

## Erich Hückel (1896–1980)

### Gray's words

*"Full many a gem of purest ray serene  
the dark unfathom'd caves of ocean bear  
Full many a flower is born to blush unseen  
and waste its sweetness on the desert air"*

strike a chord in all of us, perhaps conjuring up images of poets who spoke in forgotten tongues and creative artists who lived amongst insensitive people. We do not expect scientists to fade away unnoticed in like manner because of an unreceptive audience. Certainly not in this century! After all, religious authoritarianism does not shackle science the way it did in the middle ages. Science has also become truly international, allowing noble thoughts to come from all sides. Unfortunately, these expectations prove to be naive. Many great ideas have not found ready acceptance, in spite of their obvious merits. Erich Hückel belongs to the unfortunate category of scientists whose creativity was nipped early, mainly because his own fraternity as well as the clientele he was addressing dismissed or ignored his contributions.

Chemistry students would encounter the name of Hückel in different contexts. The simplest formulation of quantitative molecular orbital theory is the Hückel MO (HMO) method. Application of the procedure to unsaturated organic systems is a standard part of the curriculum. Even students who do not know the details of HMO theory are expected to know the ' $4n+2$  rule' for predicting the stability of cyclic conjugated systems. Hückel makes an appearance in electrochemistry too. The first successful description of the non-ideal behaviour of ionic solution is the well-known Debye-Hückel theory.

Many students react with surprise when told that it is the same Erich Hückel who is associated with both theories. While the topics are widely different, there are several common features in the approach employed. The primary goal in each case is to understand a complex, but interesting chemical problem. Drastic simplifications are made, but with well-defined physical basis. The formulation is quantitative. Most importantly, general predictions are made which are amenable to experimental verification. All the features which one would like to have in a good theory!

It would therefore come as a shock to realise that Hückel was academically humiliated and his contributions scorned during much of his lifetime. While the suffering caused to the scientist is intense, irreparable, and attracts our sympathy, the retardation caused to the progress of the scientific field is a matter of general concern. Since it is relatively recent history, it is worth examining what went wrong.

The beginnings were auspicious. Erich Hückel was born (1896) in a family with a strong interest in pure science. He married Anne, daughter of a Chemistry Professor, in 1921. His father-in-law, Richard



Zsigmondy, went on to win the Nobel Prize in 1925. Hückel obtained his DPhil at Göttingen under the guidance of Peter Debye (Nobel Prize in Chemistry, 1936) with a thesis on an experimental study of X-ray scattering. Hückel then worked with the eminent mathematician David Hilbert and returned to Debye's group at Zürich. The theory of strong electrolytes was developed during this period. It never became known who, if any, was the dominant partner. In any case, the work did not fetch Hückel an immediate faculty position. He became a wandering post-doc, first with Donnan in London, then with Niels Bohr at Copenhagen, later with Werner Heisenberg and Hund at Leipzig and finally got a position of sorts in Stuttgart in 1930. Those were the heady days when the framework of quantum mechanics was fully constructed and waiting to be applied to different problems. Bohr suggested to Hückel that chemistry would be an appropriate area in which fruitful applications may be possible. Hückel chose problems involving unsaturated carbon compounds for study, presumably because his elder brother Walter was an accomplished organic chemist.

Between 1930 and 1937 (referred to as the 'seven years of disgrace' by his wife because of his uncertain academic status), Hückel published 17 papers on the nature of bonding in carbon compounds and related problems. First, he proposed an explanation for the large barrier to rotation about carbon-carbon double bonds. Hückel extended the description of bonding in the oxygen molecule (worked out by J E Lennard-Jones) to formaldehyde and then on to ethylene. He generalised the concept of two non-equivalent  $\sigma$  and  $\pi$  bonds, rigorously valid for diatomics, to polyatomic systems as well. It provided a beautiful interpretation for van't Hoff's empirical structural proposals.

Hückel then tackled the problem of bonding in benzene. At Leipzig, he had been intimately aware of the work of a colleague, Felix Bloch, on the band structure theory of metals (Bloch went on to win the Nobel Prize in Physics for his equations in nuclear magnetic resonance). In a sweeping simplification, Hückel considered the nature of energy levels for electrons confined to a 'lattice' of just six carbon atoms in a ring. He worked out the mathematical details, which are familiar now, and showed how the system is highly stabilised. He generalised the results for all carbon chains and rings. He pointed out that the energy levels for chains are non-degenerate, while for the rings, the lowest energy level is uniquely stabilised, followed by a series of doubly degenerate levels. He correctly worked out the implications of these results. Cyclic conjugated systems would have a closed shell only with 2, 6 or 10 electrons. These electron counts would lead to aromaticity. On the other hand, presence of 4 or 8 electrons would lead to open shells. Hückel further showed that these ideas can be applied to polycyclic compounds as well. Significantly, Hückel seriously evaluated the use of valence bond (VB) theory for these problems and concluded that it was 'decisively unsuccessful'. For example, the theory in its classical form incorrectly predicts that cyclobutadiene is resonance-stabilised in the same way as benzene.

Instead of being hailed for these remarkable insights, Hückel was totally ignored for several decades. Although he got a position in Marburg, he was promoted as a full professor only in 1961, a year before



his retirement. Physicists did not have a high opinion of him. After all, in the thirties, 'second rate physicists were coming up with first rate ideas'. In any case, with all its approximations and the nature of problems examined, HMO theory was too low brow. On the other hand, chemists in Germany held (hold?) the view that 'chemistry is what chemists do'. So papers with many equations were not considered in any way relevant to their work. The well-known organic chemist Hans Meerwein (of the carbocation and rearrangement fame) was trying to get a student to make cycloheptatrienyl anion in 1950, without realising that his colleague in the physics department had predicted the ion to be an unstable triplet species. In England, a small group of theoretical chemists (notably C A Coulson and H C Longuet-Higgins) appreciated Hückel's work, but their view did not percolate to the influential organic chemists at that time. The stability of the aromatic sextet remained a puzzle for them. In USA, Linus Pauling and resonance theory dominated the scene. Hückel was relegated to a footnote in *The Nature of the Chemical Bond*. Organic chemists were quite comfortable with resonance theory. It was easy to use and they were willing to overlook the faults.

To the credit of organic chemists, they resurrected Hückel theory through their own efforts. When many natural products with the tropolone skeleton were isolated, W von E Doering saw it as proof of Hückel's prediction. The polarisation of the carbonyl group effectively results in a 7-membered ring with  $6\pi$  electrons. In the following years, the validity of the ' $4n+2$ ' rule became firmly established. The influential physical organic chemist J D Roberts, while preparing for a course, discovered the simplicity and power of HMO theory. In his autobiography, he tells the amusing story of making some German organic chemistry professors set up the secular determinant for simple systems in a public forum. M J S Dewar worked out several important results based essentially on HMO theory. K Fukui used Hückel's  $\pi$  MO's effectively in conjunction with his frontier orbital theory. R Hoffmann worked out the Extended Hückel Theory, applicable to any chemical system. The latter two shared the Nobel Prize in Chemistry in 1981 for their study of chemical reactions. The wheel has now turned full circle with some chemists striving hard to make new molecules which are not predicted to be stable by Hückel's theory.

Hückel remained bitter and withdrawn. He made some efforts to work on the theory of the nucleus, something his fellow-physicists might appreciate, but gave up soon. It is sad that his creativity ran out so early.

To make amends for the past acts of omission, the German Chemical Society and the German Physical Society jointly awarded the Otto Hahn Prize in 1966, coinciding with the centenary celebrations of Kekulé's benzene structure. Hückel accepted the award but excused himself from the ceremony, partly because of his state of health and also because he 'dreaded the pompous style in which the Kekulé symposium was planned'.

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