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Note

Information Theory in Describing the Electronic Structures of Atoms

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An information approach to the description of atoms by introducing »differential« entropy characteristics of chemical elements has been developed. These quantities clearly reflect the horizontal and vertical structure of the periodic table, and the main features of atomic electron structures, such as delay in filling d- and f-subshells, the action of Hund's first rule, the anomalies in the electronic structure of some atoms, the appearance of the first electron having a given value of some quantum number, etc. The necessity of change in the position of lanthanides and actinides in the periodic table is discussed.

INTRODUCTION

The concept of information as a quantity related to entropy appeared first in 1894. Boltzmann¹ stated that every piece of information obtained for a physical system is related to the decrease in number of its possible states: therefore, the increase of entropy means »loss of information«. In 1929, Szillard² developed this idea for the general case of information in physics. In 1932, von Neumann³ made use of the concept of information in quantum mechanics and atomic physics. In 1948, Shannon⁴ published his fundamental work on information theory. Arising as »a special theory of communications«, this theory soon exceeded its initial limits and found application in a number of scientific and technical areas.

Wiener's work⁵ on the role of information stimulated the application of information theory in biology and physiology. Some important problems of conservation, processing and transmission of information in living beings were solved, such as coding of genetic information⁶, estimation of the possibility of a spontaneous selfgeneration of life on earth⁷, formulation of the fundamental laws of biological thermodynamics⁸, analysis of the problems of bioenergetics⁹, etc.

Information theory is still of limited application in chemistry and physics, but progress has been made in this field in recent years. A number of methods for determining the information content of molecules¹⁰⁻¹³ were suggested. The problem of eventual existence of information balance in chemical reactions was examined¹⁴. An estimate of the information capacity of bioorganic molecules was also made¹⁵.

In analytical chemistry, information theory was applied to minimize errors and analytical time, to achieve higher selectivity, to estimate the efficiency of analytical methods, etc.¹⁶⁻¹⁹. The formation and growth of crystals was considered as an information process²⁰. Optimum information conditions for characterization and prediction of catalyst properties were found²¹⁻²³.

Levine and Bernstein et al.²⁴⁻²⁷ developed an information-theoretic approach to molecular dynamics which describes the behaviour of the systems far from equilibrium. The key to this approach is the concept of surprisal, the deviation from expectation on the basis of microcanonical equilibrium. This approach found various applications including the determination of branching ratios for competing reaction paths, the study of the operational characteristics of lasers, etc.

Daudel and coworkers²⁸⁻³¹ suggested the partitioning of the space of a molecular system into a number of mutually exclusive spaces called loges. The minimization of the information function was used to find most suitable loges, i. e. those which contained localized groups of electrons.

The examples of the successful application of information theory in chemistry and physics indicate an important tendency in contemporary science. Besides their substantial and energetic essence, the systems in nature and technics also have an information side. The concept of information seems to be no less general than that of matter and energy. This assertion follows from some of the classical definitions of information as »neither matter, nor energy«⁵, »a measure of the variety in a given system«³², »a measure of the non-homogeneity in distribution of matter or energy into space and time«³³, etc.

These definitions represent a sufficient basis for applying information theory to molecules and atoms. In this case one can speak of »structural information«, or »information content« or more precisely, entropy of probability distribution of electrons in atoms and molecules. This quantity is capable of characterizing all details in a given structure, as well as of correlating with the basic atomic and molecular properties. Such an information approach could also be considered as a universal language for describing systems. Even if this approach represents only a translation of known facts into a new convenient language, it allows us to infer useful analogies or common laws among systems of different nature. In such a way one might attempt, for instance, to find analogies in biology to the known chemical or physical laws. Another example is the attempt to find an information analogy between chemical elements and atomic nuclei³⁴. On this basis, studies of a new systematics of nuclides are in progress. However, the information approach is not simply a translation from one language into another; it provides an additional insight into systems and phenomena, allowing new results to be obtained. Thus, the Pauli principle and Hund's first rule were found to require the maximum information content of atoms and molecules. They appear, unexpectedly to be related to the Second Law of Thermodynamics, or more precisely, to a principle close to but not identical with the Second Law in its present form³⁵.

SOME REMARKS ON THE INFORMATION APPROACH

The aim of this work is to give an outline of an information approach to the description of atoms of chemical elements. The basis of this approach is Shannon's equation⁴

$$\bar{I} = - \sum p_i \cdot \log_2 p_i \tag{1}$$

Let us consider a system of arbitrary nature consisting of N elements. Making use of a certain criterion, the set of N elements can be partitioned into different subsets. Let a given criterion be chosen and k subsets be formed, having N_1, N_2, \dots, N_k elements, respectively. A finite probability scheme of the set can be constructed specifying a definite probability $p_i = N_i/N$ for a randomly chosen element to be in the i-th subset. Then \bar{I} will denote the mean entropy of probability distribution of elements under consideration, in bits per element (this quantity is often called the mean information content of the system).

Consider now an atom having z electrons which are partitioned into k-subsets, z_1, z_2, \dots, z_k , respectively. In such a way the average entropy of probability distribution of electrons over subsets can be defined in bits per electron:

$$\bar{I} = - \sum_{i=1}^k \frac{z_i}{z} \cdot \log_2 \frac{z_i}{z} \tag{2}$$

Using an equation derived from (2),³⁶:

$$I = z \cdot \bar{I} = z \cdot \log_2 z - \sum_{i=1}^k z_i \cdot \log_2 z_i \tag{3}$$

the total entropy of probability distribution of electrons in the atom, called the atomic information content, can also be calculated in bits.

In exposing the essence of the information approach to the electronic structure of atoms, the most important criteria for grouping of electrons must be specified. Using the one-electron approximation, we accepted as criteria the different atomic quantum numbers and some of their combinations. In this way the following subsets in the electronic structure of atoms were taken³⁷ into consideration: 1. electron shells, 2. subshells, 3. atomic orbitals, 4. spin-orbitals, 5. (nlj)-subshells, as well as groups of electrons having the same value of a given quantum number; i. e. 6. principal (n), 7. angular momentum (l) 8. magnetic (m), 9. magnetic spin (m_s), 10 inner (j), and 11. total magnetic (m_j).

The method can be developed further by introducing the so-called »differential entropy characteristics«. These are quantities expressing the increase in the entropy of electron distribution of an atom of a chemical element in comparison with an atom of an element whose atomic number is smaller by one:

$$\Delta I_x = I_x^z - I_x^{z-1}, \text{ bits/atom} \tag{4}$$

Here, the index x represents a definite set of quantum numbers expressing the manner of electron grouping in the atom. The differential information is a sensitive quantity which is capable of reflecting even the smallest details of the electronic structure of atoms.

The filling of a given electron subset (shell, subshell, etc.) begins and ends most frequently at a constant population of the preceding subsets. Then eq 4 will be transformed to:

$$\begin{aligned} \Delta I_x = z \cdot \log_2 z - (z-1) \cdot \log_2 (z-1) - (z_{k+1} \cdot \log_2 z_{k+1} - \\ - z'_{k+1} \cdot \log_2 z'_{k+1}) \end{aligned} \tag{5}$$

Obviously, the differential entropy will have a maximum value in every element in which the formation of a new subset begins ($z_{k+1} = 1, z'_{k+1} = 0$). ΔI will decrease regularly with increasing number of electrons in this subset and will have a minimum value when the subset is filled with a maximum number of electrons. In this way, the differential entropy characteristics could be used as a convenient language for describing the electronic structures of chemical elements, and the various forms of periodicity displayed in them.

DISCUSSION

Let us examine some of the diverse atomic entropy characteristics of chemical elements.

According to eq 6, the entropy function ΔI_n will reach a maximum in the initial element of every period in the periodic table since it is in this element that the populating of a new electron shell begins (Figure 1). An entropy curve common to the second and third period is obtained. Its shape is the same as that of the curve for a given period, ending in a minimum in the corresponding noble gas. In the subsequent periods the entropy curve of every period divides into different, s, p, d and f parts. At this, an inequality is valid:

$$\Delta I_n^s > \Delta I_n^p > \Delta I_n^d > \Delta I_n^f \quad (7)$$

As the type of valence electrons determines the grouping of chemical elements into main, secondary and tertiary (lanthanides, actinides) groups, one may also conclude that the entropy of probability distribution of electrons over shells, ΔI_n is capable of reflecting correctly the horizontal and vertical structure of the periodic table. In fact, the elements of each main or secondary group can be connected in Figure 1 in a common curve, to which a group entropy equation corresponds. The periodicity of atoms does not arise from some information theoretical conditions but is well reflected in the functions used.

The differential entropy of probability distribution of electrons over shells reflects not only the delay in filling f- and d-subshells but also such features of the electronic structure of atoms as the cases of $ns \rightarrow (n-1)d$ and $(n-2)f \rightarrow (n-1)d$ electron transitions. These anomalies lead to a smaller increase of

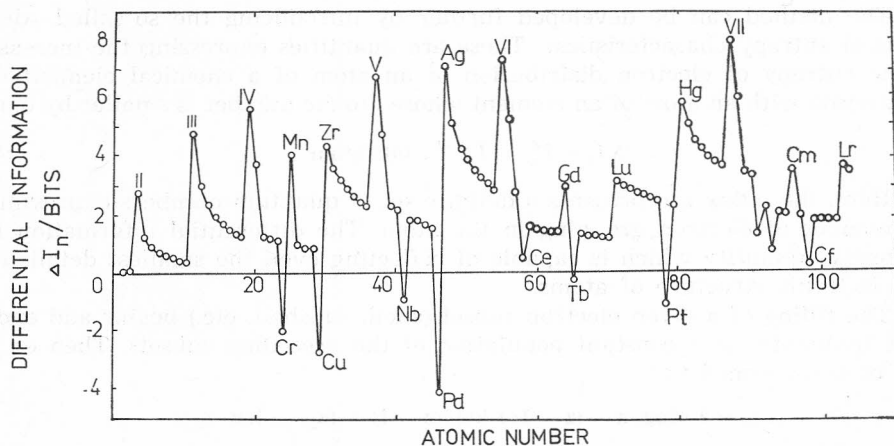


Figure 1.

entropy function and to deeper minima in Figure 1 at $ns \rightarrow (n-1)d$ transitions, since in these cases the electron drops from an outer into an inner shell (Cr, Cu, Nb, Pd, Pt). The restoration of the normal electron configuration, taking place in the subsequent chemical element, sharply increases the entropy index (Mn, Zn, Ag, Hg). When the anomalous transition of an electron continues in the subsequent elements, medium values of ΔI_n are obtained which coincide with the normal electron configuration of elements, (Mo, Tc, Ru, Rh, Au). The dependence is exactly opposite at $(n-2)f \rightarrow (n-1)d$ electron transitions. There are maxima in elements with an anomalous structure (La, Gd, Ac, Th, Cm) and minima at the restoration of the normal structure (Tb, Pa, Nb, Cf), and again medium values are obtained when the anomaly continues to occur in the subsequent element (U, Bk).

The regularity in reflecting the beginning and end of electron shells and subshells by maximum and minimum values of ΔI respectively, established by eq 5 and Figure 1, allows us to express our opinion on the controversial question where the 4f- and 5f- elements begin and end. In the literature³⁸, the view prevails that lanthanides begin at N58, Ce and end with N71, Lu, and, by analogy, for actinides — from N90, Th, to N103, Lw. Our data indicate a maximum instead of a minimum value of ΔI_n in Lu and Lr; therefore, Lu and Lr should be considered as initial elements in a new subshell (5d or 6d), but not as the last elements in another subshell (4f or 5f). By analogy, lanthanides and actinides should end in Yb and No, respectively (N70 and 102), with the entropy function reaching a minimum. These results agree with Villar's suggestion³⁹ on lanthanides and actinides. The presence of a d^1 - instead of an f^1 -electron configuration in the initial element of these series (La and Ac) can be explained by $(n-2)f \rightarrow (n-1)d$ electron transition in analogy with other elements of these series (Gd, Cm, etc.). This view is additionally supported by the presence of a minimum of ΔI_n at Ce and Pa (Figure 1), indicating a restoration of the normal electron configuration, violated by an $f \rightarrow d$ electron transition in La, Ac and Th.

The differential entropy of probability distribution of electrons over subshells, ΔI_{nl} , is a function of the atomic number Z (Figure 2), similarly to ΔI_n . This includes both the grouping of elements into periods and groups and the reflecting of anomalies in atomic electron structure. Again, every period begins with a maximum of the corresponding ns -level and ends with a minimum of

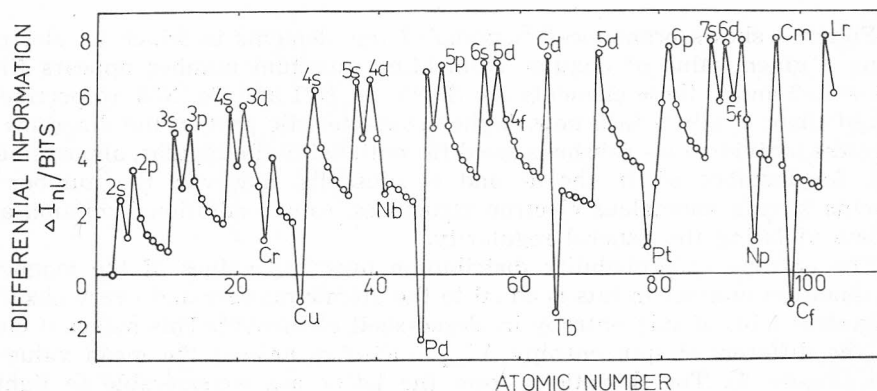


Figure 2.

the np-level. Every s, p, d and f- subshell forms a separate part of the total entropy curve, and by analyzing their positions one can easily come to the same conclusion as above, concerning lanthanides and actinides. The elements of every main or secondary group can be connected in Figure 1 by a common curve to which a group entropy equation corresponds. These group equations are specific instances of eq 5, in which the group constant z_{k+1} equals $1 \div 8$ for the eight main groups and equals $1 \div 10$ for the secondary groups.

In Figure 3 the differential entropy of probability distribution of electrons over atomic orbitals, ΔI_{nlm} , is already a monotonous function of the atomic number. The total curve consists of two parallel branches. The upper branch includes the elements in which, in accordance with Hund's first rule, every AO in a given subshell is populated by single electrons only. These are one s-, three p-, five d- and seven f- elements. The lower branch of the differential curve includes the same number of elements, but from the second half of the subshells, in which every new electron forms an electron pair. The two branches can be described by eq 5, taking $z_{k+1} = 1$ and 2, respectively. From this one can find that the difference between them is constant and equals 2 bits. In such a way the data shown in Figure 3 can be treated as an illustration of Hund's rule, which demands a maximum value of ΔI_{nlm} . It may be expected that these data will correlate with the magnetic properties of atoms.

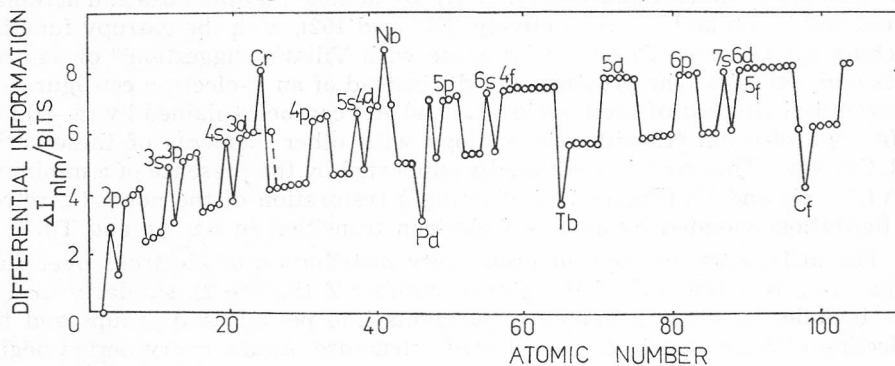


Figure 3.

Figure 4 shows pronounced maxima of the elements in which an electron having a given value of angular momentum quantum number appears first. For $l = 1, 2$ and 3, these elements are B, N5; Sc, N21 and Ce, N58, respectively. Each of them is initial in a new, higher characteristic part in the diagrams in which the individual nl -subshells are differentiated in the regular, almost linear parts, for instance p^6 . In the d- and f- subshells, however, the number of elements having anomalous electron structures, causes additional minima and maxima violating the general regularity.

The entropy of probability distribution over the values of the magnetic spin quantum number in bits is equal to the atomic number and every electron has exactly 1 bit of spin entropy in closed-shell elements⁴⁰. This makes it clear why the differential spin entropy ΔI_{m_s} fluctuates around the mean value of 1 bit (Figure 5). The deviations from the latter are considerable in lighter elements, but they decrease gradually with increasing atomic number. It can

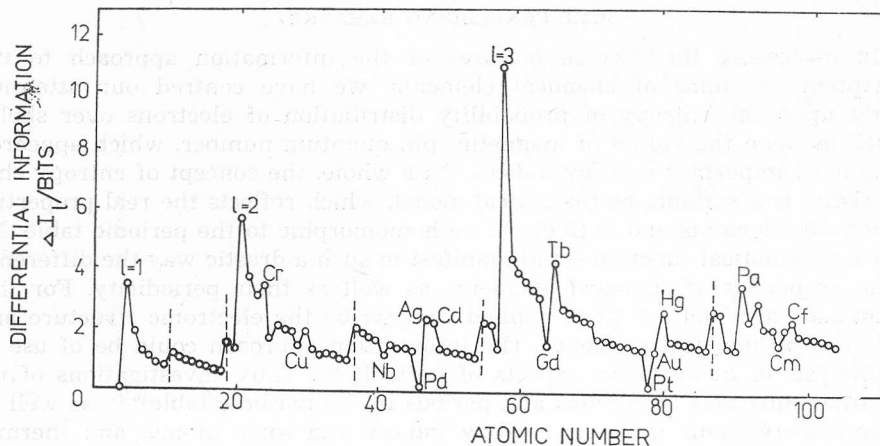


Figure 4.

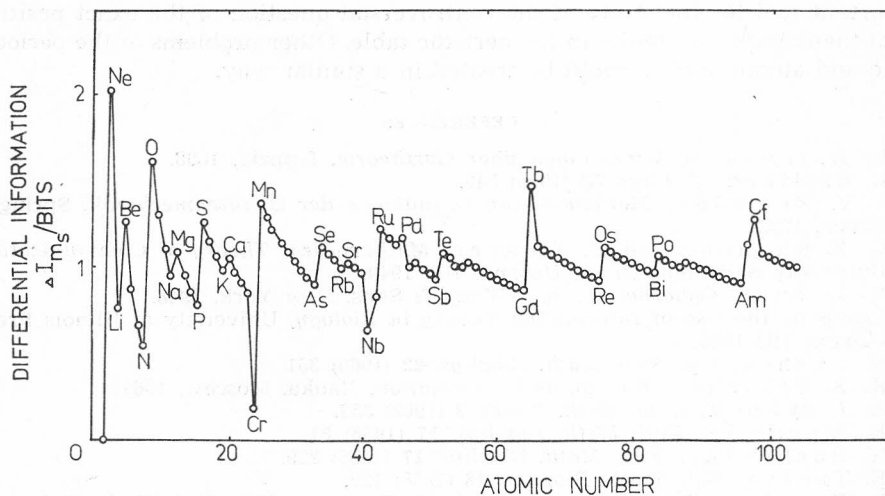


Figure 5.

be estimated that the entropy curve will merge with the line $\Delta I_{m_s} = 1$ bit, but only at such values of Z which considerably exceed the theoretical limits of the periodic table.

The zigzag trend of the differential curve is due to Hund's first rule. The subsequent population of the electron subshells by three p-, five d- or seven f- electrons is accomplished by electrons with parallel spin, and this reduces the entropy of each electron. Deep minima in the curve occur in elements having a maximum number of single electrons in a given subshell: N (2p), P (3p), Cr (3d), Gd (4f), etc. Every minimum is followed by a maximum, since electrons having antiparallel spin appear after some interruption, and the relative increase in spin entropy is large (O, S, Mn, Tb, etc.). It can also be noticed that the differential spin entropy is a very sensitive indicator of the elements (Cr, Nb, Gd) with a large number of single electrons.

SOME CONCLUDING REMARKS

In discussing the diverse features of the information approach to the description of atoms of chemical elements, we have centred our attention mainly upon the entropy of probability distribution of electrons over shells, as well as upon the values of magnetic spin quantum number, which appeared as the most important entropy indices. As a whole, the concept of entropy characteristics is a suitable mathematical model, which reflects the real properties of chemical elements and is likely to be homomorphic to the periodic table. No other mathematical function could manifest in such a drastic way the difference in the properties of chemical elements, as well as their periodicity. For this reason such a model has been applied to describe the electronic structure and properties of chemical elements. The information approach could be of use in the analysis of quantitative aspects of periodicity. Thus, investigations of information equations for groups and periods in the periodic table^{40,41}, as well as of some correlations between entropy indices and some atomic and thermodynamic properties of chemical elements are in progress. Using the entropy function ΔI_n , it has been shown in this paper that information theory is an important tool for the study of the controversial question of the exact position of lanthanides and actinides in the periodic table. Other problems of the periodic table and atomic theory could be treated in a similar way.

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SAŽETAK

Upotreba teorije informacije u opisivanju elektronske strukture atoma

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Razvijen je postupak koji se temelji na teoriji informacije, za opisivanje elektronske strukture atoma. Izveden je pojam »diferencijalnih« entropijskih karakteristika kemijskih elemenata koje jasno odražavaju horizontalnu i vertikalnu strukturu periodnog sustava elemenata. Raspravlja se i pitanje točnog položaja lantanida i aktinida u periodnom sustavu.

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