

Concluding remarks

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I begin my closing remarks with a quotation from István Mayer's paper,¹ What he says is:

*For chemists, molecules consist of atoms held together by bonds; quantum chemists treat them as systems of electrons and nuclei. It is not trivial to bridge these images—both of which are legitimate in their own context—because there is no strict quantum mechanical definition of an atom **within** a molecule.*

It seems to me too that a very similar point was being made by Claude Lecomte and his co-workers.² I thought also that, implicitly, it makes another uncomfortable point that, from a quantum mechanical standpoint, the separation of a system of nuclei and electrons into *molecules* interacting by van der Waals forces and the like, involves an equally non-trivial bridging process.

Roy McWeeny in the Spiers Memorial Lecture³ with which he opened this meeting, reminded us of how we Quantum Chemists got to be where we are, describing the rather more than seventy years of development from the work of Heitler and London to the present. Although we know where we are and we surely know what we are doing, it is clear that differences remain between our way of looking at atoms and molecules and the way that chemists generally look at them. How then did the chemists' ideas arise before the advent of quantum mechanics and how might that affect the way that we go about things?

Chemistry is about synthesis. Physical Chemistry, Chemical Physics, Theoretical Chemistry, though endlessly interesting in their own right to those who choose to practice them, are, for the vast majority of working chemists, simply aids to synthesis. They need not be direct aids, this would be too much to ask, but they must somehow aid in the rationalising process by which a synthesis can be anticipated or its outcome understood. Traditionally the chemical bond has been a major element in this rationalising process. Where did that idea come from?

In the early 1800s there were perhaps a few hundred chemical compounds known but by 2004, according to Chemical Abstracts, *CAS Databases*, about 24 million were known. The major expansion in synthesis came after the Karlsruhe Conference of 1860 where Cannizzaro convinced the participants of the value of Avogadro's work and hence enabled agreement on a set of atomic "weights" (masses) in the light of which a theory of valency could develop in a less controversial environment. The idea of a chemical bond, introduced by Frankland somewhat earlier than this, developing the line notation of Crum Brown to provide diagrammatic formulae, and of the idea of valence saturation capacity of atoms, became central to chemical thought and enabled the anticipation on paper of possible synthetic outcomes. Those interested in the history of these developments can consult the excellent book by Colin Russell, *The History of Valency*.⁴

The problem at this stage was to relate this Chemical theory of atoms to the then current Physical theory. It was Helmholtz, who in his famous Faraday lecture of 1881 tried to persuade chemists to take seriously Faraday's 1839 insight that bonding might have an electrical origin. But it was not until the construction of the atom containing electrons, that a coherent theory was developed in the work of

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Lewis. In this theory, bonding was described as electron pairing and valence saturation expressed in terms of the realisation of electron octets and so on. This did not, of course win approval from physicists because it assumed stationary electrons, but physicists were in enough trouble over moving electrons before the work of Bohr that the battle was not really joined until the 1920s. The results of that battle are summed up in Sidgwick's *Electronic Theory of Valency*.⁵ The book was published the year after Schrödinger's first paper and in the year that Heitler and London's calculation on H₂ using wave-mechanics was published. Physics and Chemistry were then back together with bonding accountable for by means of a Physical theory. That the nuclei had to be thought of as claspable classical particles in this approach was not seen by physicists as an objection because such an approach was vital to their approach to solids. And this is where Roy McWeeny began. A summary account of this part of the history can be found in my review.⁶

The work that has been presented at this meeting can, I think be seen in two groups. That aimed at elucidation in contemporary terms of traditional chemical concepts and that aimed at constructing novel concepts that it is hoped will be useful in chemical synthesis. The first kind I see as developing ideas of the chemical bond from the work of Heitler and London. The second kind I see as following in the path of those pioneers like Pauling, who took the orbital from the mathematics of the theory to the molecular structure diagram.

When we try to elucidate traditional chemical concepts we should perhaps remember what Charles Coulson said in his 1951 Tilden Lecture:

I described a bond, a normal chemical bond; and I gave many details of its character (and could have given many more). Sometimes it seems to me that a bond between two atoms has become so real, so tangible, so friendly, that I can almost see it. And then I awake with a little shock: for a chemical bond is not a real thing: it does not exist: no-one has ever seen it, no-one ever can. It is a figment of our own imagination.

A certain scepticism, perhaps not quite as marked as in the quote above, also found its place in Coulson's after-dinner speech entitled *The Present State of Molecular Structure Calculations* made at the Boulder Conference in 1959 of which Paul Ayers⁷ has already reminded us. He said there:

The concepts of classical chemistry were never completely precise Thus when we carry these concepts over into quantum chemistry we must be prepared to discover just the same mathematical unsatisfactoriness.

I think that there can be no doubt that Charles Coulson, with his usual perspicacity, neatly anticipated the origin of those differences between us and the general chemists on such matters. In my view we must just learn to live with this imprecision. A particular contribution may lead us to look at a certain form of bonding, a particular occurrence of aromaticity, a peculiar sort of charge transfer, in a new and helpful way. However, the ideas here are essentially chemical and operational ones so no final or exclusive status could possibly be claimed for an account of them originating in quantum mechanics. Almost by definition, these ideas will lack a firm theoretical basis.

As Roy McWeeny made clear, the great new concepts that came into Chemistry after Heitler and London were that of the *orbital* which chemists took to heart and deployed and still deploy to incredibly good effect in their synthetic endeavours and that of the *independent-particle model* (IPM) of electronic behaviour. There certainly would have been no Woodward-Hoffman rules if orbitals and the IPM hadn't got in on the act. Nor would there have any VSEPR rules either. But the idea of employing orbitals within the IPM is not an uncontroversial one. It was subjected to withering fire in the article "There are No Such Things as Orbitals" by John Ogilvie⁸ that proved so provoking that Linus Pauling arose from his sick bed to provide a magisterial reply.⁹ It is not to take sides here. It is simply to note that the mathematical unsatisfactoriness anticipated by Coulson can call into question the status of chemically important innovations. Problems of a similar nature arise in the independent-particle approach when correlation is taken seriously.

With the widespread development of the molecular orbital method, alluded to by Roy McWeeny³ in his lecture, I was not clear if the ideas of perfect pairing and resonance which developed from Pauling and later Wheeland's deployment of valence bond concepts, had retained a hold on the chemists' imagination. It would seem from the discussion that indeed they have. And it is nice to see that valence bond ideas are still stimulating interest among theoreticians. The four papers that have been presented to us here seem to show that, with suitable care, the non-orthogonality problem can be managed. If I may interpolate a personal note to express regret that Joe Gerratt's untimely death prevented him from sharing in the recognition that would surely have been his for his tireless devotion to the development of a computationally feasible valence bond method.

In the sixties Roy McWeeny and Per-Olov Löwdin worked hard to establish density matrices as the preferred means of describing molecules and, a little later, Richard Bader argued persuasively for densities as a means of describing bonding, but the wavefunction continued to dominate the thought of theoreticians chiefly because of its computational utility. However with the advent, in the early seventies, of density functional theory (DFT) ideas began to change because, with the aid of powerful small-scale and affordable computers and the availability of effective program packages, useful computations could be performed by a chemist on a molecule big enough to be synthetically interesting. Such calculations are not at the same "pencil and paper" level that was possible with orbitals. But nevertheless they have provided tools for chemists generally to aid synthetic endeavours. Indeed DFT methods have probably become quite central to computer-aided synthetic endeavours. These developments seem to be mirrored in the many papers using DFT methods that we have heard here. Naturally enough there is "Coulson imprecision" here too, some of it generated by choice of density functional form but some arising in the usual way.

If I may hazard a guess, I think that when the next Discussion is held on this topic in perhaps fifty years' time, this approach will be seen as the one that really got into Chemistry, as did orbitals and the IPM fifty years ago.

Our discussions I found vigorous, stimulating and provocative and I feel sure that this will be reflected in their published form. At times I was swept back to my youth listening in meetings to arguments between followers of Robert Robinson and those of Christopher Ingold about who really invented the theory of organic mechanisms or between the followers of Sinanoglu and those of Nesbet about who was right about pair theories. And I thought, forty years later, "Who now cares?" The subject moves on and some of the ideas get incorporated into the subject and some do not. I know that as working scientists we tend to be suspicious of philosophy but we would do well to remember Wittgenstein's ideas on language communities and realise that we can use language usefully only in a community of shared experience and just so long as a large portion of the chemical community does not share our linguistic experience of what an "atom" is or what a "molecule" is we must anticipate a lack of understanding of our language. We are perhaps as quantum chemists a bit like a community of religious believers or, from a more Derridian perspective, those who read the text in the same way.

Roy McWeeny faced the EPR paradox head on in its relationship to modern Quantum Chemistry and, of course, it must be faced. I am convinced by his argument that, for the purposes of energy calculations, one can ignore the symmetry couplings and hence conservation rules. Of course the results of some experiments, such as those of Aspect on photons, seem to show that you can't always do this. Perhaps photons aren't chemical! But I do think that one should take symmetry couplings seriously when thinking about inter-molecular forces. I wonder if computational work is able to show just how far apart molecules must be for us to be able to neglect antisymmetrising the electrons between the molecules? It is not quite as easy as it is for the hydrogen molecule.

It is also a curious fact of Quantum Chemistry that we nearly always treat identical nuclei as distinguishable particles and hence establish the idea of a molecular structure with a particular point group symmetry. Indeed, if we are to clamp the nuclei in order to perform electronic structure calculations then we must distinguish between identical nuclei. We usually glide over all the difficulties here by saying that we are working within the Born–Oppenheimer approximation. Is this because we feel that we can ignore the nuclear permutational symmetry coupling in the context of molecular electronic structure calculations? If so, why do we think this? Are the traditional *feasibility* arguments secure here?

Has anything that might have been considered, been missed at this meeting?

I had rather expected to hear more than we have heard on relativistic work. The field did, of course, suffer a setback with Bernd Hess's premature death, but I am aware of interesting and, I would have thought, relevant work by, for example, Kutzelnigg¹⁰ and by Sadlej¹¹ in the past ten years or so. Perhaps nothing in the way of chemical concepts has yet been achieved in that work.

I had rather expected too that there might have been more upon concepts in reaction kinetics arising from constructed potential energy surfaces. There seems to me to have been a great deal of work in this area also in the past ten years, particularly for reactions explained in terms of intersecting potential surfaces. I think that surface crossing is a concept that has come into its own in Chemistry, developing the older ideas of Landau–Zener hopping. Among those who have contributed here I would think particularly of Stuart Rice¹² and of Michael Robb.¹³

I was not surprised that no one spoke of any conceptual implications for Chemistry that might arise in attempting to calculate without making the Born–Oppenheimer approximation although recently there has been a revival of all-particle (moving nuclei and electrons) calculations in the work of Adamowicz,¹⁴ of Sherrill¹⁵ and of Nakai¹⁶ and of Hammes-Schiffer.¹⁷ In the light of the results of this work, admittedly preliminary and only on very simple systems, I have some anxiety about how the bond is to be recovered from it because clearly all modern density-based approaches depend upon clamping the nuclei.

But there is only time for so much and for what has passed here and for what I have learned from it I should like to express my grateful thanks to all who have participated.

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