

Letters

Have Orbitals Really Been Observed?

I would like to thank Spence et al. for their response (1) to my article (2), in which I criticized what I, and others, took to be a claim for the observation of atomic orbitals. I am relieved to hear that the authors agree with me that it is not orbitals that can be observed but only charge density. Given this apparent agreement it is surprising that the observation of orbitals was mentioned even once, let alone four times as the authors admit to doing in their response. I am also still concerned to learn that Spence et al. wish to attach any significance whatsoever to what they claim to be a striking similarity between the observed charge density and “textbook images of a d_z^2 orbital”. If orbitals cannot be observed, as they agree, I fail to see why they might still be equivocating over this point. Nor do I believe that the one-electron model has received any additional validation in the case of transition metal oxides, or any other system for that matter, from the claimed similarity between the images obtained and the charge density corresponding to a d_z^2 orbital. In fact the usefulness of the orbital model has never been in question, or in need of observational support, regardless of whether this might be direct or otherwise.

Spence et al. also claim that it is acceptable to use words like “orbital” in different senses, provided that this does not lead to confusion. However, it was precisely because I thought that the conflation of the terms orbital and charge density *does* cause confusion that I wrote the article to which they have now responded. For example, there is currently some theoretical interest directed at performing orbital-free density functional calculations (3). To the researchers in this field the distinction between orbitals and charge density is the very *raison d'être* of their endeavor. But the audience most likely to be confused by the conflation of terms that the authors are condoning is the chemical education community. Up to this point we have had the difficult task of trying to stress to students that according to quantum mechanics electrons may no longer be regarded as having definite trajectories or paths. This property after all is the only categorical reason for denying the observability of orbitals, rather than appealing to their approximate nature in many-electron systems. Indeed, according to conventional quantum mechanics, orbitals are even

unobservable in the case of the hydrogen atom.

But in order not to seem too dogmatic, it must be said that some alternative interpretations of quantum mechanics, such as Bohm's theory, do regard electrons as having definite trajectories. However, this theory has not yet received any experimental evidence that might lead one to prefer it to the currently accepted Copenhagen interpretation.

Given the well-known distortions of scientific terms that occur in nontechnical dictionaries, the appeal by Spence et al. to the *New Shorter Oxford Dictionary* is a little surprising. Without wishing to contradict the quoted phrase by Wittgenstein that “meaning is use”, I would just add that the use of scientific terms, in particular, is not subject to the vagaries of popular use, or misuse, but tends to be governed by conventional agreement. Rather than “the expulsion of all one-electron language from chemistry”, which Spence et al. seem to believe I am advocating, the only thing I would wish to expel is the making of false claims regarding the *observation* of orbitals.

Finally, I would like to point out that my efforts to discuss this episode have been favorably commented upon by the doyen of experimental studies on charge density and chemical bonding, namely Professor P. Coppens, whom the authors themselves cited in their primary article in *Nature* magazine (4).

Literature Cited

1. Spence, J. C. H.; O'Keeffe, M.; Zuo, J. M. *J. Chem. Educ.* **2001**, *78*, 877.
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