-time permutation patterns researchers. Similarly, the quasi-polynomial sequence obtained for $\nu(123, \widehat{I_k})$ had no previous interpretation in the literature other than as a sequence of atomic numbers. What, if any, chemical interpretation is there for $\nu(123, \widehat{I_k})$ when $k > 10$? What other chemical or physical structures can be described in terms of pattern packing or pattern avoidance? Are there other combinatorial structures that give alternate ways to generate the sequences of atomic numbers of particular groups of chemical elements? The variety of applications of permutation patterns has grown tremendously in recent decades, and modeling electron orbitals can now be added to the list.

References

[1] M. H. Albert, M. D. Atkinson, C. C. Handley, D. A. Holton, and W. Stromquist, On packing densities of permutations, *Electron. J. Combin.* **9** (2002), R5.

[2] D. André, Developpments de sec x et de tan x. *Comptes Rendus Acad. Sci. Paris* **88** (1879), 965–967.

[3] D. André, Mèmoire sur les permutations alterneées, *J. Math.* **7** (1881), 167–184.

[4] R. Barton, Packing Densities of Patterns, *Electron. J. Combin.* **11** (2004), R80.

[5] C. Battiste Presutti and W. Stromquist, Packing rates of measures and a conjecture for the packing density of 2413, in Permutation Patterns (2010), S. Linton, N. Ruskuc, and V. Vatter, Eds., vol. 376 of London Mathematical Society Lecture Note Series, Cambridge University Press, pp. 287–316.

[6] M. Bóna, Exact enumeration of 1342-avoiding permutations: a close link with labeled trees and planar maps, *J. Combin. Theory Ser. A* **80 (2)** (1997), 257–272.

[7] M. Bóna, *Combinatorics of Permutations*, Chapman & Hall, 2004.

[8] A. Burstein, P. Hästö, T. Mansour, Packing patterns into words, *Electron. J. Combin.* **9.2** (2003), R20.

[9] Erdős and G. Szekeres, A combinatorial problem in geometry, *Compositio Mathematica*, **2** (1935), 463–470.

[10] I. Gessel, Symmetric functions and P-recursiveness, *J. Combin. Theory Ser. A* **53 (2)** (1990), 257–285.

[11] P. A. Hästö, The packing density of other layered patterns, *Electron. J. Combin.* **9.2** (2003), R1.

[12] D. Knuth, *The Art of Computer Programming: Volume 1*, Addison-Wesley, 1968.

[13] G. Miessler and D. Tarr, *Inorganic Chemistry*, 2nd edition, Prentice Hall, 1998.

[14] OEIS Foundation Inc. (2019), The On-Line Encyclopedia of Integer Sequences, `http://oeis.org/A168380`.

[15] A. Price, Packing densities of layered patterns, Ph.D. thesis, University of Pennsylvania, 1997.

[16] R. Stanley, *Catalan Numbers*, Cambridge University Press, 2015.

[17] W. Stromquist, Packing layered posets into posets, preprint, 1993. Available at `http://walterstromquist.com/publications.html`.

[18] D. Warren, Optimal Packing Behavior of Some 2-Block Patterns, *Ann. Comb.* **8.3** (2004), 355–367.

[19] D. Warren, Optimizing the packing behavior of layered permutation patterns, Ph.D. thesis, University of Florida, 2005.

[20] D. Warren, Packing densities of more 2-block patterns, *Adv. Appl. Math.* **36.2** (2006), 202–211.