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Resonant Atom Model and the Formation of Valence Bonds

Yu. B. Magarshak

MathTech Inc., New York, USA

The nature of the valence bond is traditionally attributed to the displacement of electronic orbitals in space between interacting atoms. At the same time, a number of experimental facts, in particular, the existence of four-dimensional structural symmetry between the filling of electron shells and periodical properties of elements require a change in the standard valence concept. A model in which valence bonds are caused by the resonant interaction between the shell electrons of one atom and the protons of another atom seems to be more adequate.

Introduction

In 1939, Linus Pauling in his classical book *The Nature of the Chemical Bond and the Structure of Molecules and Crystals: An Introduction to Modern Structural Chemistry* [1] proposed valence theory according to which (disregarding details) the valence bond is formed due either to the collectivization of the wave function by atoms (covalence bond) or to the transition of the electronic cloud from one atom to another. If such transition is complete, the bond is called ionic; otherwise, it is called polar. In this case, a number of additional effects and phenomena such as the hybridization of orbitals, the electronegativity scale of elements, resonant valence bonds (as, for instance, in the benzene molecule) may appear. However, according to Pauling, the nature of the chemical bond causing these and many other processes is in the aforementioned displacement of the functions. Pauling's valence model is now standard in spite of some obvious difficulties. One of them is presented by coordination numbers [2]. It was found that one electron in some compounds can interact with several atoms (e.g. magnesium and iron atoms interact with four nitrogen atoms in chlorophyll and hemoglobin molecules, respectively), and the number of atoms with which one electron in so-called coordination compounds interacts can reach 12. The explanation that the wave function of an electron localized in one of the atoms is redistributed between a large number of nearby atoms is an obviously strained interpretation and directly contradicts the third of six Pauling's valence rules [1, 3]: "*An electron involved in the formation of a bond cannot be involved in other bonds.*" (which actually was later revised). The explanation of the hydrogen bond in the Pauling model also seems artificial. It is found that the single electron of a hydrogen atom in many molecules (e.g. in protein molecules) can form not only the basic bond, but also the second weaker bond in the direction opposite to the former bond. The location of the stationary wave function of the electron on "crest" between two atoms, which is of key importance, in particular for the structure of proteins, seems to require a more natural explanation. Thus, although the Pauling model (which constitutes the core of the modern valence concept) well explains the structure of many molecules and provides evident representation of the corresponding processes, the further development of valence theory by analyzing data collected for more than half-century since its appearance seems to be natural and necessary, particularly because the nature of the valence bond is of fundamental importance not only in chemistry,

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but also in molecular biology, solid state physics, and many other fields of natural sciences.

Another difficulty follows from the analysis of the periodic properties of chemical elements and the structural symmetry of the electronic configurations of atoms. In 1869, Mendeleev [4, 5] showed that the properties of elements periodically repeat. He managed to place elements in a rectangular table consisting of eight groups (in the current interpretation, with valences increasing from +1 in the first group to +7 (or –1) in the seventh group; these groups end with noble gases, which have zero valence in most cases and are not involved in compounds). In addition, Mendeleev predicted the properties of several elements opened later. The main features of the Periodic Table remain unchanged to date. However, some questions remain unanswered. Let us mention two of them. First, why the number of elements on the k -th shell is equal to $2k^2$, i.e. increases parabolically, while the basic part of the Periodic Table (where elements are divided into periods and groups) is rectangular? Second, why the Periodic Table is two-dimensional, while the number of quantum numbers is known to be equal to four? Maybe the structure of the periodicity of the properties of elements simply is flat, because Mendeleev searched it in such form from the very beginning in order to ensure optimal visualization? Whether substantial elements of the structure of periodically repeating properties are lost in such visually clear form? Answers to these questions were given in [6, 7]. The key to the answer is the presence of two coexisting reference systems in the plane of the principal n and orbital l quantum numbers in the set of atoms and elements (as chemists conventionally call atoms involved in valence interaction with each other) [7]. To visualize these structures, it is necessary to specially order the electronic configurations of all known elements at four hierarchical levels (see Fig. 1):

$$\textit{Supercycle} \Rightarrow \textit{Cycle} \Rightarrow \textit{Subshell} \Rightarrow \textit{Chemical element} \tag{1}$$

in contrast to the traditional ordering at three hierarchical levels (see Fig. 2):

$$\textit{Shell} \Rightarrow \textit{Subshell} \Rightarrow \textit{Chemical element} \tag{2}$$

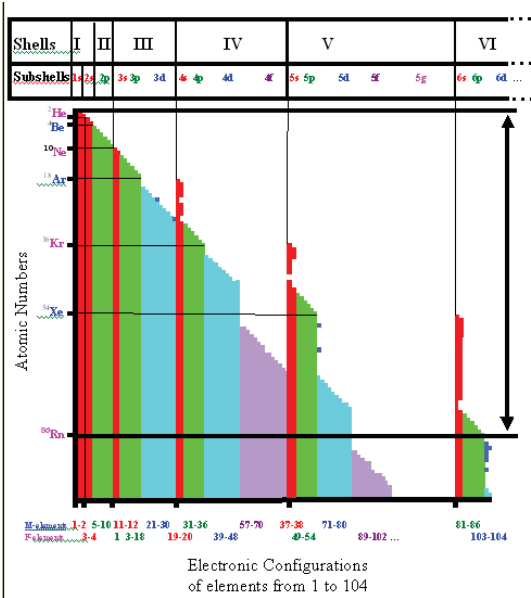


Figure 1. Electron configurations of the first 104 elements of the Periodic Table that are ordered in the following sequence: *Supercycle* $\Rightarrow$ *Cycle* $\Rightarrow$ *Subshell* $\Rightarrow$ *Chemical element*. For the definition of the cycle, supercycle, and the detailed discussion of the structures associated with them, see [1].

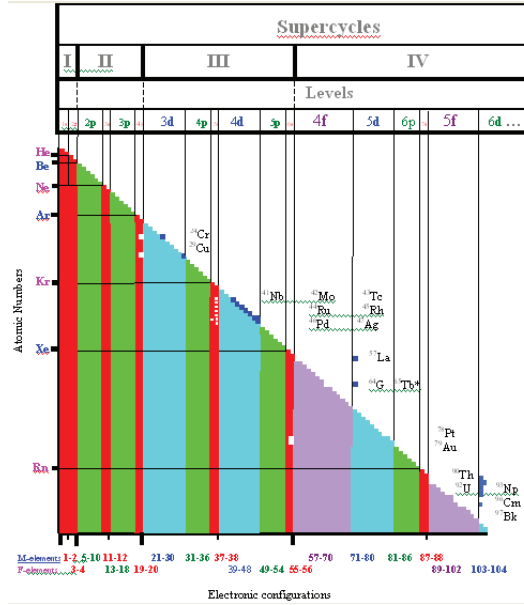


Figure 2. Electron configurations of the first 104 elements of the Periodic Table that are ordered in the following sequence: *Shell* $\Rightarrow$ *Subshell* $\Rightarrow$ *Chemical element* forming a subshell.

No structure is observed in Fig. 2, but it is obviously seen in Fig. 1. It is worth noting that shells are absent among levels forming the structure in Fig. 1 and in relations (1). For this reason, the term *subshell* (i.e. a part of the shell) traditionally used in physics (and almost not used in chemistry) seems to be inappropriate. According to Fig. 1, the subshell is the structure element of the classification of the electronic states of the set of atoms and is the basis for the classification of chemical elements. In [7], subshells were called *cells* in order to emphasize that, first, they are independent of shells and, second, they are structural “blocks” of the “building” of the Periodic Table of chemical elements so as atoms are the structural elements of molecules. Dividing the structure in the upper part of Fig. 1 into several rows and appropriately displacing these rows, one can represent the arrangement of subshells in Fig. 1 in the form [7]

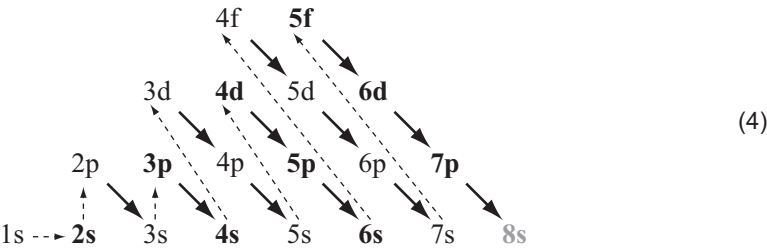
$$\begin{aligned}
 &5f \rightarrow 6d \rightarrow 7p \rightarrow 8s \\
 &4f \rightarrow 5d \rightarrow 6p \rightarrow 7s \rightarrow \\
 &\quad 4d \rightarrow 5p \rightarrow 6s \rightarrow \\
 &\quad 3d \rightarrow 4p \rightarrow 5s \rightarrow \\
 &\quad 3p \rightarrow 4s \rightarrow \\
 &\quad 2p \rightarrow 3s \rightarrow \\
 &\quad 2s \rightarrow \\
 &\quad 1s \rightarrow
 \end{aligned} \tag{3}$$

In this representation, vertical, horizontal, and diagonal structures of indices are clearly seen. It is also seen that every odd row and following even row (from bottom to top) contain the same number of chemical elements and are identically structured in subshells (but the orbital quantum number l in even rows is one unit larger than that in odd rows). The elements entering into a pair of rows with the numbers $2k - 1$ and $2k$, where $k = 1, 2, 3$, and 4 are called **supercycles** [7]. The first (lowest) and second rows of a supercycle are referred to as ***M*** and ***F*** ***cycles***, respectively. The rows of relations (1) are called ***levels***. Thus, all currently known 118 elements form eight levels dividing into four supercycles (rather than seven periods as in the traditional classification of elements by according to Mendeleev), consisting of four ***M*** cycles and

four F cycles. Thus, a pyramid of atomic electron configurations appears with four hierarchically ordered structural levels:

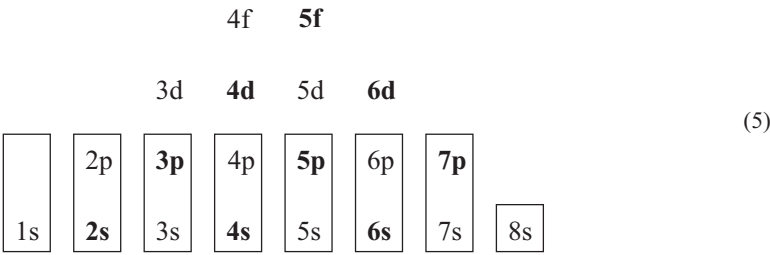
$$\textit{Supercycle} \Rightarrow \textit{Cycle} \Rightarrow \textit{Subshell} \Rightarrow \textit{Chemical element}.$$

In order to pass to the standard quantum-mechanical representation in the (n, l) coordinates, it is necessary “to rotate” relations (1) by an angle of $\pi/4$: where boldface



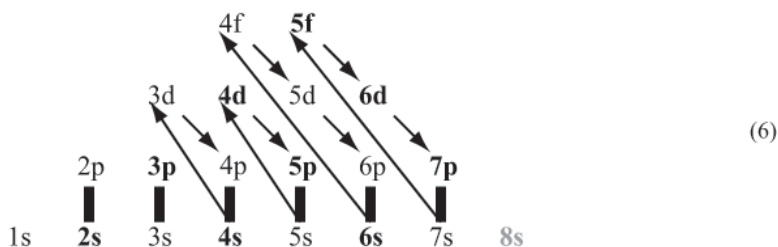
indicates the subshells of F cycles (ending supercycles), solid arrows specify the order of transitions between subshells (cells) in a cycle (also called a level), and dashed arrows indicate the order of transitions between cycles as a function of the charge of a nucleus. According to relations (1) and (2), the set of atomic electron configurations can be structured in two coordinate systems (n, l) and $(n + l, n - l)$.

Let us now analyze the connection between the electronic configurations of atoms and the chemical properties of elements (as traditionally called atoms involved in the valence interaction with each other). Imposing the Mendeleev’s Periodic Table of elements on relations (4) for the electronic configurations of atoms, one obtains [8]



The elements of the Periodic-Table groups from the first to eight that form valence bonds are given in frames. The filling of subshells (cells) inside a cycle occurs in parallel to the main diagonal from top to bottom and from left to right. Cycles are filled along the secondary diagonal of the pyramid from bottom to top and from left to right, beginning with the 1s subshell consisting of hydrogen and helium. Thus, in addition to the four structural levels including supercycles, cycles, subshells, and chemical elements in the $(n + l, n - l)$ coordinates, the set of atoms and chemical elements also has the structure of the valence properties of the chemical elements in the (n, l) coordinates. These structures, which can be represented both in the (n, l) coordinates [relations (5)] and in the $(n + l, n - l)$ coordinates [relations (3)], coexist and supplement each other. If chemical elements forming subshells are represented in relations (5) by introducing an additional dimension, a pyramidal structure appears. Then, separating M cycles from F cycles by displacing the latter, for example, deeper into the figure by half the edge of cubes symbolizing chemical elements, we arrive at the four-dimensional pyramid of atoms and elements (Figs. 3, 4, and 5). However, not all elements are on the surface of the pyramid in these figures. If, for better visualization, the chemical elements belonging to one subshell are represented vertically rather than perpendicularly to the figure, the pyramid of atoms and elements that is similar to skyscraper is obtained (see Fig. 6) [7]. The groups of the Periodic Table are located vertically on the first eight “floors” of the pyramid of atoms and elements. In this “3.5-dimensional” representation, alkali metals and noble gases are located on the first and eighth floors of the step pyramid, respectively.

The pyramid of elements (in which a structure appears both in the (n, l) coordinates and in the $(n + l, n - l)$ coordinates) differs from the Periodic Law not only in the dimension of the structure (four rather than two hierarchical levels), but also in the way of dividing elements into structural blocks. In particular, the second period according to Mendeleev consists of eight elements, whereas the second level of relations (3) (the F cycle of the first supercycle) contains two elements (lithium and beryllium) and the first supercycle includes four elements H, He, Li, and Be [7]. Which of the pyramid-forming coordinate systems, (n, l) or $(n + l, n - l)$, is dominant in chemistry? By the tradition going back to Mendeleev, the periods begin with s terms and end with p terms, whereas the last elements in division into levels are s terms ending a cycle. The division of elements into the periods in the (n, l) coordinates is represented as



The group subshells entering into a period (according to Mendeleev's classification) are connected by thick line segments. They specify the subshells that begin and end periods, whereas the order of the filling of the subshells in the periods is specified by a sequence of arrows that begin on the first floor and end on the second floor. The comparison of the composition of solid arrows in relations (4) (the *levels*, which are also called *cycles*, which are disposed parallel to the main diagonal) with the disposition of arrows in the relations (6), shows that Mendeleev's choice of the beginning and end of the cyclically repeating process seems to be geometrically and logically artificial. It seems more natural to begin the periods with the subshell from which the filling of the cycle starts. However, when quantum mechanics and, later, quantum chemistry appeared, the hybridization of orbitals was found to occur in the (n, l) coordinates on the first two floors of relations (5) in vertical and from bottom to top [see frames in relations (5)] [8]. In particular, this is the way of the hybridization of two s and two p orbitals in the carbon atom. Owing to this hybridization, organic molecules are formed and life becomes possible [9]. Thus, we have to value Mendeleev's intuition who had constructed the Periodic Table in the (n, l) coordinates half-century before the development of quantum mechanics. However, the chemical properties of elements and electron shells can be structured in both coordinate systems, which are called *fundamental*. To date, it is not clear whether the monotonic increase in valences in the Periodic Table from 1 to 7 and the end of the periods with noble gases having eight electrons on the outer shell are due to any physical mechanism or this is simply one of the possible choices of the beginning and end of the cyclically repeating process at which the filling of subshells from the first floor (alkali and alkali earth metals, $l = 0$) in the periods can pass to the *fourth floor* (lanthanides and actinides, $l = 3$), then/or to the *third floor* (transition metals $l = 2$), and only then comes back to the *second floor* ($l = 1$), in groups of which valence begins with 3. In the latter case, **the monotonic increase in valence with the ordinal number of the groups of the Periodic Table is nothing else than an artifact of this choice.**

1. Pyramids of Elements and the Nature of the Valence Bond

In the light of the analysis performed in the preceding section, an additional disadvantage of standard valence theory is obvious. None of relations (3)—(6) follows from Pauling's theory. Moreover, the presence of the rotation by $\pi/4$, the existence of two

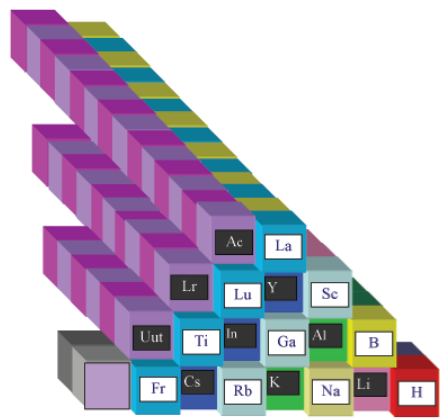


Figure 3. Four-dimensional pyramid of atoms and elements in the level (cycle) representation (cubes representing the elements of the F levels are displaced deeper into the figure by half the cube edge).

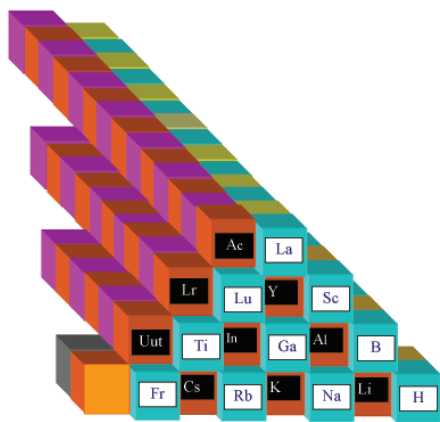


Figure 4. Four-dimensional pyramid of atoms and elements in the cluster representation.

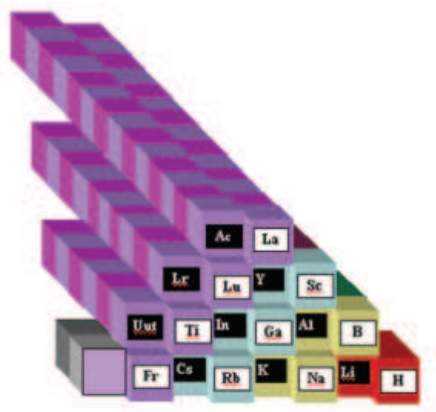


Figure 5. Four-dimensional pyramid of atoms and elements in the supercyclic representation.

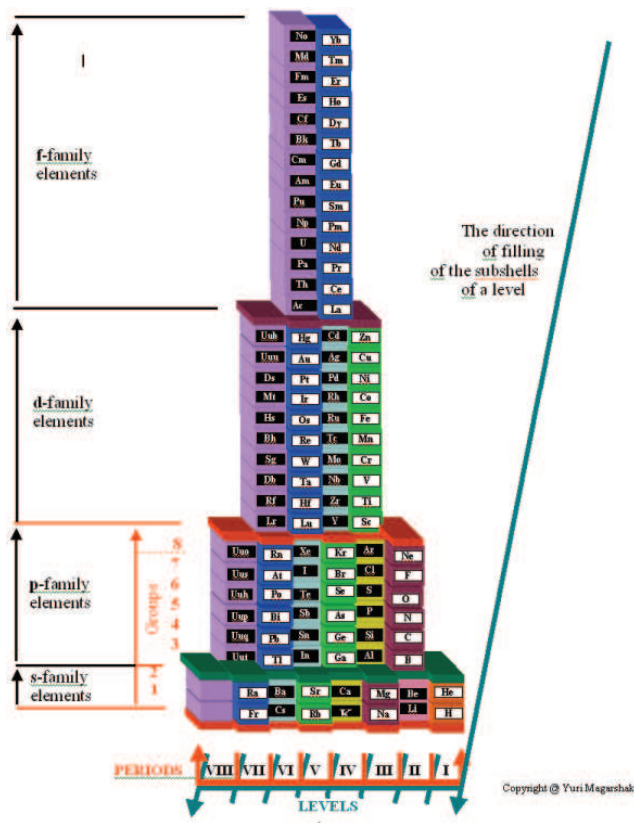


Figure 6. Pyramid of elements in the “3.5-dimensional representation”, in which (in contrast to four-dimensional representation on Figs. 3–5) all elements of the Periodic Table are shown. Colors designate the division of the elements into the periods (according to the tradition going back to Mendeleev). Steps correspond to the division of the elements into levels (cycles) and supersteps (pairs of odd and next even steps) correspond to the division in supercycles. The elements of the M cluster in the 3.5-dimensional representation, as well as in the four-dimensional pyramid, are displaced forward (perpendicularly to the figure plane) by half the cube edge with respect to the corresponding elements of F clusters.

reference systems (n, l) and $(n + l, n - l)$, the presence of the triangular structure in the arrangement at the four hierarchical levels shown in Fig. 1, and the existence of four-dimensional pyramids of elements (Figs 3–5 and Fig. 6) also do not follow from this theory. From the nature of chemical bonds as it is understood now, it is fundamentally unclear why the filling of electron shells occurs in one system of quantum numbers, whereas the valence properties of elements, as well as atomic spectra, are determined in the other system of quantum numbers that is related to the former system by rotation (by the angle $\pi/4$). The model of the valence bond that is due to the hybridization of orbitals and to the displacement of wave functions does not answer the question: “*Why does the set of elements in Figs. 1 and 3–5, as well as in relations (3), (5), and (6) (multielectron problems), behave similarly to one electron in the formation of atomic spectra, i.e. so as if all elements are the states of a certain hyperparticle?*” To explain all listed phenomena and femtochemical experiments, which will be briefly reviewed below, a physicochemical valence model that differs from the standard model is proposed in this work.

2. Presence of Several Coexisting Symmetries and the Commutation of Operators

As follows from the preceding sections, the set of atomic electron configurations can be structured in two systems of coordinates (n, l) and $(n + l, n - l)$, which are rotated by an angle of $\pi/4$ in the plane of the principal and orbital quantum numbers. This property of the system is not trivial. A question of under which conditions a physical system (and the corresponding differential equations and Hamiltonians describing it) has two coexisting symmetries that do not asymptotically displace one another in the $t \rightarrow \infty$ limit seems to be very important. When searching for an answer to this question, it was proved that, **for two symmetries to coexist in the system described by differential equations (and/or by Hamiltonians), operators generating these symmetries must commute with one another** [8].

A more precise formulation of this theorem is as follows. Let the structures and symmetries that are described above and shown in Figs. 1, 3–5 and 6 be generated by a pair of Hamiltonian-type operators, which naturally appear in the presence of two commutative Lie symmetry algebras in the quantum system. From the existence of simple commutative Lie symmetry algebras in a physical problem, it follows the existence of a single commuting pair of energy-type operators for localized quantum states.

Let us consider a finite-dimensional complex representation of the product of semisimple Lie algebras. Any such representation V of $g_1 \times g_2$ decomposes into a direct sum of tensor products $V_k \times W_j$, where V_k are irreducible representations of g_1 and W_j are representations of g_2 .

Theorem 1. *Assume that g_1, g_2 are simple Lie algebras. Then there is a canonically defined pair of commuting operators Δ_1, Δ_2 such that both $\Delta_i, i = 1, 2$ commute also with the action of g_1, g_2 and have integer nonnegative eigenvalues on V .*

This theorem was proved in [8]. Thus, to explain symmetry between the properties of elements and filling of electron shells within the rotation on the plane of the principal and orbital quantum numbers, **two commuting operators are required**. One of these operators is specified by the Schrödinger equation. Since an atom consists of a shell and a nucleus, which contains protons and neutrons, the only possible generator of the second operator can be the interaction of the electrons of the shell with the protons of the nucleus. Owing to the negligible smallness of the probability of the random appearance of structures (1), (3), (4) and (6), as well as of their appearance due to any “empirical rule” (the term used, in particular, for Hund’s “rule”) rather than a process fundamental for the atomic structure, the hypothesis of the existence of physical mechanisms that generate the second operator and ensure the appearance of these structures seems to have no alternative to explain the above phenomena.

3. Resonant Atom Model

Postulate 1. In atoms there are no stationary electronic states.

Postulate 2. All electrons, which constitute the shell of the atom, are involved in the process with the following basic steps (collectively called **resonant path**):

- (i) The $\psi\beta$ -capture of a shell electron by atom nuclei.
- (ii) Proton–Electron $\rightarrow$ Neutron resonance interaction (**pen-resonance**) of the shell electron with the proton of the nucleus: $e + p \rightarrow n$
- (iii) $\beta\psi$ -release of the electron from the nuclei and its return to nonlocalized ψ -state in the shell.

Postulate 3. The physical nature of $\psi\beta$ -shell electron capture by nuclei, and $\beta\psi$ -electron release from nuclei, is not the same. $\psi\beta$ -capture takes place due to the overlap of the electronic ψ -function with the volume occupied by atom nuclei. $\beta\psi$ -release of the electron from nuclei is possible only at energies determined by Schrödinger equation for the space around the nuclei, in which electronic shell is disposed.

Comments.

- 1) According to the resonance atom model, the stationary Schrödinger equation is valid only because electron-nuclei cyclic processes is very quick, much quicker than the measurement time.
- 2) At present, unidirectional processes of the field interaction between electrons, protons, and neutrons are well known. These processes are, first, K-capture at which an electron from the shell nearest to the nucleus interacts with a proton of the nucleus and, as a result, a neutron appears and the atomic number of the element decreases by one, and, second, β -decay at which the nucleus emits an electron and the atomic number of the element increases by one [2]. According to the resonance atom hypothesis, K-capture and β -decay are comparatively rare irreversible processes that are easily detectable and constitute the “top of the iceberg” of frequent reversible interactions between the proton, neutron, and electron.
- 3) A consequence of quantum mechanics is wave-particle dualism due to which the electron at the time of measurement exhibits corpuscular properties and is located in a volume that is approximately 10^{15} times smaller than the volume occupied by its orbital. On the other hand, the overlap of the electronic ψ -state with the volume occupied by the nuclei can provide the localization of the electron inside the nuclei. Such localization is a necessary condition for the beginning of the *pen*-resonance process. For these reasons, localization of a shell electron in the nucleus, necessary for the (presumably resonant) interaction between proton in the nuclei with shell electron, is undoubtedly possible.
- 4) Other particles (in particular, neutrinos) can be involved in the *pen*-resonance process.

4. Superresonant Nature of the Valence Bond

Postulate 1. In the valence interaction between the atoms in a molecule, an electron on the shell of one of the atoms is involved in the *pen*-resonant interaction with a proton in the nucleus of another atom.

Postulate 2. A valence bond is formed due to jumps of the electron of the shell between the nuclei connected by the valence bond, and each of jumps to a certain nucleus is of *pen*-resonance nature.

Postulate 3. In molecules consisting of more than two atoms, resonances between resonances can occur. The number of the hierarchical levels of resonances in nature is unlimited.

Comments.

- 1) According to the superresonant valence model, the physical nature of the valence bond is the same as the nature of the atom: it is superresonance that is resonance between *pen*-resonances with nuclei participating in the bond formation.
- 2) According to the postulates of the (super)resonant nature of valence, covalent, ionic, and polar bonds, as well as the presence of hybrid orbitals and resonances in molecules, are explained not as in the traditional model. These explanations are as follows.
 - Covalence bonds, in which a common electron pair is formed between atoms, arise when the electron of the outer shell of each of two atoms resonantly interacts with the nucleus of the atom with which the valence bond is formed with the same, or approximately the same, energy and frequency as those of the interaction with the nucleus of the “parent atom”.
 - The ionic bond between two atoms in a molecule is formed when the outer electron of one atom resonantly interacts with the nucleus of another atom and completely leaves resonance with the nucleus of the parent atom.
 - The polar bond appears when the ratio of the probabilities of the resonance localization of the electron in the nucleus of the “parent” atom and in the nucleus of the atom with which the valence bond is formed is between zero and one and differs from $1/2$.

- The hybridization of orbitals is determined by correlation in superresonant jumps of several electrons between the nuclei of the atoms connected by the valence bond.
 - Resonant valence bonds (e.g. in the benzene molecule in which resonance occurs between the single and double bonds) are attributed to the resonance of superresonant jumps of electrons between the nuclei of the atoms which take part in the multi-atomic resonance (for example, between the atoms of the six-membered benzene ring in the case of the benzene molecule).
- 3) Time in which atoms diverge at a distance where the formation of the valence bond is impossible is of the same order of magnitude as the period of atomic vibrations in molecules (10^{-15} – 10^{-12} s). If the **superresonant cycle** (which includes at least two *pen*-resonances with nuclei which form the bond) is several orders of magnitude faster than the upper limit of this range, the electron has more than enough time to form the valence bond that holds the atoms connected by this bond. In a similar way, i.e. by means of the superresonant interactions between the shell electrons of all atoms of a molecule with the nuclei of the atoms connected by valence bonds, the formation of molecules of any size occurs.
 - 4) According to the superresonance model, an electron may not only vibrate between the nuclei of two atoms, but also “travel” between the nuclei of the atoms along a certain trajectory. In particular, the existence of chemical compounds with coordination numbers in which an electron of one atom is connected by valence bonds with several neighboring atoms is explained by the fact that the valence bonding is a fast nonstationary process. If the time of the superresonant bonding of an electron on an atomic shell with each of the atoms coordinationally connected with this coordinating atom is several orders of magnitude shorter than the period of the oscillations of the atoms, the electron coordinating the configuration of the molecule has more than enough time to sequentially couple with all atoms with nuclei of which it superresonantly interacts.
 - 5) The resonance model of the atom suggests the possibility of the existence of the hierarchy of resonances. The first-level *pen*-resonance provides the existence of atoms. The second-level resonance ensure the formation of valence bonds between atoms. The third-level resonances provide the synchronization of the formation of bonds between atomic nuclei (forming, e.g. a ring as in benzene). This process can be continued. There is likely no restriction imposed by nature on the number of hierarchical levels of resonances. For this reason, the application of resonance atom concept, which generate higher levels resonances, to explain the functioning of biological systems, in particular, electronic transport in macromolecules and enzymatic activity, as well as the levels of the organization of matter in living organisms that are higher than biological macromolecules seems to deserve a detailed investigation.
According to the atomic resonance concept, resonances underlie not only the structures of atoms and valence bond, but also the general structure of matter at all levels beginning with the atomic structure.
 - 6) The resonance atom model and superresonant bond model provide an explanation of structural symmetries in relations (4) and (6) between (i) the valence properties of chemical elements, (ii) the properties of electron shells of atoms, and (iii) atomic spectra. This explanation is that the existence of **two** fundamental processes different in nature that underlie the structure of atoms and valence bonds gives rise to the existence two operators (Hamiltonian) that can have properties required for the satisfaction of relations (3), (4) and (6), in particular, can commute with one another [9].
 - 7) Superresonant bonds can provide the basis for the formation of not only molecules, but also solids. However, the discussion of this problem is beyond the scope of this paper.

5. Estimation of the Parameters of the Superresonance Valence Model

A small difference between the rest masses of the neutron and proton, which is less than $1/700$ of the mass of these particles, is explained in the framework of the resonance atom model of the structure of matter. Such ratio of the masses is a necessary condition for the possibility of the occurrence of the *pen*-resonance and is determined by the time–energy uncertainty relation [10, 11]

$$\Delta E \Delta t \approx \hbar, \quad (4)$$

where Δt is interval between the beginning and the end of the process and ΔE is related to the rest masses of the electron, neutron, and proton as $\Delta E = c^2 (m_n - m_p - m_e)$. The substitution of the neutron mass value $m_n = 939.5731$ MeV, proton mass value $m_p = 938.2796$ MeV, and electron mass value $m_e = 0.5110034$ MeV, the Planck's constant, and electron charge yields the value $\Delta t \cong 8 \cdot 10^{-22}$ s, which is close to the frequency range in which resonances between elementary particles occur (10^{22} – 10^{24} s $^{-1}$)¹. Thus, **the closeness of the masses of the neutron and proton (the cause of which remains mysterious in many respects) is a necessary condition for the existence of atoms according to the resonance atom model. Moreover, according to the hypothesis of the superresonance nature of the valence bond, this closeness is a necessary condition for the existence of not only atoms, but also molecules and solids.**

What is the frequency of the occurrence of the *pen*-resonance? Light covers the distance from the nucleus to the outer electron orbit in time $\tau = 5.3 \cdot 10^{-11}$ m/($3 \cdot 10^8$ m/s) = $1.8 \cdot 10^{-19}$ s. It is natural to assume that the frequency with which resonance occurs between the electron localized in the nucleus and the electron delocalized on the shell is lower than this value. Thus, the electron is in the state described by the Schrödinger equation for a time that are several orders of magnitude longer than the time for which the electron is in the state localized in the nucleus. This relation completely corresponds to the fact that, in experiments where measurement is performed for a time that are several orders of magnitude longer than the time of fundamental resonances, the electron states are described by the time-independent Schrödinger equation and the number of protons in the nucleus is equal to the number of electrons on the shell. At the same time, for valence bonds to be formed due to superresonances, the superresonance cycle frequency must be larger than the maximum atomic vibration frequency, i.e. in the range 10^{15} – 10^{18} s $^{-1}$.

6. History of the Development of Representations of the Nature of the Valence Bond

Walter Heitler and Fritz London [12] were the first physicists who applied the principles of quantum mechanics to determine the nature of the chemical bond in the hydrogen molecule. According to their model, when atoms approach each other, a negatively charged electron of one atom is attracted to the positive nucleus of another atom due to the Heisenberg exchange energy. As a result, beginning with a certain distance between the atoms, electrons oscillate between the nuclei of the atoms. Thus, according to the model, electrons in the hydrogen molecule belong to both atoms, forming the valence bond, whose length and energy are calculated from the Schrödinger equation.

In 1928, London [13] applied an approach based on the Heisenberg exchange energy to H_3 triatomic molecule. He showed that electrons in this case also oscillate between the nuclei. In the next several years, Polanyi and Wigner [14] and Henry Eyring and Michael Polanyi [15] formulated transition-state theory. In addition, using the London

¹More accurate estimations, in particular, with the inclusion of other particles (e.g. neutrinos), which involvement in the superresonance process might be discovered experimentally in the future, can only refine this estimate, but cannot change it by several orders of magnitude.

equation, Eyring and Polanyi [15] for the first time introduced the concepts of reaction dynamics and potential energy surface. The Arrhenius-like equations, which take into consideration both statistical mechanics and quantum theory, have been derived. The chemical reaction rate k in the van't Hoff equation [16] was expressed in terms of the Boltzmann constant k_B , Planck's constant h , absolute temperature T and Gibbs free energy of activation ΔG^{**} . It was shown that the maximum rate $k_{\max}$ of a chemical reaction (which was defined in transition-state theory as the frequency of penetration through the potential barrier)

$$k = k_{\max} \cdot e^{-\Delta G^{**}/RT} = k_B T/h \cdot e^{-\Delta G^{**}/RT} \quad (5)$$

limited by the pre-exponential factor in Eq. (5), is equal to about $k_B T/h$ [17]. Its value $6 \times 10^{12} \text{ s}^{-1}$ at room temperature is in the range of atomic vibration frequencies in molecules (from 0.01 ps to 0.1 ps). The hopping frequency of the electron forming the valence bond between the nuclei was estimated in these works as $> 10^{12} \text{ s}^{-1}$.

In 1929, Pauling published a work in which the concept of the hybridization of orbitals was introduced for the first time in application to the carbon atom. In 1931, He formulated six rules valid for valence bonds [1]:

- (i) A valence bond is formed as a result of the interaction of uncoupled electrons, one of each atom.
- (ii) The spins of the electrons forming the valence bond should be oppositely directed.
- (iii) The electron that forms a bond cannot be involved in other bonds.
- (iv) One and only one wave function from each atom is involved in the formation of a bond.
- (v) The electron having the minimum energy forms the strongest valence bond.
- (vi) Among two orbitals of an atom, an orbital that has the largest overlapping with the atomic orbital of another atom forms the stronger bond, which is directed toward the overlapping of the orbitals.

The comparison of rules (i)–(iii) (based on works by Heitler and London) with rules (iv)–(vi) (which opened by Pauling) obviously shows that Pauling oriented to the needs of practical chemistry, where it was difficult to apply the conceptual results obtained by Heitler and London. Simultaneously with the work published by Pauling in 1931, Slater published paper [18] in which he tried to justify a model of the valence bond that was based on the fundamental physical principles and was similar to Pauling's model. In the 1930s, Pauling published seven papers under the general title *The Nature of the Chemical Bond*, which have become classical and, considered together, created the basis of the present canonical chemical bond model. Those papers are as follows.

- *The Nature of the Chemical Bond. Application of Results Obtained from the Quantum Mechanics and from a Theory of Paramagnetic Susceptibility to the Structure of Molecules.* April 1931.
- *The Nature of the Chemical Bond. II. The One-Electron Bond and the Three-Electron Bond.* September 1931.
- *The Nature of the Chemical Bond. III. The transition from One Extreme Bond Type to Another.* March 1932.
- *The Nature of the Chemical Bond. IV. The energy of Single Bonds and the Relative Electronegativity of Atoms.* September 1932.
- *The Nature of the Chemical Bond. V. The Quantum-Mechanical Calculation of the Resonance Energy of Benzene and Naphthalene and the Hydrocarbon Free Radicals.* June 1933.
- *The Nature of the Chemical Bond. VI. The Calculation from Thermochemical Data of the Energy of Resonance of Molecules Among Several Electronic Structures.* August 1933.
- *The Nature of the Chemical Bond. VII. The Calculation of Resonance Energy in Conjugated Systems.* October 1933.

In each of these works, practically useful rules were proposed and they were not all be derived from the fundamental principles of quantum mechanics or from the Schrödinger equation. The most important of them are as follows.

- a) The introduction of the concept of hybrid bond.

- b) The introduction of the concept of electronegativity, which for the first time allowed chemists to predict the energy of a chemical bond arising between elements by using the tables composed by Pauling instead of using the Schrödinger equation and wave functions.
- c) The introduction of the concept of resonant structures in which the resonance occurs between single and double valence bonds. By the example of the benzene molecule, it has been shown how resonance occurs between five canonical conformations. According to Pauling, the properties of a resonant structure are the average properties of states between which resonance occurs. (*The Nature of the Chemical Bond. V. The Quantum-Mechanical Calculation of the Resonance Energy of Benzene and Naphthalene and the Hydrocarbon Free Radicals*).
- d) The introduction of the concept of resonance between the ionic and covalence bonds. Owing to this resonance, valence bonds can cease to be integer (single, double, or triple) and can have intermediate values (*The Nature of the Chemical Bond. VI. The Calculation from Thermochemical Data of the Energy of Resonance of Molecules Among Several Electronic Structures*).
- e) The concept of stabilizing resonance in the conjugate systems, in which single and double bonds alternate (*The Nature of the Chemical Bond. VII. The Calculation of Resonance Energy in Conjugated Systems*) and a number of practical rules for calculating the parameters of such systems have been proposed.

These results were summarized in classical book [1] published in 1939. Many of rules proposed by Pauling, which appeared to be highly efficient in applied chemistry, were based on semiempirical reasons and their justification continues to be criticized. Nevertheless, Pauling's theory of chemical bonding is considered now as standard to a much greater degree than Pauling might think, developing it step by step.

An alternative approach to the nature of the chemical bond was developed by Friedrich Hund, Born's pupil, who studied atomic spectra in 1926 and opened the order of the filling of electron shells with changing in the charge of a nucleus (Hund's rule [19]). Studying molecular spectra, Hund found that molecular emission and absorption spectra are in many respects similar to the spectra of free atoms. As a result, Hund and Mulliken [20–26] proposed a model of molecular orbitals according to which electrons are located on the surface of a molecule. Hund and Mulliken represented a molecule as an atom with several nuclei that are separated in space and surrounded by an electron shell common for all nuclei. Thus, in the Hund & Mulliken model of the molecular structure, the difference between atoms and molecules is not radical. This concept was significantly different from the Heitler–London–Pauling model; however, it was confirmed in molecular spectroscopy experiments.

Despite significant differences between the Heitler–London–Pauling valence bond model and the Hund–Mulliken representation of molecules as atoms with the separated nuclei surrounded by molecular orbitals, both results can be derived from the Schrödinger equation as it was shown in the next decade. At present, the concepts of molecular orbitals (proposed by Hund and Mulliken) and valence based on works by Pauling, coexist.

Experimental data collected in the last decade due to the creation of femtosecond lasers and to the development of femtosecond transition-state spectroscopy force us to return to the problem of the nature of bonding between atoms in molecules. In particular, the presence of resonance transitions between covalent and ionic configurations in the atoms of the NaI and NaBr molecules was shown in the real-time experiment [27, 28]. Thus, the concept that the chemical bond is stationary, follows from the time-independent Schrödinger equation, and is caused by the stationary states obtained by solving this equation appears to be in doubt, although it is presented as standard in all school and high school textbooks and most monographs. Investigation of the rupture of the valence bond in real time is another area of fundamental interest. Using femtosecond spectroscopy, A. Zewail [28] analyzed the rupture of the I-CN bond in the ICN molecule. This analysis made it possible to experimentally follow the trajectory of the reaction, including the dynamics of the transition through a potential barrier. The irradiation of molecules by femtosecond pulses with a length of about 0.05 Å (the characteristic sizes of analyzed molecules are Angstroms) in order

to generate and analyzes Single-Molecule-Type Dynamics is the third research area that seems to be most promising for the analysis of the nature of the chemical bond. The action of such short pulses whose length is less than one hundredth of the atomic size almost does not perturb the ground state except for a small part of a molecule. This circumstance allows the real-time analysis of the propagation of perturbations in the molecule [28, 29]. Zewail and his coworkers believe that the creation of attosecond (10^{-18} s) lasers will make it possible to follow the trajectory of the electron during chemical reactions in real time [28]. Thus, direct experimental proofs of the validity or invalidity of the valence-bond models both reviewed above and proposed in this work can be obtained in the next decade.

7. Comparison of the Superresonance Valence Model with the Heitler–London, Hund–Mulliken, and Pauling Models

In the first decade after the development of quantum mechanics, Heitler, London, Polanyi, Hund, Mulliken, Slater, Wigner, and others seriously tried to explain chemistry using the fundamental physical principles. Nevertheless, the conceptual gap between physics and chemistry exists to date. The superresonance model includes a number of elements of the previous models.

- 1) As well as in the Heitler–London model, the valence bond is based on the motion of an electron between nuclei with very high frequency. However, in contrast to the Heitler–London model, the superresonance model of the formation of molecules attributes this motion not to the Heisenberg exchange energy, but to the *pen*-resonance between elementary particles, with a frequency characteristic of resonances between particles (10^{22} – 10^{24} s $^{-1}$) which is a number of orders of magnitude higher than Heitler–London evaluation.
- 2) As well as in the work by Hund and Mulliken, the structure of molecules in the superresonant model is determined by nuclei. Therefore, the consideration of molecules “*as atoms with more than one nucleus*” in both models has both physical and chemical senses. However, the physics of the formation of the electron shell in the superresonant valence model — the resonant interaction of electrons with protons in a nucleus — differs from the physical representations underlying the Hund–Mulliken model.
- 3) The superresonant bond model, as well as Pauling’s rules, provides the possibility of the occurrence of resonance structures. However, in contrast to the standard model, the superresonant valence model considers resonances not only as the cause of the formation of resonant bonds in some molecules (such as the benzene molecule), but also as the physical basis of the chemical bond itself. Moreover, according to the model proposed in this work, resonances constitute the physical mechanism that is responsible for the appearance and existence of not only molecules, but also atoms.

Discussion

- 1) The efficiency of the Occam’s razor principle (according to which new concepts should be introduced only if they are absolutely necessary) has been manifested during centuries in various sciences. The introduction of new models and concepts is not required if the existing representations successfully explain the basic experiments. However, too many questions concerning mechanisms of the formation of chemical compounds are collected. The consideration of alternative models becomes necessary. The superresonance hypothesis of the nature of valence seems to be most adequate and “soft” among all mechanisms listed in the review. On the one hand, it can hold the quantum-mechanical results, which are described by the Schrödinger equation whenever one is applicable (in particular, in the adiabatic approximation). On the other hand, the efficiency of the application of

Butlerov's "hyphens" becomes understandable, because electrons (according to the superresonant valence model) are involved one by one in *pen*-resonance with the nucleus, forming an inter-nucleic "bridge". Thus, the efficiency of the widespread chemical representation of atoms as spheres and points, which proved to be highly effective in numerous applications, is directly explained in the physics of resonant processes underlying (according to the superresonance hypothesis) the formations of molecules. The superresonant model most naturally explains the hybridization of orbitals, the hydrogen bond, and coordination numbers. Femto-chemical results, which directly demonstrate the inadequacy of the representation of the chemical bond as a stationary process, are completely consistent with the existence of the fundamental resonances underlying the nature of the valence bond. Moreover, the existence of structural symmetries in relations (3)–(6), as well as the representation of the set of electronic configurations and the periodical properties of chemical elements in the form of four-dimensional pyramids, can be strictly explained in the framework of the superresonance model.

- 2) According to the superresonant valence model, the interaction between atoms in molecules is caused either by the resonant interaction of valence electrons with the nuclei of both valently connected atoms (covalent and polar bonds) or by the complete transition of an electron of one atom to interaction with the nucleus of the other atom (ionic bond). In the latter case, the atoms become oppositely charged, which is equivalent to the appearance of the Coulomb interaction between the centers of these atoms in the classical approach. This fully corresponds to the empirical representation of the atomic structure that is accepted by chemists whose practical experience forces them skeptically estimate the utility of the use of quantum-mechanical calculations in chemistry. However, in the light of the proposed superresonant valence model, the skepticism by practical chemists concerning the adequacy of the current way of the application of atomic theory in their science seems to be completely justified.
- 3) According to the resonance hypothesis, the structure of matter is based on resonances, resonances between resonances, interaction between resonances, and the hierarchy of resonances. At the most general understanding level, such representation is similar, on the one hand, to the ideas underlying string theory and, on the other hand, to philosophical representations of the harmonic structure of the universe beginning with Plato and Pythagoras. However, string theory is applied to a scale of about 10^{-35} m, whereas the characteristic sizes of atoms and molecules are 10^{25} – 10^{27} times larger.
- 4) Resonance model of the structure of atoms and molecules establishes a straight connection between chemistry and the theory of elementary particles, molecular biology, and nuclear resonance states. The role of relativistic effects in the superresonant process may also be essential [9].
- 5) The increase in entropy is now explained by the fact that nearby trajectories at multiple atomic collisions diverge exponentially such as it is shown both analytically and in computer simulation for the Sinai billiard [30] and Bunimovich stadium [31]. However, the problem of the consistency between the time reversibility of the Newtonian equations of motion and the irreversibility of the entropy increase, strictly speaking, remains. If at least some colliding atoms interact not only as elastic spheres (traditional model in the kinetic theory of gases), but also *pen*-resonantly, these collisions cease to be reversible under time reversal in the Newtonian equations of motion, already because the duration of the *pen*-resonance is a random variable with dispersion. Moreover, since time of the *pen*-resonance is small but nonzero, this duration is enough for the interacting nuclei to move in space. Therefore, the model of collisions between atoms as elastic spheres is inapplicable at least for collisions at which *pen*-resonance occurs (whose energy, in contrast to valence bonds in molecules, is insufficient to hold atoms). Thus, if *pen*-resonances occur at least in some atomic collisions, the entropy of the system increases.
- 6) The superresonance model of valence bonds forces us to revise both understanding and modeling of the enzymatic activity and functioning of biological molecules in

vivo. The traditional bond model compels specialists in molecular-biology simulations to reduce molecular dynamics, including the enzymatic activity, to the Coulomb law and Newton's law of gravity with the selection of the corresponding coefficients. This approach, although numerically effective, seems to be inadequate and too simplified. Representation that bonds between atoms are caused by resonances, as well as the possibility of the existence of hierarchical resonances in molecules, provides a new sight and new opportunities both for explaining existing processes and for designing molecules with given properties. Possible connection of enzymatic activity with the theory of elementary particles (on which proton-electron-neutron-resonances are based according to the proposed model) is equally intriguing and stimulating.

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Резонансная модель атома и формирование валентных связей

Ю. Б. Магаршак

МатТек Инк., Нью-Йорк, США

Природу валентных связей традиционно объясняют смещением электронных орбиталей в пространстве между взаимодействующими атомами. В то же время ряд экспериментальных фактов, например, существование четырехмерной симметрии между заполнением электронных оболочек и периодическими свойствами химических элементов, требует пересмотра стандартной концепции валентности. Модель, в которой валентные связи вызываются резонансным взаимодействием между электронной оболочкой одного атома и протонами другого атома, представляется более адекватной.