Bonding and Geometry

Reply to the Comments of Gillespie and Popelier

*Gernot Frenking**

Stichwörter:
bond theory · correspondence · density functional calculations · molecular geometry

I want to reply to the two instances where my comments are said to be "unjustified and unfair". This is the case at the end of the paragraph on page 3454, column 2. The authors state that I cited unpublished calculations in my review. This is not true! The calculations I am referring to concern the energies which are necessary to distort BF_3 and BCl_3 from the planar equilibrium geometry to the pyramidal structure in the complexes $F_3B{-}NH_3$ and $Cl_3B{-}NH_3$. Unlike in the 1999 paper by Gillespie and co-workers (*Inorg. Chem.* **1999**, *38*, 4659) who used model structures, the calculations of the real molecules show that the distortion energy for BF_3 is smaller than for BCl_3. This was already published by Politzer and co-workers in 1993 (*Inorg. Chem.* **1993**, *32*, 2622). The latter work was cited in the 1999 paper by Gillespie and co-workers, but apparently this part of the paper has escaped their attention.

The second instance where my comments are called "unjustified and unfair" concerns the explanation of the geometry of CF_3O^- in terms of the LCP model. The significant sentence in the book by Gillespie and Popelier reads (page 205, first paragraph): "Because the CO bond is so short, the CF bonds are necessarily longer than in CF_4." Here the authors take the short C–O bond, which "is not much longer than in methanal" (page 204, second paragraph) as the starting point for an explanation of the geometry of CF_3O^-. I call this deceptive because there is no explanation *why* the C–O bond is so short. The atomic charge of oxygen in CF_3O^- is nearly the same as in CH_3OH.

Furthermore, I must make a comment about my sentence "the mathematical object Ψ is too abstract and too elusive for the human imagination to grasp to allow it to become the focus of orthodox chemistry, which instead strives for pictures that are accessible for the human senses" because it was cited in a way which twists my intention in the book review. The meaning of this sentence is not something which must be admitted, but which has to be recognized as a fundamental perception about the material world at the molecular scale, which is the very object of chemistry. The wavefunction Ψ, which is fundamental for our science, is a mathematical object which is not accessible to human senses. Many chemists have problems with recognizing this. Chemistry has a long history of using pictures and models which are attempts to use human imagination for chemical objects. However, the perceptivity of the human senses is restricted in time and space. The scientific discovery that the laws of electrostatic force in the microscopic range are fundamentally different from classical laws and, therefore, are not accessible to human senses, has come as a shock not only to scientists. Chemists have for a long time ignored the revolution which came with quantum theory, because the heuristic models of human imagination had proven very successful as an ordering scheme and a predictive tool for synthetic chemistry. Organic chemists eventually accepted the wave function as a helpful quantity because the important class of pericyclic reactions could only be explained with MO theoretical arguments using the symmetry of Ψ. To recognize symmetry it is necessary to know the *sign* of the wave function. However, the sign and thereby the symmetry is lost when the product $\Psi\Psi^*$ is formed, which after integration yields the electron density ρ! This is one reason why Ψ is more fundamental than ρ which is *not* open to dispute.

Roald Hoffmann has shown that approximate orbital models, even as simple as EHT, may be used to understand chemical reactions and molecular structures which were totally incomprehensible for classical bonding models. With the sentence "in our opinion the electron density which is an easily understandable property of a molecule, that can be obtained directly from the wavefunction, is much more useful for understanding chemical bonding and molecular geometry than its wavefunction", the authors use the easiness of understanding as the reason for choosing ρ as a basis for bonding models. This is misleading, because it ignores the progress in the understanding of chemical bonding that has been gained by quantum chemistry in the last decades which showed that Ψ is the basis for a true understanding of molecular electronic structure.

I see no point to continue arguing about the examples presented in the reply. I encourage interested readers to study the book by Gillespie and Popelier together with my review and then to make their own judgement. There is no reason for me to change anything that I wrote.

[*] Prof. Dr. G. Frenking
Fachbereich Chemie
Philipps-Universität Marburg
Hans-Meerwein-Strasse
35043 Marburg (Germany)
Fax: (+49) 6421-282-5566
E-mail: frenking@chemie.uni-marburg.de

  DOI: 10.1002/ange.200320070