The Conversation Continues II

Dear Roald, Sason, and Philippe:

I read your recent "Conversation"[1] with interest and would like to extend some of Jack Roberts's comments. I realize that you did not plan to write a history of the roles of MO and VB theory in chemistry. But your presentation carries the *impression* of such a history in a fashion that I think is misleading. First, I think you seriously underplay Michael Dewar's role in this story. He is barely mentioned once in your article, and you three do not appreciate the influence he had on the chemistry of the 1950s and 1960s. Of course, this is understandable since Sason and Philippe were barely born at this time. You mention Moffitt almost in passing but have no idea how significant his paper[2] on ferrocene was. I still remember the pleasure I felt reading it (like the pleasure in a work of art!)—it explained the stability of ferrocene and its chemistry in a way that the resonance or VB theory of the time couldn't touch. Moreover, it had predictability, such as my later extension of the same picture to f-orbitals and the discovery of uranocene.[3]

Your treatment also fails to appreciate the role that perturbation theory (as developed in part by Fukui but mostly in chemical terms by Dewar) has played. There is no counterpart in resonance theory to the landmark 1952 *J. Am. Chem. Soc.* papers of Dewar[4] (which are not mentioned in your Conversation). It's true that the formalism presented (theorems and proofs) kept them from having much of a direct effect on practicing chemists, but the fundamental basis was laid, and Dewar himself-made subsequent direct use of these principles. Perturbation theory as applied to reactivity, pericyclic reactions, etc. is so straightforward in terms of HOMO−LUMO interactions that the resonance (and VB) theory of the time couldn't come close. The Möbius strip analogy used so brilliantly by Zimmerman[5] is an example that again has no simple counterpart in resonance/VB theory. It's true that I myself did not appreciate this aspect of perturbation theory at this time and did not dwell on it in my 1961 book, but it played a major role not long thereafter—and makes Woodward−Hoffmann clearer and simpler as I pointed out in my *Science* paper interpreting the Nobel prize to Roald Hoffmann and Kenichi Fukui.[6] Jack Roberts points out that our books[7,8] had a major impact at the time and that you gloss over this role. But they were very popular and my book particularly has been highly cited. I recall that Springer was thinking about a German translation but discovered that everyone in Germany already had the English version! One reason for its popularity was perhaps that it documented the many quantitative correlations that even simple Hückel theory provides for many physical, chemical, and reactivity properties of conjugated molecules. Resonance/VB theory simply could not provide comparable quantitative correlations.

The $4n + 2$ rule that comes so simply from even the simplest MO theory had a major impact on the organic chemistry of the immediate post-war era starting with Dewar's deduction of the structure of stipitatic acid[9] and including the syntheses of many novel conjugated compounds and ions. This was a brilliant era of synthetic organic chemistry to which many experimental chemists contributed and in which VB theory played essentially no role.

Finally, Jack has already mentioned how Wheland explained resonance in terms of oscillating pendulums, hardly less chemically intuitive than vibrating strings! But, vibrating strings in a circle lead directly to the $4n + 2$ rule and to the nodal properties of cyclic conjugated systems and those that can be considered as perturbed circles. My late colleague George Pimentel pointed out to me long ago how much chemistry can be explained simply by such nodal properties. In fact, I taught this in my physical organic course for many years.

In short, your conversation might give a suitable present picture of the current MO−VB dichotomy, especially from the point of view of two of the present VB practitioners, but it does not give an accurate picture of how the theories actually developed in the chemistry of the late 1940s until virtually the present time.

Best regards,

Andrew Streitwieser
University of California, Berkeley

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