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RESEARCH NEWS

Beyond Mendeleev

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Undoubtedly one of the greatest intellectual triumphs of the last century is the classification of elements by Mendeleev. This classification had two mysterious features, viz. eight-fold periodicity and gaps. Mendeleev reserved the gaps for the elements to be discovered. Thus, he, in particular, predicted the element now called scandinavium.

Later Bohr found a rationale behind the classification of elements. This was largely a consequence of his atomic model wherein electrons were filled in successive shells of increasing energy. Interestingly, elements that occurred in the same group turned out to have identical electronic configurations for the outermost electrons. For example, all the elements of group '1' from hydrogen to francium have their outermost, single electron, in the 's' state. It also became clear, on this model, that the chemistry of an atom is decided by its outermost electrons. Later investigations confirmed many other implications of the Bohr model. In one stroke Bohr had unveiled the mystery surrounding the periodicity and the groups in the Mendeleev's classification. Figure 1 shows a modern version of the Periodic Table.

However, Bohr's explanation is too simple-minded to account for certain glaring ambiguities. For example, in transition elements instead of completing the '3d' state every extra electron goes into the '4s' state. We find such an anomaly in rare earths and in actinides

group / period	Ia	IIa	IIIb	IVb	Vb	VIb	VIIb	VIII			Ib	IIb	IIIa	IVa	Va	VIa	VIIa	0
1	1 H																1 H	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La *	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac **	104 *Rf*	105 *Ha*													

* 6	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
** 7	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Figure 1. The classical periodic table The thick zig-zag line is the 'diagonal line'.

as well. In other words the simple rule of filling successive shells breaks down. For such irregularities Bohr came up with an interesting explanation. He argued that it is energetically less favourable to accommodate successive electrons in the same shell and that they would rather go to the next higher shell. Later the unfilled states of the inner shells get filled. But these arguments cannot resolve the other peculiarities associated with the periodic table. For example, the belief that the elements of the same group are chemically identical is clearly belied. For instance in the 4th group, carbon (C) has nothing much in common with tin (Sn) or lead (Pb). Generally, it is tempting to conclude that the number of outermost electrons is the oxidation state of an element. This works all right for some elements, but completely misleads us when we came to N, O, F, Cl, Br, He, Ne, Ar and Kr. Again as we descend down a group in the 'p' block the elements become increasingly metallic. Another important related question pertains to the existence of the diagonal line separating the metals from the non-metals. In short, this beautiful citadel of elements has cracks all over.

The obsession to have a better periodic table of elements has urged some crusaders to suggest ways and means of overcoming some, if not all, of these deficiencies. The recent adventurist being Leland C. Allen of Princeton University. He suggests[1] that one more dimension is necessary to complete the periodic table. This dimension, in his opinion, is the configurational energy defined by

$$E_c = (a\,\varepsilon_s + b\,\varepsilon_p)/(a+b),$$

where a and b are occupancies and ε_s and ε_p are the ionization potentials of 's' and 'p' states of the representative atoms in the 'p' block elements. For 'd' block elements ε_p gets replaced by ε_d of $(n-1)$ shell. It so happens that a large value of E_c also means large energy level separation. According to Allen this parameter E_c answers many of the questions raised earlier. For example, E_c for all the elements to the right of the diagonal is always higher than E_c for all elements to the left of the diagonal. And for the metalloid band made up of B, Si, Ge, As, Sb and Te, Allen finds E_c to be nearly a constant. All the elements of higher E_c have higher energy level separation and are thus non-metals while low E_c elements have low energy separation and are therefore good candidates to be metals. Now as one descends down a group the atomic size increases. Hence the magnitude of the average valence energy level decreases. In addition, the spacing between the levels also decreases. We can convince ourself that these effects are plausible, by appealing to the elementary model of an electron in a box. In addition, the bond-directions lose significance since s, p and d levels become increasingly degenerate. Thus, the elements become more and more metallic as we go down the same group. Again, it is found that the values of E_c of N, O, F, Cl, Br and the noble gases are pretty high compared to all other elements. Therefore they have correspondingly large energy gaps between the levels occupied by their outermost electrons and the next unoccupied levels. This considerably restricts formation of chemical bonds by the outermost electrons. The bonding will be either partial, as in the case of N, O, F, Cl and Br where only a few outer electrons take part in bonding, or totally absent as in the case of noble gases.

All these arguments could have been undertaken with any other atomic parameter like the atomic radius, polarizability or ionization potential, etc. In fact, these have been employed in the previous attempts at understanding the periodic table. But Allen states that none of these can compete with E_c when one is looking for a third coordinate for every atom. This coordinate is an addition to its already established coordinates, viz. period and group. It must be remarked that Allen identified E_c with the electronegativity of the atom, which was introduced by Linus Pauling[2] nearly half a century ago as independent additional parameter. Pauling analysed the periodic table in terms of this parameter. This work of Allen stimulated a

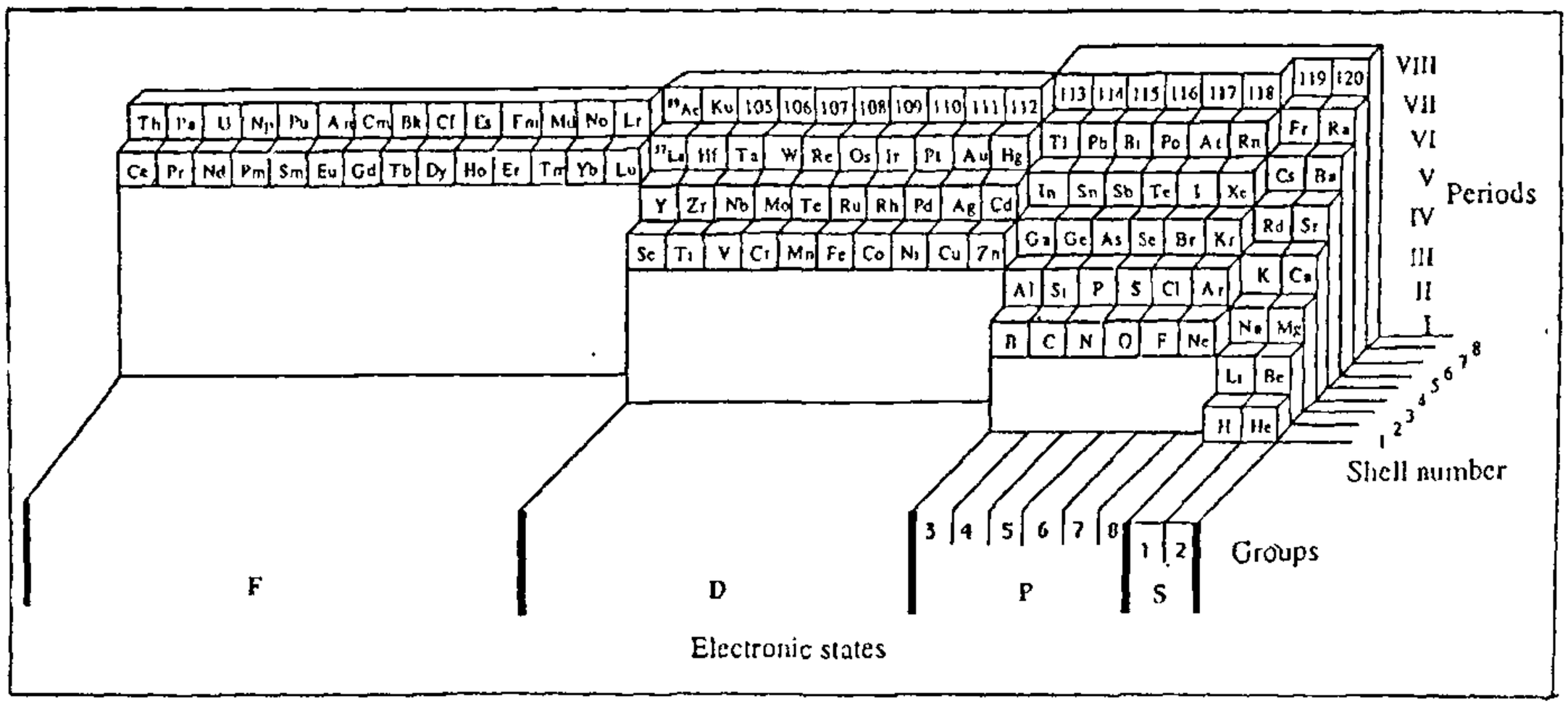

Figure 2. Three dimensional periodic table of elements built in accordance with Hund's rule (After Magarshak and Malinsky[4])

skeptical response from John Maddox[3] of *Nature* who wondered whether the configurational energy E_c was powerful enough to resolve the many inconsistencies of the classical classification.

More recently there has been an altogether different approach to this problem. Magarshak and Malinsky of the Department of Mathematics of the Mount Sinai School of Medicine, New York, have come up with a 'genuinely three dimensional' periodic table. They suggest[4] a three-dimensional stacking of elements based on Hund's rule[5] according to which a spectroscopic term of largest total spin S will be of the lowest energy. And among such terms the ones with largest total angular momentum L are of lowest energy. Since these terms are all well-documented[2,6] it is not difficult to get the three-dimensional table shown in Figure 2. The number of chemical elements in successive periods is given by:

2, 2, 8, 8, 18, 32, 32.

Thus, for instance, in the first period only H and He exist. The second consists of only Li and Be. In the three-dimensional periodic table the third dimension is the periodic number $(n+1)$. All the elements at the same level have same $(n+1)$. A period corresponds to passing from one element to another at the same height from left to right. Group numbers are the accepted classical ones. Projection of this figure along the axis of shell number gives the traditional two-dimensional periodic table. Projection along the axis of period gives a two dimensional realization of Hund's rule. Magarshak and Malinsky conclude: 'We believe that our three dimensional representation is a useful tool for visualizing properties of chemical elements and is in complete agreement with quantum mechanics.'

Interestingly the game started long back by Mendeleev is still enchanting to some. There appears to be still a lot to be probed into.

1. Allen, L. C., *J. Am. Chem. Soc.*, 1992, **114**, 1510.
2. Pauling, L., *The Nature of the Chemical Bond*, Cornell Univ. Press, 1940.
3. Maddox, J., *Nature*, 1992, **356**, 13.
4. Magarshak, Y. and Malinsky, J., *Nature*, 1992, **360**, 114.
5. Hund, F., *Linenspectren und Perodisches System der Elemente*, Berlin, 1927.
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On the right *trk*

Mahendra Rao

Nerve growth factor (NGF) is a prototypic member of a family of trophic molecules that include. brain-derived neurotrophic factor (BDNF), neurotrophin-3 (NT-3) and neurotrophin-4/5 (NT-4/5). These low-molecular peptide molecules share structural and topological homology and have both overlapping and distinct effects on the survival of various neuronal subsects.

Two classes of receptors based on binding affinity have been identified — low affinity binding which has a KD in the nanomolar range and a high affinity binding in the picomolar range. The protein which is responsible for the low affinity binding, low affinity NGF receptor (P75LNGFR) has been identified and cloned and shown to bind to all the neurotrophins tested with roughly the same KD. High-affinity binding receptors for the neurotrophins (the TRKs have also been identified. Expression cloning and scatchard analysis have shown partial specificity for neurotrophin binding. For example, TRK-A binds NGF preferentially. But will also bind NT-3 and NT-4/5. Other experiments have shown that TRK expression is both necessary and sufficient to mediate high affinity binding and signal transduction *in vitro*.

These results have left the role of the LNGFR unclear. Several functions have been postulated including aiding in the discrimination between neurotrophins and/or forming high-affinity-receptor complexes (see ref. 1 for review). The first paper discussed demonstrates an important role for the LNGFR and the second paper demonstrates a difference in the specificity of trophin binding to naturally occurring dorsal root ganglion cells and TRK receptors expressed on cell lines by transfection.

Lee *et al.*[2] have disrupted the LNGFR gene and generated transgenic mice which lack detectable LNGFR expression. Analysis of the mice shows that LNGFR plays an important role in neuronal development. Homozygous LNGFR negative mice show a pronounced sensory deficit. Examination of the dorsal root ganglion suggests that this is due to a loss of a subset of sensory neurons. In contrast, sympathetic neurons that are also NGF-dependent appear normal in number and project to appropriate targets. Thus while some trophin functions seem to require LNGFR expression others seem to be independent.

Carroll *et al.*[3] also noted a loss of a specific subset of neurons in the dorsal root ganglion after injecting NGF antibodies *in utero*. The authors were able to demonstrate that the neurons lost were specifically those that expressed the TRK-A receptor (relatively NGF-specific), suggesting that *in vivo* (as *in vitro*) NGF acts selectively on TRK-A expressing neurons. Equally importantly other neurotrophic molecules which are present (and presumably support the non-NGF dependent cells) cannot substitute for NGF in the NGF-dependent cells, suggesting that other neurotrophins cannot bind the TRK-A receptor *in vivo*. Consistent with this result are supporting data from binding studies in primary DRG neurons suggesting a far greater discrimination by TRK receptors, between trophins, than that suggested by the binding data from transfected cells[4]. Further, since the LNGFR is present on both TRK-A expressing and non-expressing cells and since only TRK-A expressing cells are lost after NGF antibody treatment, the LNGFR is not the primary effector of NGF action *in vivo*.

The two papers taken together suggest a possible function for the LNGFR and provide a model for testing this hypothesis. *In vivo* the LNGFR may serve to