

The Computational Perspective

DO YOU BELIEVE IN WAVEFUNCTIONS?

In just what terms do chemists think when doing basic analysis? Do they have, dancing about in their heads pictures of s and p – or perhaps little d – orbitals? Are they trying to visualize what sort of orbital hybridization might be possible and therefore what sort of chemistry to expect? Do they ponder what will happen to the wavefunction of a molecule when a different substituent is added in a certain position on a ring? Probably not! For chemists to be thinking in this manner, they would have to think in *terms* of wavefunctions – and there is a sizable body of evidence which suggests that many chemists do not really believe in wavefunctions. In what, then, *do* they believe?

To put it plainly and simply, they believe in structure. This belief is reflected in the language of chemistry. Open any text on organic chemistry and you will find a field described in terms of bond lengths, bond angles and torsional angles. In short, organic chemistry is a field organized by considerations of structure. It is usually presented in terms of families of compounds called alkanes, alkenes, alkynes, etc. There is good reason for this, certainly, as structure also happens to classify the compounds with regard to physical and chemical properties. Practicing chemists have, additionally, a special term to let everyone know that they are looking at the three-dimensional structure of a molecule; they refer to a molecule's 'stereochemistry'.

There is a good reason for this orientation – it has been largely very successful. Things have come a long way since the alchemists spoke of the Green Dragon. Given their success vis-a-vis structure, is there any reason why they should extend the type of analysis they do? Why should they bother with wavefunctions? Let's look for a moment at what they would have to contend with in order to conduct an analysis in terms of wavefunctions.

The first (and quite possibly the most important) point that computational chemists can make is that structure is a direct consequence of wavefunction. When the wavefunction is changed, the structure of the molecule is changed. We can further argue that, when structure changes, charge distribution within the molecule also changes and, thereby, the chemistry of the molecule is changed. It is at this point that the bench chemist and the computational chemist may well part company.

In the first place, no chemist can *see* the change in a wavefunction. Indeed, according to quantum mechanics, the wavefunction itself is not observable! Computational chemistry is a field which depends heavily on the analysis of charge distributions, but these charge distributions are not, in fact, measurable. . . . Is it any wonder that chemists work in terms of structure, which, after all is very real and measurable? Wavefunction looks more like a mental construct to provide employment for mathematically oriented chemists. From a bench chemist's point of view, the wavefunction is more a quasi-religious belief than a present reality.

The question which immediately suggests itself at this point is whether there is any valid reason to worry about wavefunctions. Would our chemistry be any better or more insightful if we were to think at the level of the wavefunction, rather than at the level of one of its alleged consequen-

ces? My own personal bias would be to answer in the affirmative. I would, however, be hard pressed to prove it.

It could well be that, in focusing so diligently on structure, we are overlooking opportunities to extend our reach. The manner in which we ask questions is doubtless conditioned by the fact that we make so much use of structure considerations. We could be overlooking major opportunities, but we will never know until we have the facilities to look at some pictorial representation of wavefunction information on a routine basis. We need, in short, the ability to visualize these wavefunctions.

Current graphics tools allow us to have space-filling models in which we have something like small charge clouds of the size of the Van der Waals radii for the atoms contained in the molecule. While this might provide a sort of qualitative feel, it must be emphasized that a wavefunction for a molecule would probably look very different. Our present tools give us so-called 'ball-and-stick' representations which enable us to rotate these images in space. This capability certainly adds some insight. We cannot, however, view and manipulate segments of molecular orbitals (as would be required for large molecules). Such tools do exist to some extent, but, as with most graphics, they are tied to a given manufacturer's equipment. This limitation is disappearing, albeit slowly.

It is in this area of visualization that computational chemistry will make a major contribution in this decade. Currently, the computer visualization tools we see routinely focus on structure. This is changing, and will likely change significantly in the next few years. As wavefunction visualization techniques become commonplace, we will have our answer as to whether we can extend our reach and what new opportunities we may discover as a result.

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