

# Chemists come in from the cold

*New developments in understanding high-temperature superconductivity have given theoretical chemistry a new lease of life, which Linus Pauling has been quick to recognise.*

HIGH-TEMPERATURE superconductivity has at least two considerable achievements to its credit already. Predictably, perhaps, there has been a renewed flurry of excitement in solid-state physics. People seem to be measuring anything they can, and not always with one of the ternary copper oxides as the substrate. Sensibly, the several oxides of copper are favourites, but anything with a layered or, ideally, a perovskite structure is a natural. Even if the temperature of bulk superconductivity is never increased above 90 K or so, surely something must come out of all that.

But the most remarkable of the transformations of the past few months is that chemists have once again been welcome in august society. (That should not be taken to imply that chemists have ever ceased to be powerful; the present president of the Royal Society of London, for example, like two out of the three physical scientists who previously held that post, is a chemist.) They, after all, are the people who know about atomic radii, bond lengths, valency, coordination numbers and electronegativity, all of them concepts a little more shadowy than when they are first written on the schoolroom blackboard. In passing, these same people may help with telling how to put one's hands on a little ytterbium, or gadolinium, if the competition should become even rougher.

It is nevertheless amusing to witness the way in which hardliners in the field, people who know about the Meissner effect and how to measure it, appear now to be willing to take instruction on chemists' topics such as valence-bond theory from people they would not ordinarily (or even now) trust to calibrate an electrometer. They even let Linus Pauling read them a lesson on just that subject the other week in *Physical Review Letters* (59, 225; 1987). But even Pauling seems not quite sure whether resonating valence bonds will account for high-temperature superconductivity; there is a splendid giveaway phrase in his paper, a conjunction that goes, "Whatever may be the mechanism of superconductivity, it is certain that..." Can there ever have been clearer proof that people are at a loss?

True superconductivists may therefore be comforted to know that valence-bond theory has not always been popular, even among chemists. Pauling's own great book (with A.H. Wilson), *The theory of the chemical bond*, now more than half a century old, had the curious effect of turn-

ing disciples into detractors. It was for many people a splendid way of learning wave-mechanics, but it turned out also to be a demonstration that precious little could be calculated; only supercomputers have materially changed that.

Forty years ago, the name of everybody's game was to calculate the properties of systems with more than one atom using the wavefunctions of hydrogen, or of atoms like it with a nuclear charge that might be different from unity. The valence-bond route required one to enumerate all possible ways in which the available electrons might be distributed among the available nuclei, however unphysical they might seem. The valence-bond calculation of the hydrogen molecule ion as a resonating mixture of two equivalent states of a free proton and an intact hydrogen atom (the electron can be interchanged) was obviously a kind of a joke with a serious message (because it can be made to work).

How to get better wavefunctions? Then, as now, people were at sixes and sevens. Linear Combinations of Atomic Orbitals (LCAO) were convenient, in the sense of being easy to construct, calculate and fit to the few known facts by the adjustment of a few parameters. The obvious snags were the adjustable parameters and, more philosophically, the circumstance that the molecular orbitals that, for example, made it a fact of life that the outer electrons of a molecule such as benzene are utterly delocalized, did not comprise a strictly orthogonal set, which is what people had been told was a necessary condition for using them. At the time, the chemists appear not to have appreciated that people like Léon Brillouin had made striking progress on a complicated version of a similar problem simply by representing the state of an electron in a metal as that of a particle in a box and using heuristic (or hand-waving) arguments to show that the result is bound to be a band structure of some kind.

Intrinsically, all three ways of calculating macroscopic systems should yield the same result if they were soundly based and were able to take account of enough terms in the inevitable perturbation series. Over a long interval, heroic work has been done by those who reckoned at an early stage that there would be benefits (for others, not often themselves) in finding wave equations representing electrons in the outer shells of complicated atoms. Now, it

is all so much easier. Those who use up-to-date atomic wavefunctions refer to them by four- or six-character alphanumeric codes and expect their readers to know precisely what they mean.

The physics of the problem has, unfortunately, not been much changed. The better the machines become, the larger the number of terms that can be included in approximations to the truth and, thus, the greater the difficulty in telling what they signify. In the end, it will not matter much; the approximations will converge. Meanwhile, there is this urgent problem of telling what explains the high transition temperature to superconductivity in the ternary copper oxides...

Pauling's answer is magisterial; he senses that the square arrays of oxygen atoms surrounding each copper atom in what is presumed to be the superconduction plane of the ternary oxides are the means by which pairs of electrons are assembled and then able to move together from one inter-copper space to another. In passing, he figures out that scandium should be better than barium as a temporary storage place for (or donor of) electrons in the active superconducting plane.

Other ruminations show common cause. For example, J. E. Hirsch, from the University of California at San Diego, building on an earlier suggestion by V.J. Emery, has shown how electrons may be held together physically in pairs (and thus made subject to Bose-Einstein condensation) when moving in an antiferromagnetic lattice by the penalty of having to break nearest-neighbour antiferromagnetic bonds as they go (*Phys. Rev. Lett.* 59, 228; 1987). The fun in that is that Hirsch appears not to know that his antiferromagnetic bonds (oppositely directed electron spins) are what Pauling calls valence bonds. It may be a smaller world than we think.

Meanwhile, the question will remain of whether it will be possible to calculate these structures: if the valence-bond method is so often hampered by the number of alternative structures that must be included in the basis set, will even Crays suffice? It is also strange that, so far, the chemists have been remarkably silent on a question that might be thought to interest them most — why should marked departure from stoichiometry matter so much? Perhaps there is still a lot to learn.

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