is to be any recovery. The mechanism by which active fibres can apparently displace inactive fibres is obviously of great importance and as yet not understood.

This knowledge of the organisation of the primary visual cortex is being used to understand the activities of other visual areas and is forcing reconsideration of present ideas on the *modus operandi* of all other cortical areas. □

Rules for chemical reactions

from Graham Richards

One half of the Nobel Prize in Chemistry was awarded to *Kenichi Fukui,* Kyoto University and the other half to *Roald Hoffmann,* Cornell University, for their theories concerning the course of chemical reactions.

THEORETICAL CHEMISTS often seem to work at one of two extreme ends of the same problem. Either they do highly accurate calculations on small molecules or crude, even qualitative, investigations of larger molecules which are closer to the molecules synthesized and used at the laboratory bench. Both Fukui and Hoffmann belong to the latter school. Their work has added an excitement to broad areas of organic chemistry. The culmination of their research in the form of the Woodward–Hoffmann rules represents what is perhaps the most significant single step in organic chemistry in the post-war period.

The chemistry of a molecule is determined by the distribution of its electrons and by how tightly these electrons are held at particular locations in the molecule. Fukui's method of frontier molecular orbitals concentrates on the electrons which are the most loosely bound. If a reactant is involved in donating electrons to form bonds then the electrons involved are most likely to be those most easily removed. Conversely, if a molecule reacts by virtue of acceptance of electrons into a previously unoccupied molecular orbital then the bond will be created in the region where the extra charge is most readily accepted. Frontier molecular orbital theory then looks quantitatively at electron density distributions in the occupied molecular orbital which is highest in energy terms and at the lowest unoccupied molecular orbital. The new acronyms HOMO and LUMO abound in current literature on organic and medicinal chemistry.

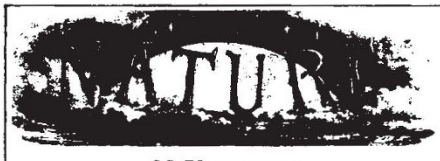
Frontier orbital theory is based on the perturbation treatment of molecular orbital theory introduced by Coulson and Longuet-Higgins. It deduces conclusions about chemical reactions by looking at the interaction of the reactants, assuming that the position of the transition state on the potential energy surface can be deduced from the initial slope along the reaction coordinate; the smallest slope is identified with the lowest energy transition state and consequently the fastest reaction or preponderance of products. Fukui's ideas were developed and exploited in the early days when theoreticians were not blessed with large computers and in consequence restricted to pi-electron systems and the simple Hückel molecular orbital method. This limitation nonetheless allows consideration of the reactivities of all the aromatic molecules of orgnic chemistry since their reactions are largely those of the delocalised pi-electron system built from atomic 2p atomic orbitals.

Hoffmann's first major contribution to theoretical chemistry was to extend the formalism of the pi-electron Hückel theory to include sigma electrons. Thus molecules of the aliphatic type such as ethane could be considered as well as aromatics such as benzene. This simple semi-empirical molecular orbital technique is still widely used since it can treat very large molecular systems without demanding anti-social amounts of computer time.

Experience gained from extended Hückel calculations led to the now famous Woodward–Hoffmann rules which Fukui showed could be explained by frontier orbital theory, (although there are other explanations including symmetry arguments). The idea of Hoffmann and the late Nobel laureate R.B. Woodward explains why, for example, maleic anhydride reacts easily with butadiene but not at all easily with ethylene. In the former case two new carbon–carbon bonds are made simultaneously and the electrons which are involved complete a circuit. Concerted and cyclic reactions of this type are called pericyclic and this example is a cycloaddition. Woodward and Hoffmann's rules start with a consideration of the molecular orbitals of the reactants and match up the electron densities in occupied and unoccupied molecular orbitals. A correlation diagram permits a simple decision to be made as to whether a particular reaction is allowed or not.

Vast numbers of applications of the Woodward–Hoffmann rules are to be found in recent literature and perhaps the best testament to the power and range of applicability of these rules is to quote in its entirety the first paragraph of chapter 12 from the eponymous pair's book *Conservation of Orbital Symmetry*; Chapter 12, Violations "There are none!" □

Graham Richards is lecturer in Physical Chemistry at Oxford University.

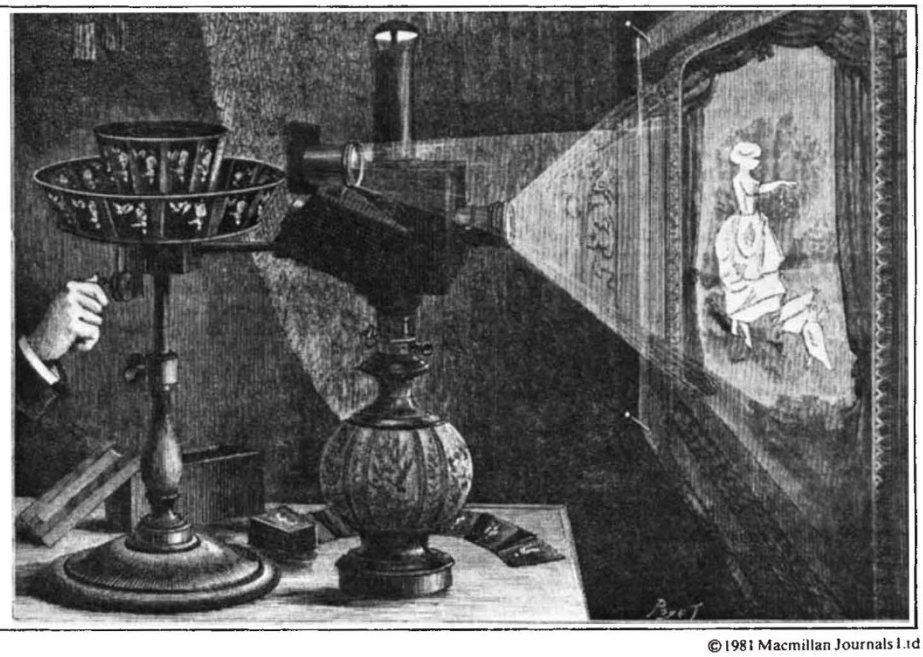


99 Years ago

THE PROJECTION PRAXINOSCOPE

M. Gaston Tissandier describes in *La Nature* an ingenious adaptation of the praxinoscope by means of which the images are projected on a screen, and are visible to a large assembly. M. Reynaud, the inventor obtains at once the projection of the scene or background — by the object-glass which is seen at the side of the lantern — and of the subject, by another object-glass which is shown in front of and a little above the same lantern. In making the two parts of the apparatus converge slightly, the animated subject is brought into the middle of the background, where it then appears to gambol. A hand-lever on the foot of the instrument allows a moderate and regular rotation to be communicated.

From *Nature* **27**, 61, November 16, 1882.



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