# The Periodic Table is Misleading, Incomplete, and Unduly Neglected

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The Periodic Table has been in its present form approximately 70 years and it remains the single most powerful means for organizing the electronic structure of matter and the principal agent for introducing chemical science to young students. Because of its vast exposure and familiarity, it has been treated as an icon and seldom examined critically. Nevertheless, everyone knows that energy is the governing parameter in determining the structure of molecules and solids and therefore it is surprising that some manifestation of atomic energy is not a part of it. Since the Periodic Table is made up of the valence electron configurations of ground state free atoms, the appropriate energies are the *configuration energies* and when these are added to complete the Table its misleading features are removed and its predominant role in ordering chemical phenomena is considerably enhanced. Thus, such troublesome problems as: (a) why the chemistry of groups is not independent of row, (b) why all of the valence electrons in N, O, F, Cl and Br cannot be utilized in bonding, (c) the origin of the diagonal line separating metals from nonmetals and what determines its position, (d) why multiple bonding is more prevalent in the first row than in higher rows, are readily answered by the pattern and properties of configuration energies. The use of configuration energies also can be taken beyond the Periodic Table and applied to specific atoms in specific solids and molecules. Two methods of accomplishing this are described.

## INTRODUCTION

This article is dedicated to Professor Linus Pauling in honor of his 90th birthday, and his many contributions to the understanding of chemical bonding. In the period from the late 1920s until the outbreak of World War II. Pauling, along with a few others that included Heitler, London, Slater, Mulliken, Lennard-Jones, Coulson, and Brillouin, laid most of the ground work for contemporary research in molecular structure and reactivity. The collection of mathematically simple, valence bond-like models created by Pauling, *e.g.*, resonance, hybridization, maximum overlap, the electrostatic valence rule, the bond order-bond distance relationship, percent ionic character, and

electronegativity, have dominated the thinking pattern of chemists for more than 60 years. Although the computer revolution has permitted theoretical chemistry to obtain wavefunctions for small to medium sized molecules whose accuracy is far beyond that generated by any models of the 1930s, the sheer complexity of the molecules and solids of interest to chemists remains so great that many of Pauling's qualitative chemical pictures, and further development of his models, are more needed now than every before. In this paper we give one example, an extension of Pauling's electronegativity definition. We have found that Pauling's set of values (and those of Allred and Rochow, the two scales used almost exclusively by practicing chemists) can be closely matched by the orbital occupancy weighted average ionization potential of the valence electrons for ground state free atoms. This quantity, atomic configuration energy is a new dimension to the Periodic Table. Electronegativity is thus converted into configuration energy (*CE*) and it can be shown that atomic energy level spacings are strongly correlated with them, a fact which adds greatly to their usefulness. In this article we also give two methods by which configuration energies can be taken beyond the Periodic Table and applied to determining the charges and valence energies of atoms as they exist in molecules and solids.

It is to be noted that our article, along with others in this international collection to honor Pauling's 90th birthday, is being published by one of the leading scientific journals in Croatia, a country currently experiencing intense uncertainty concerning its future. It is a tribute to *Croatica Chemica Acta* and, in particular, to Professor Zvonimir B. Maksić, one of the guest-editors of this issue, that open scientific exchange is being maintained during this severe crisis. Science helps promote a humane society most rapidly when free scientific interchange is possible and Linus Pauling has been an outstanding exemplar of this theme.

## CONFIGURATION ENERGIES

Chemists and physicists view the Periodic Table differently and a comparison helps bring out the need for configuration energies. For chemists the combining properties of atoms is the paramount concern. The set of groups with approximately common chemistry and s, p, d, and f blocks with their characteristic behaviors generate the two dimensional array which display all atoms and therefore appears complete. Physicists, on the other hand, see a set of valence electron configurations ordered according to the Periodic Table build-up principle which depict the shell structure of atoms. The two quantum numbers, $n$ and $l$, designate more than the labels of blocks and more than the size and shape of orbitals: their primary role is energy specification. When valence orbital occupancy is taken into account and put on a per electron basis, this yields configuration energy (*CE*). Under the assumptions that atoms are spherical and that a single determinant wavefunction is adequate for qualitative understanding of atomic properties, it can be argued that adding configuration energy as a third dimension is a necessary and sufficient condition for achieving an internally consistent description of the Periodic Table. For representative elements:

$$CE = (a\varepsilon_s + b\varepsilon_p)/(a + b)$$

where a, b are the number of s and p electrons, $\varepsilon_s$, $\varepsilon_p$ their spherically averaged ionization potentials. This is just the ionization potential of an average valence electron and Table 1 lists configuration energies (in electron volts) for a large collection of atoms.

These numbers were obtained from the U.S. National Bureau of Standards high resolution energy level tabulation using the multiplet averaging technique given by Slater.[1,2] Values for the transition elements can be obtained by the same expression for s and d electrons except $\varepsilon_s$ and $\varepsilon_d$ are defined by the Hyper Hartree-Fock equations,[3] and a division between that fraction of the d electrons which are 'core' and which 'valence' must be made. This is discussed elsewhere.[4]

Beyond its definition as the one-electron energy of the configurations which make up the Periodic Table, CE possess another equally important property: it is strongly correlated with the spacings of the one-electron energy levels (both occupied and unoccupied) of the atom in question. Large CE goes with large energy level separations, thus making a close connection between the magnitude of CE and the density of states in solids and molecules. This correlation follows immediately from the fact that the effective potential seen by an electron in an atom is funnel-shaped: deeper funnels have more widely spaced energy levels (this characteristic is familiar from the textbook example of the hydrogen atom and is shown schematically as Figure 7 of reference 2). In the paragraph below we discuss seven puzzling, and often misleading, features of the Periodic Table which are clarified by configuration energies.

## CONFIGURATION ENERGIES: CONSEQUENCES FOR THE PERIODIC TABLE

### Diagonal Line

The diagonal line in the Periodic Table, which separates metals from nonmetals, runs through the metalloid band containing the elements B, Si, Ge, As, Sb, and Te. Configuration energies precisely define this band and the division between metal and nonmetals: all elements to the right of the metalloids have higher CEs and are nonmetals, all those to the left have lower CEs and are metals. The band itself has an almost constant value of 12 ev (close to the middle of the CE scale) and it is the only nearly flat surface in the three dimensional Table (a variation of only 7% of the CE range).

### Metallization

As a group is descended in the p-block the chemistry of the elements does not remain constant, but experiences a progressive increase in metallic-like behavior, a well-known fact noted in every inorganic textbook. The atomic physics of this change is also understood: the size of the atoms is increasing, therefore both the magnitude of the average valence energy level and the spacings of the levels are decreasing. Bonding directionality is being lost because the s, p, and d levels are becoming nearly degenerate, allowing mixing in many combinations, and larger orbits encompass more neighbors, thus less directionality. These changes are precisely quantified by configuration energies.

### Radius

Radius, like energy, is another property that one might expect to be intimately associated with the Periodic Table. Almost all of the definitions, including those for positive and negative ions, have employed self-consistently defined dividing lines between atoms in known crystals. Another free atom based definition, the radial maxima of the outermost atomic orbital, has been recognized ever since the beginning of quantum

mechanics, and Slater[5] has shown that there exist a close parallel between these two different approaches. We have discussed and given plots[4] showing that for representative elements the outer radial maxima, $r_M$, is an inverse function of $CE$:

$$r_M = \text{constant} \, (CE)^{-b}$$

where b is a positive number between 1 and 2 varying smoothly with group number. Thus, this fundamental property can also be brought quantitatively into the compass of the Periodic Table.

## Oxidation State Limitation

Of the representative atoms, N, O, F, Cl, Br, He, Ne, Ar, and Kr are the only ones whose valence electrons cannot all be engaged in bonding, i.e., their fluorides cannot reach their group oxidation state. This is immediately explained by their $CE$s: these atoms have the nine highest values and they hold some or all of their electrons so tightly as to prevent them from being engaged in bonding. Because of their high $CE$ they have a correspondingly large energy gap to the first available unoccupied level, likewise discouraging bonding. The late transition metals also are unable to reach their group oxidation states, but this occurs for an entirely different reason. In this latter case some fraction of the d orbitals become core instead of valence. This is manifest both in $CE$ values and radial extent and is discussed more fully elsewhere.[4]

## Closed Shells

It is, of course, well known that closed subshells themselves do not prevent bonding, as illustrated by group II atoms. The possibility of closed subshell bonding is determined by relative configuration energies. Mg $3s^2$ has a low $CE$ and closely spaced levels, leading to a metallic solid. Ar $sp^6$ has a high $CE$ and widely spaced levels, leading to an inert gas.

## Multiple Bonding

In representative atoms, multiple bonding mostly involves first row p-block elements. This arises because the ratio of valence electron radial maxima to core electron radial maxima is very much greater for first row atoms than for the others and therefore two first row atoms or a first and second atom can get close enough together so that the nucleus of one atom is not far from the center of a perpendicular p orbital lobe on an adjacent atom. Large valence to core radius ratio is accompanied by large configuration energy therefore producing a low potential energy region of $\pi$ symmetry between the atoms. Transition metal multiple bonding is a more complex topic which awaits further calculations on transition metal $CE$s.[4]

## Van Arkel-Ketelaar Triangles

One version of these very useful Periodic Table aids is given as Figure 1. Everyone knows that the variations in bonding organized by the Periodic Table embraces the ionic (I), covalent (C), and metallic (M) extremes, and everyone knows that binary salts e.g., NaCl, are made by combining an atom from the left side with one from the right side, but the simple systematization of binary possibilities shown in these triangles can be illuminating, especially because of their quantification by $CE$ and $\Delta CE$. The

regions near the center of each leg are particularly interesting. Along a row in the Periodic Table, the horizontal M to C leg, the center corresponds to the metalloids (binary compounds can be designated inside the triangle as well as along its edges; Figure 1 does not show these for pedagogical simplicity) and to the binary compounds surrounding the diagonal line, *e.g.*, GaAs, AlP, InSb. Many of these compounds are commercially important semiconductors and photonic materials. Along the I–C leg there are well-known ionic and covalent solids and molecules, but in the middle, *e.g.*, $AlF_3$, there are fascinating complex polymers with a number of practical applications. Along the M–I leg are some of the least explored and exploited compounds of all: those combining atoms from Group I and II with those from Groups III, IV and V. These are the intermetallic Zintl phases which to date have been almost exclusively investigated by German preparative inorganic chemists.[6] Many of these are metallic-looking, ceramic-like semiconductors that have yet to find commercial application. A simple approach to the electronic charge distribution in these novel materials using *CE*s is given later in this article.
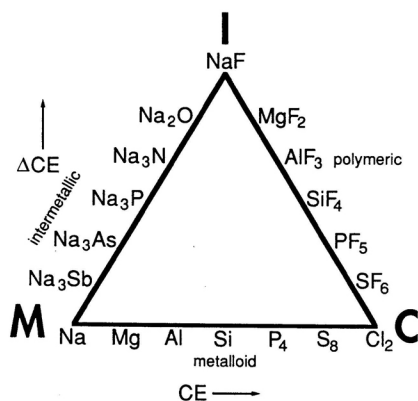


Figure 1. Van Arkel-Ketelaar Triangle illustrated for some Second Row atoms. M≡Metallic, C≡Covalent, I≡Ionic. *CE* ≡Configuration Energy.

## CONFIGURATION ENERGY AND ELECTRONEGATIVITY

Configuration energy was called spectroscopic electronegativity, $X_{spec}$, in a previous paper,[2] but at that time we did not realize the full implications of its intimate relationship to the Periodic Table. *CE* is conceptually and practically the most useful definition of electronegativity, but it now has a considerably enhanced role resulting from recognition of its strong correlation with energy level spacings and its function as the Periodic Table's third dimension. Its definition as electronegativity is best established by the close match between the Pauling's scale[7] and the Allred and Rochow scale.[8] This is shown graphically as Figure 3 in the previously noted paper.[2] For the representative elements, $X_{spec}$ »takes the average« of these two classic scales. $X_{spec}$ might even be said to adjudicate them, because there are two or three numbers of each scale that seem out of line, and in each case $X_{spec}$ comes closest to the most reasonable choice between the two, (*e.g.*, I, Br, and Cl in the Pauling scale, Al and In in the Allred and Rochow scale). A detailed search of the literature: textbooks, monographs, review articles, and

numerous individual research articles, from 1932 to the present, reveals that practicing chemists have overwhelmingly employed the Pauling and Allred and Rochow scales to rationalize chemical bonding phenomena (this is in sharp contrast, however, to most purely theoretical papers during the last 40 years, which have strongly favored the Mulliken definition[9]). It may also be noted that between the previous paper[2] and the present article, a change in units also has been put into effect. Pauling's arbitrary choice of values between 1 and 4 has proved to be too cramped: most physically useful scales (*e.g.*, dipole moment and Bohr atomic units) span a range of 1 to 10 or 1 to 20 and this is satisfied when electron volts are used. Most important, however, has been widespread recognition during the last five years that electronegativity is an *energy*,
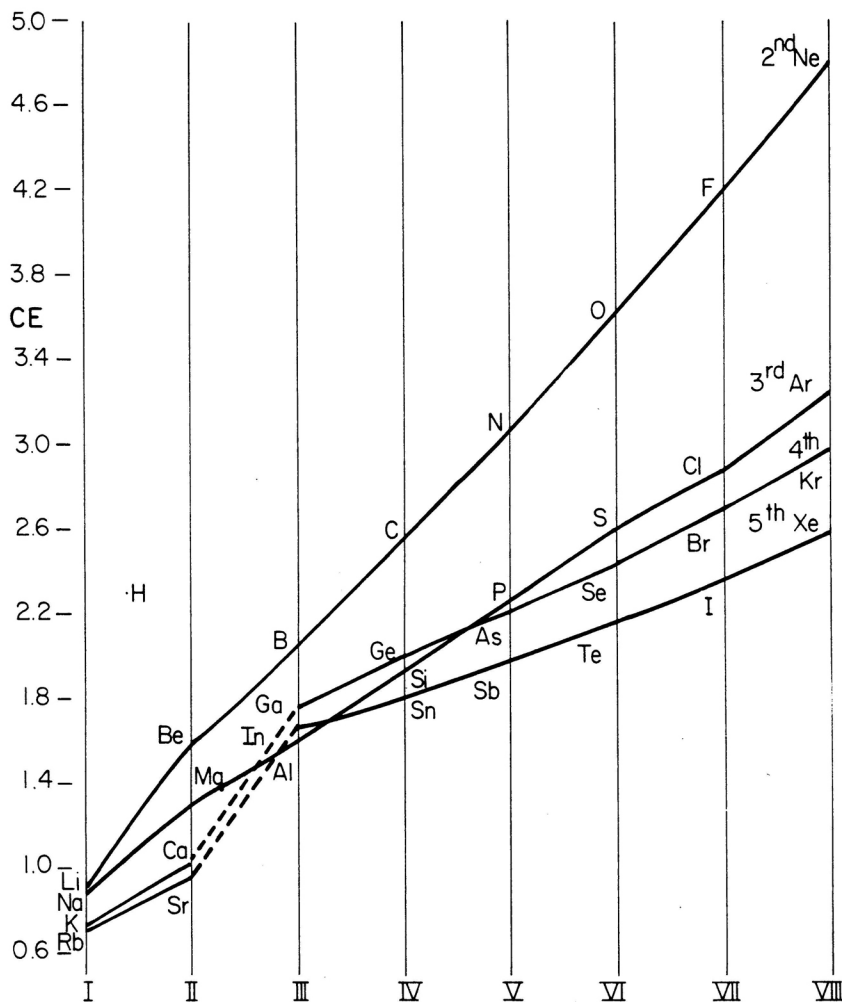


Figure 2. Configuration Energies *versus* Group Number. The scale for *CE* in this figure is Pauling units as given in Reference 2. To convert to electron volts multiply by 5.9152.

and because this energy is an average ionization potential, electron volts is the obviously appropriate choice.

An especially attractive feature of the free atom based $CE$s as electronegativity is the opportunity to take advantage of the truly high accuracy energy level data available from the National Bureau of Standards tables. (Detailed references to this data, and how it is processed, has been given in the previous electronegativity paper[2]). Figure 2, $CE$ *versus* Group, points out the quite significant advantage of high accuracy for these values: many of the materials science applications of these numbers involve the atoms Ga, In, Al, Ge, Si, Ge, As, and P. This new recognition of the utility of more precise electronegativity is a notable contrast to the long standing presumption of most organic chemists.

## CONFIGURATION ENERGIES: BEYOND THE PERIODIC TABLE

For many years there has been an over interpretation of Pauling's qualitative description of electronegativity as »the power of an atom *in a molecule* to attract electrons to itself«.[10] This was introduced seven years after his original, 1932, quantitative definition[7] (that resulted in quite accurate *atomic* values for 10 atoms). Thus, for almost the entire history of electronegativity there has been a search for scales that incorporate some molecular or solid state aspect (*e.g.*, bond energies, vibrational frequencies, dipole moments). Not surprisingly, the large collection of disparate, but qualitatively similar, set of values have led chemists to believe that electronegativity was an inherently 'fuzzy', ill-defined concept. This has been re-enforced by the large variety of units in which the proposed scales have been expressed. At the time of Pauling's early researches it was not possible to anticipate the truly remarkable bonding categorization and codification ability of the Periodic Table. Now, however, that vast store of empirical and computational data establishes without question the simple, zeroth order hypothesis that molecules and solids are made out of atoms (and LCAO wavefunctions) as the single most useful systematization of the structure of matter. It follows that »in a molecule« means the Periodic Table itself.

If one accepts the argument in the paragraph above, it then becomes even more interesting and relevant to go beyond the Periodic Table and attempt to translate $CE$ into a definition applicable to atoms as they exist in solids and molecules. This is clearly desirable because we are now able to start with the correct zeroth order approximation and systematically move to a higher order where we focus on a specific atom in a specific molecule. To achieve an *in situ* definition of $CE$ we need a molecular or solid state electronic wavefunction. We have accomplished this by devising a quantum mechanical projection operator whose expectation value yields the desired average one-electron energy of an atom in a molecule or solid.[11] This quantity has been designated $EI_A$, the Energy Index for atom A, and it is proving useful in explaining and unifying various physical organic properties such as rotation and inversion barriers and the anomeric effect[12] as well as bond polarities.

### Lewis-Langmuir Atomic Charges

As noted above, when one attempts to go from free atom $CE$ or electronegativities to the corresponding quantity for a specific atom in a specific molecule or solid, one needs a representation of the electronic structure of the molecule or solid in question. This point may seem obvious, but in the history of electronegativity there has been

TABLE I

*Configuration energies (electron volts)*

| Atom | Config. Energy[a] | Atom | Config. Energy[a] |
|------|------------------|------|------------------|
| H | 13.61 | K | 4.34 |
| He | 24.59 | Ca | 6.11 |
| | | Ga | 10.39 |
| Li | 5.39 | Ge | 11.80 |
| Be | 9.32 | As | 13.08 |
| B | 12.13 | Se | 14.34 |
| C | 15.05 | Br | 15.88 |
| N | 18.13 | Kr | 17.54 |
| O | 21.36 | | |
| F | 24.80 | Rb | 4.18 |
| Ne | 28.31 | Sr | 5.70 |
| | | In | 9.79 |
| Na | 5.14 | Sn | 10.79 |
| Mg | 7.65 | Sb | 11.74 |
| Al | 9.54 | Te | 12.76 |
| Si | 11.33 | I | 13.95 |
| P | 13.33 | Xe | 15.27 |
| S | 15.31 | | |
| Cl | 16.97 | Cs | 3.89 |
| Ar | 19.17 | Ba | 5.21 |
| | | | |
| | | Zn | 9.39 |
| | | Cd | 8.99 |
| | | Hg | 10.44 |

[a] Energy level data from National Bureau of Standards tables and A. A. Radzig, and B. M. Smirnov, *Reference Data on Atoms, Molecules and Ions.* Springer-Verlag, 1985. See ref. 1 of ref. 2 for detailed listing of sources, method for using data, and conversion to other units.

considerable confusion and wishful thinking on this matter. Part of this has arisen because those who have devised electronegativity definitions derived from molecular properties such as vibrational frequency, dipole moment, radius, electron affinity, and bond energies, have believed that their values were for 'an atom in a molecule'. But the molecular information content of any of these definitions is small compared to that required for the many environments possible for an atom in a molecule.[13] Likewise, such adjustment schemes as equalization of electronegativity are far too simple to adequately reflect molecular electronic structure.[14] On the other hand, the large inconvenience of generating and interpreting even simple electronic wavefunctions is a significant impediment to experimental chemists seeking quantitatively useful data on molecular charge distributions. This quandary can be resolved by using the simplest electronic structure model that has had a major influence on chemists' thinking: Lewis Dot structures. These structures are based on the assumption of pure homonuclear covalent links, therefore, no bond polarity information is present. This is reflected in the fact that formal charges ($FC$) are equal to zero for most atoms in most circumstances. (In cases for which $FC \neq$ e.g., $H_3\overset{\ominus}{B}-\overset{\oplus}{N}H_3$, the formal charges arise because the electron counting scheme only works when each atom of the bond contributes one electron and

is thus incorrect for coordinate covalent bonds and electron transfer situations). We have shown previously[15] that the formal charge formula can be extended so that atomic charges for polar bonds can be obtained from Lewis Dot structures. These have been designated as Lewis-Langmuir atomic charges:

$$LL_A = \begin{pmatrix} \text{Group} \\ \text{number} \\ \text{of A} \end{pmatrix} - \begin{pmatrix} \text{Number of} \\ \text{unshared} \\ \text{electrons on A} \end{pmatrix} - \left( 2 \sum_B \frac{CE_A}{CE_A + CE_B} \right)$$

For cases where $FC \neq 0$ the group number (effective nuclear charge), $n_A$, is referenced to zero to make $LL_A$ independent of the origin of the bonding electrons. E.g., $H_3BNH_3$, $FC_B = -1$ $\therefore$ $n_B = 3 + 1 = 4$, $FC_N = +1$, $\therefore$ $n_N = 3 + 1 = 4$ and:

$$LL_B = 4 - \frac{6CE_B}{CE_B + CE_H} - \frac{2CE_B}{CE_B + CE_N} = +0.370$$

Similarly, $LL_N = -0.626$, $LL_H(B) = -0.057$, $LL_H(N) = +0.143$. These charges are quite similar to those obtained by *ab initio* calculations (as are those for numerous other molecules[15]).

## $LL_A$ Charges for Zintl Phases

We have noted that the M–I leg of van Arkel-Ketelaar triangles contain the under investigated Zintl phases, and $LL_A$ charges can give useful insight into these potentially interesting technological materials. The nature of the bonding in these compounds is thought to obey the Zintl-Klemm model which posits an anionic covalent bond network of Group III, IV or V atoms interspersed by Group I or II cations. The coordination around the anions follows the 8-$N$ rule. NaTl is a classic example, and is formulated as $Na^+$ $Tl^-$. The Tl anions form a diamond-like covalent network ($N = 3 + 1$) and the imbedded $Na^+$ provide local electrical neutrality. Three stoichiometries of calcium silicon compounds illustrate the range of M-I materials, $Ca_2Si$, $CaSi$, and $CaSi_2$. Table IIA gives their structures and charge distributions. Table IIB gives results for CaSi, SrSi, and BaSi, and shows the effect of electronegativity changes on the cation. These two tables illustrate how use of configuration energies can greatly modify formally assigned charges. Although insufficient physical measurements have been made to date, it is hoped that $LL_A$ charges may be correlated with energy gaps.

TABLE II

*Atomic Charges for Zintl Phases*

| IIA | 8–N | Structure | $FC_{Ca}$ | $LL_{Ca}$ | $FC_{Si}$ | $LL_{Si}$ |
|---|---|---|---|---|---|---|
| $Ca_2Si$ | 0 | Separate Ions (Salts) | +2 | +0.598 | −4 | −1.196 |
| $CaSi$ | 2 | Planar Zig-Zag Chains | +2 | +0.598 | −2 | −0.598 |
| $CaSi_2$ | 3 | Hexane-like Sheets | +2 | +0.598 | −1 | −0.299 |
| **IIB** | | | | | | |
| CaSi | 2 | Planar Zig-Zag Chains | +2 | +0.598 | −2 | −0.598 |
| SrSi | 2 | Planar Zig-Zag Chains | +2 | +0.661 | −2 | −0.661 |
| BaSi | 2 | Planar Zig-Zag Chains | +2 | +0.740 | −2 | −0.740 |

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## SAŽETAK

### Periodni sustav elemenata navodi na krive zaključke, nekompletan je i neopravdano zanemaren

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Autor predlaže da se u periodni sustav uključe konfiguracijske energije atoma. One su povezane s mnogim atomskim svojstvima i objašnjavaju njihove promjene na prirodan način.