Extra-mural research funding at present estimates is about Rs 250 crores. There is an estimated need to double the grants for sponsored research. Do you want to comment on this?

It is always desirable to have more funds for sponsored research. In technology, if the research is not sponsored, then one does not know its commercial value. It must come from the industry, mostly.

The Prime Minister, in his inaugural address at the Indian Science Congress of 3 January 2001, stated that the government would hike investments in the R&D sector to 2% of GDP from its present level of about 0.92%, within the next five years. When can we expect a perceptible change?

When it becomes 1.25.

Is the government considering raising (doubling) the renumeration of JRF/SRF fellows and research associates?

At present, there is no such plan on the board. There are also very special scholarships available (S. P. Mukherjee scholarships, 25 in all), five in each

discipline. These in itself are a good number. We are also having a CSIR students' scheme. We can only do as much as funds will permit. We wish to do it but....

On some broader issues

Can you elaborate on the necessity for having both a SAC-C and a Cabinet Committee on S&T? To the S&T on-looker, the SAC-C appears to be mostly non-functional. Your comments?

SAC-C is making reports, many of its contents do not come in the limelight. They are working. They hold meetings and they make reports.

There is a feeling that agencies are not treated at par. In fact, there is an unwritten 'social order' that is said to prevail. In this context, some of the agencies such as IMD (doing important monsoon research, vital to India), ICMR, ICAR, Survey of India, Zoological and Botanical Surveys of India need far greater support than they receive at present. What is your feeling?

All scientific activities need support.

On international cooperation

Today China is an academically advanced society. There is a China–US Academic Programme. Are you also thinking on the same lines ?

I do not copy programmes. We also have established an Indo-US Joint S&T Forum.

Are there any new plans afoot for regional cooperation in S&T especially with South-East Asian countries?

We have many programmes, we are helping them. Their students are coming here. Also some of our institutions are going there, for example, Manipal is going to Malaysia, Indonesia, Bhutan and Nepal. Dabur has gone to Nepal. We have good scientific exchange with Bangladesh. And also with Myanmar. Whatever we have, we are willing to share with our neighbours.

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RESEARCH NEWS

A molecular abacus for electrons

A. G. Samuelson

Counting electrons has been a favourite pastime for chemists. And for good reason. It was Mendeleev's intuitive counting, even before electrons were discovered, that gave birth to the periodic table of the elements. On the basis of magic numbers of electrons around an atom (2, 8 or 18), one could systematize a vast body of chemistry. The electronic properties of most compounds, complex as they may be, could be rationalized by counting the number of electrons.

Extra stability associated with planar conjugated structures containing a ring of atoms was pointed out by Hückel. If

$4n + 2\pi$ electrons were present, the ring had unusual stability and it was considered aromatic. Much later, Woodward and Hoffmann showed the importance $4n + 2\pi$ electrons in reactions. The magic numbers associated with cage structures such as boranes were more difficult to unravel. Lipscomb was the pioneer in organizing the growing body of information in the sixties and seventies. The most succinct exposition of the rules governing three-dimensional structures came from Wade[1]. Wade's rules helped in understanding the electronic requirements of boranes, carboranes and other heteroboranes. In

conjunction with the isolobal analogy of Hoffmann, the stability of very complex polyhedral structures could be understood and predicted.

Extension of Wades' $n + 1$ skeletal electron pair rule, where n is the number of vertices in a closed polyhedral structure, to a collection of polyhedra condensed to each other was not simple. The plethora of crystallographically characterized macro-polynuclear clusters involving metalloboranes, metallocenes and other heteroboranes kept many computational chemists busy, but no unifying principle seemed to emerge. The variety of ways cages are put
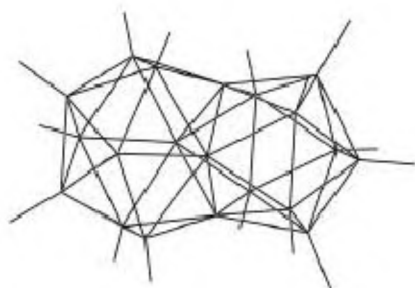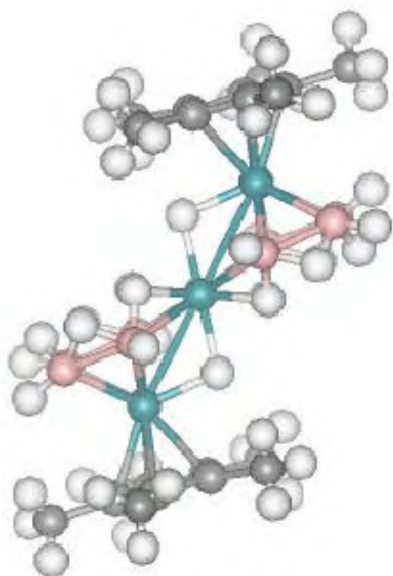
Figure 1. A stick diagram of $B_{20}H_{16}$.

Figure 2. A ball-and-stick model of $Cp^*RuB_4H_{10}Ru\ B_4H_{10}RuCp^*$.

Box 1. Chemistry and counting.

Mendeleev	1869	Periodicity in properties of elements noted!
G. N. Lewis and I. Langmuir	1916	Stable shells of electrons 2, 8, 18.
Hückel	1931	$(4n + 2)\pi$ electrons in planar conjugated systems
Woodward and Hoffman	1965	$(4n + 2)\pi$ electrons in transition states.
Wade's rules	1976	$(n + 1)$ electron pairs for skeletal bonding.
Jemmis rules	2001	*mno* rule for macro polyhedral structures.

B1. Dmitrii Mendeleev, *Z. Chem.*, 1869, **12**, 405.
B2. (a) Gilbert N. Lewis, *J. Am. Chem. Soc.*, 1916, **38**, 762; (b) Irving Langmuir, *J. Am. Chem. Soc.*, 1919, **41**, 868.
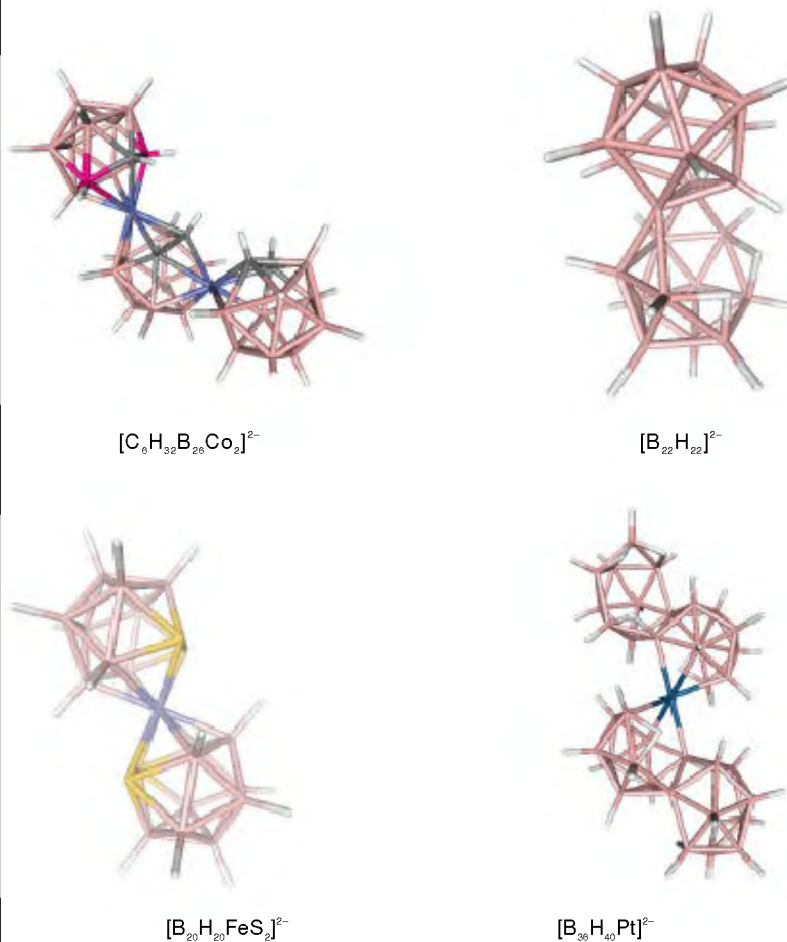B3. Hückel, E., *Z. Phys.*, 1931, **72**, 204.
B4. Woodward, R. B. and Hoffman, R., *J. Am. Chem. Soc.*, 1965, **87**, 2511.
B5. Wade, K., *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1.
B6. Jemmis, E. D., Balakrishnarajan, M. M. and Pancharatna, P. D., *J. Am. Chem. Soc.*, 2001, **123**, 4313.

Box 2. Macropolyhedral heteroboranes.

$[C_6H_{32}B_{26}Co_2]^{2-}$

$[B_{22}H_{22}]^{2-}$

$[B_{20}H_{20}FeS_2]^{2-}$

$[B_{36}H_{40}Pt]^{2-}$

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together makes a single uniform princi-
ple virtually impossible. But that is
precisely what Jemmis from the Univer-
sity of Hyderabad has achieved[2]! In a
recent issue of the *Journal of the
American Chemical Society* he has
propounded a new electron counting
scheme for three-dimensional cages
linked together[3].

The beauty of the rule lies in its
simplicity. It only requires one to count
the clusters, the pairs of electrons in
each cluster and the vertices shared
between clusters. In the case of borane-
based clusters, the number of B-H units
translate to the pairs of electrons. A C-
H instead of B-H increases the number
of electron pairs for a vertex to 1.5.
Jemmis makes it sound as simple as A,
B, C. Only the alphabets of this electron
counting rule begin much later at *m*, *n*

and o! A few modifications are made for the vertices that are missed identified by the letter p and the extra caps by the letter q.

The utility of the rule is easily seen from the following examples. For the icosahedral $B_{12}H_{12}^{-2}$, $m = 1$, $n = 12$ and $o = 0$, so that the simple Wade's $n + 1$ rule is obtained. Twelve BH groups (each contributes an electron pair) and the -2 charge together makes the $n + 1$ electron pairs. The $B_{20}H_{16}$ has two polyhedra (Figure 1) so that $m = 2$. The number of vertices is 20. There is no single-vertex bridge so that $o = 0$. Thus 22 electron pairs are expected. The 16 BH groups provide 16 and the four boron atoms provide 6 electron pairs so that $B_{20}H_{16}$ must be neutral as indeed is found experimentally. Ferrocene, $C_5H_5FeC_5H_5$, can be treated as two pentagonal bipyramids (pbps) connected through the vertex Fe, except for the absence of the two apical atoms along the five-fold axis which would have completed the two pbps. Thus, $m = 2$, $n = 11$, $o = 1$, $p = 2$. The 16 electron pairs come from 10 CH groups and the divalent Fe. The necessity of the mno rule is easily seen with the molecule $Cp^*RuB_4H_{10}RuB_4H_{10}RuCp^*$, where Cp^* stands for pentamethylcylcopenta-dienyl ligand (Figure 2). One cannot use Wade's rules on the molecule as a whole. Although it is symmetrical, it is not easy to break this molecule into easily understood fragments. While the familiar Cp^*Ru^+ fragment is discernible at either end, the central framework containing two boron cages joined together with Ru is not readily understood. The rules devised by Jemmis elegantly explain why this 64 electron cluster is stable. The cluster has 4 cages ($m = 4$) and there are 21 vertices ($n = 21$). The four clusters are joined together at three vertices and so that requires 3 more pairs of electrons

($o = 3$). Finally, to make each of these clusters a closo-unit-one has to add four vertices. This requires 4 electron pairs more ($p = 4$). So the total number of electron pairs needed for this cluster would be 32, and that is exactly what this molecule has. Ruthenium has 8 d-electrons but it hides 6 electrons in a t_{2g} shell. So each Ru is equivalent to a B-H unit and gives 2 electrons. Each C-Me unit is isolobal with a C-H and so gives 3 electrons.

The rule is comprehensive in its scope and explains the stability of horrendous boron-based cages 20 Å long and 100 atoms big. What is interesting is that a wide variety of elements could be used to link these cages together. With transition elements one has to count only the electrons involved in skeletal bonding. Apart from this complication, the rule is easy enough for a back-of-the-envelope calculation. The mno rule reduces to the $4n + 2\pi$ electron rule for condensed systems where condensation is through edge-sharing.

The structural relations that exist between benzene, condensed aromatics and graphite in group 14, can be extended to group 13, as seen in the now famous MgB_2. But the polymorphs formed by boron which are covalent solids, are not so easily understood. For the first time, the electronic requirements of the thermodynamically most favourable polymorph of elemental boron, the β-rhombohedral boron has been explained using the mno rule[4]. The idealized unit cell of this polymorph has 105 atoms. These can be divided into two groups of 48 and 57 atoms. Careful X-ray structural studies had shown that the B_{57} unit has always partial occupancies corresponding approximately to a vacancy of one boron atom so that there are three electrons less. On the other hand several large formally vacant holes in the B_{48} part has partial occupancies

which total to $B_{2.66}$ which equals 8 ($3 \times 2.66 = 8$) electrons. Why should there be vacancies and extra atoms at the same time?

The B_{48} unit is the equivalent of 4 B_{12} units obtained by breaking 2c–2e bonds. Each of these B_{12} units requires 2 additional electrons, analogous to the $B_{12}H_{12}^{2-}$ ion. Thus this B_{48} unit is electron deficient to the tune of 8 electrons! The B_{57} unit which cannot be further divided into smaller fragments by breaking 2c–2e bonds has to be treated as such. According to the mno rule the B_{57} unit has three additional electrons than it requires. That explains why there are vacancies. The new electron counting rule has solved a long standing mystery.

Apart from the fact that it accommodates old rules, and explains difficult structures, it is satisfying to note that Jemmis has rationalized the new rules using fragment molecular orbital theory. One hopes that Jemmis would follow up this beautiful explanatory work with predictions on how new clusters can be strung together to form a necklace on the face of modern chemistry. Where else could it come from but from Hyderabad, the home of pearls?

1. Wade, K., *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1.
2. Ritter, S. K., *Chem. Eng. News*, 2001, **79**, 53.
3. Jemmis, E. D., Balakrishnarajan, M. M., and Pancharatna, P. D., *J. Am. Chem. Soc.*, 2001, **123**, 4313.
4. Jemmis, E. D., Balakrishnarajan, M. M., *J. Am. Chem. Soc.*, 2001, **123**, 4324.

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