"Chemical Bonding and Molecular Geometry": Comments on a Book Review

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

In a recent review[1a] of our book "Chemical Bonding and Molecular Geometry"[1b] Frenking praised certain features such as our treatment of the connection between dipole moments and the charge distribution of a molecule as well as the discussion of the Pauli principle as fundamental to the understanding of the electronic structure of molecules. However, he severely criticizes our use of the electron density rather than the wave function approach and our use of the VSEPR and LCP models as a basis for understanding chemical bonding. He cites many statements described as "absurdities" that we show are either incorrect quotations from the book, statements taken out of context, or statements that he has simply misunderstood.

We do not agree with Frenking's claim that chemical bonding and molecular geometry can be understood only in terms of the wave function and not in terms of the electron density. The electron density can not only be obtained directly from the wave function, it can also be obtained by experiment. In one of his early papers Schrodinger[2] states clearly that the quantity of physical interest is $\psi\psi^*$ (from which the density is obtained) and not the wave function ψ, which Frenking himself admits is "too abstract and too elusive for the human imagination to grasp". Nevertheless he states that "it is only the wave function that gives an explanation for the chemical bond, whereas all attempts to explain the chemical bond in terms of the electron density have failed", although he gives no justification for this sweeping statement. Furthermore, in apparent contradiction, he states that the AIM theory, which is based on topological analysis of electron density "has become an important tool among other methods for analyzing the bonding situation in molecules". This is because, in contrast to the wave function which is "too abstract … to grasp", electron density is easily understood and pictured.

Slater[3] has shown that the force that accounts for chemical bonding is the electrostatic force, in particular the electrostatic attraction of the nuclei for the electrons (which is expressible in terms of the electron density) and the repulsions between the electrons and between the nuclei.

There is no "exchange force" nor any force resulting from the "resonance of the wave function". According to Slater,[4] the exchange integral of Heitler and London[5] "can be given a physical interpretation: it rises from the exchange charge which piles up between the atoms, and which is attracted strongly to the nuclei, since it tends to be localized between them". All the points concerning the wave function and the electron density that we have mentioned have been thoroughly discussed in a recent paper by Bader.[6] Finally it should be noted that Frenking's arguments are not, in fact, based on the wave function, but on arbitrary and approximate orbital models and the atomic-centred basis functions used in their expansion, which have no more physical reality than the wave function itself.

Now we deal with some of Frenking's more specific criticisms which are directed mainly at the VSEPR and LCP models. These models, we should note, are independent of any quantum-mechanical arguments and of the electron density, although they are supported by quantum mechanics, particularly, the importance of the Pauli principle in leading to the formation of electron pairs as described in Chapter 4 of our book and by the analysis of the electron density using the AIM theory[7,8] as described in Chapters 6 and 7 of our book. In the following sections the italic headers refer to locations in the review.

Page 144, column 1: With regard to our discussion of dipole moments and charge distribution, Frenking states "This part is well done and worth reading but then on page 39 one finds some statements about the bonding situation in BF_3 and SiF_4 which involve contradictory and selective arguments". Although we stated that in the resonance structures the positive charges at the fluorine atoms do not agree with the large calculated negative charges, we did not give this as a *reason* why the resonance structure description of these molecules involving double bonds is an inadequate description. We merely stated that these formal charges are inconsistent with the real charges. The real reason for the apparently short bonds in these molecules is, as we state clearly on page 39, "because of the (strong) attraction between the atoms due to their (large and opposite) atomic charges" for example, B +2.43, F −0.81. We are well aware that formal charges are not real charges, as we state clearly on page 17.

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DOI: 10.1002/ange.200320066

However, when resonance structures are written to describe bonding, the formal charges *are* then usually regarded as real charges, as, for example, when the polarity of the bond in HF is described by a combination of the two resonance structures H–F and $H^+ F^-$. It is in this sense that we stated that these resonance structures which place positive charges on the fluorine atoms are inconsistent with the calculated charges.

Page 144, column 3: "When finally one reads that the orbital model with σ and π bonds would not predict that the ethylene molecule is planar, it becomes clear that the view point of the authors is biased." We maintain that our viewpoint is not biased and that this statement is correct because the σ–π model is only a *description* of the bonding based on the *known* planarity of the molecule. Indeed this description is in general only valid for planar molecules. The description of the σ bonds as sp^2 is based on the knowledge of the planarity of the molecule. An alternative, but equivalent, orbital description of the bonding in ethylene can be given in terms of sp^3 orbitals and two bent bonds between the carbon atoms, as is clearly explained on pages 76 to 79 of our book. In fact neither of these descriptions of the bonding is exact in that the HCH bond angle in ethylene is 116 and not 120° as is assumed by the sigma–pi description, nor is it 109.5° as assumed by the bent-bond description. A state of hybridization in between sp^2 and sp^3 must be presupposed to give a description that corresponds to the observed bond angle.

Page 144, column 3 (bottom): Frenking criticizes our explanation of the decrease in bond angles with increasing electronegativity difference between the ligand and the central atom on the grounds that bond angles in AH_3 and AF_3 are not always consistent with this explanation. This is because this is one of the cases where ligand–ligand interactions are important and may override the predictions of the VSEPR model. In the case of the hydrides, the small size of the hydrogen atom allows bond angles to be unusually small when the hydrogen ligands are repelled close to each other by a lone pair, as occurs in AH_3 molecules. However, there are many examples where bond angles do decrease consistently with this electronegativity difference, as for example among all the halides listed in Table 4.3 (page 96), where we see, for example, that the bond angles of the fluorides and the chlorides decrease consistently from N to Sb.

We fully realize that there are some exceptions to the VSEPR model, many of which can be accounted for in terms of ligand–ligand interactions, and so we follow the chapter on VSEPR with a chapter on the ligand close packing (LCP) model. It is not to be expected that a qualitative model such as the VSEPR model would be without exceptions, and we do not claim this. Nevertheless, as Frenking states, "the heuristic VSEPR model has become an important standard model for understanding the structures of inorganic molcular compounds". Moreover, as Frenking also states, "the VSEPR model receives a quantum mechanical justification and explanation that is based on the AIM theory". We admit that it has some deficiences but, as we show, they are not nearly as numerous or as serious as Frenking leads readers to believe. Moreover, there are, in most cases, good explanations for these exceptions.

Page 145, column 1: Frenking states that the LCP model "appears rather odd" because "a large number of quantum mechanical calculations show that the bonded distance between two atoms is determined mainly by their direct electronic interactions". The LCP model does not claim that the bonding distance is determined only by packing considerations but claims only that bonds in four-coordinated molecules are longer than in three-coordinated molecules because three ligands can pack more closely than four. In other words, ligand–ligand interactions may affect bond lengths but they are not the primary determining factor. The LCP model provides an alternative explanation to the conventional explanation based on the change in hybridization from sp^2 to sp^3, which, as we have already pointed out, cannot be regarded as a true *explanation* because hybridization is not a physical phenomenon but only provides the basis for a particular *description* of the bonding. Frenking states that the LCP model fails for heavier main-group elements because the A···X distances for A = Al, Si, P, S and X = F, Cl, O become shorter, not longer, as the coordination number increases. However, he quotes only the fact that the P–F bond is longer in PF_3 than in PF_4^+. Here, Frenking ignores two important concepts of the LCP and VSEPR models that are clearly explained in our book and that are widely accepted, namely that lone pairs are regarded as pseudo ligands and contribute to the coordination number, so that both PF_3 and PF_4^+ are four coordinate, and that they lengthen adjacent bonds. In fact, if we consider a series of molecules in which the coordination number does indeed increase and in which there are no lone pairs then we find that bond lengths do increase with coordination number, as is evident in the following examples: AlF_4^- (169.9 pm), AlF_6^{3-} (189.7 pm); SiF_4 (157.0 pm), SiF_6^{2-} (172.9 pm); PF_4^+ (145.7 pm), PF_6^- (158.0 pm). The variation of bond length with coordination number is also discussed and illustrated with other examples on pages 122 and 123.

Page 145, column 3: Frenking states that our assertion that the attraction between the two atoms in a pure covalent bond is due only to the electron density accumulated between their nuclei is "completely wrong". This claim is contrary to the opinion of Slater and, moreover, is in apparent contradiction with Frenking's statement in the previous column that "the bonding line between two atoms is revealed (in the AIM theory) without making more or less arbitrary assumptions", because this bonding line is the line along which the density is larger than in any other direction; in other words, it shows where the density is accumulated between the two nuclei. Since the only forces operative in a molecule are the electrostatic forces between the charge density and the nuclei as well as between the nuclei themselves, it is reasonable to claim that the bonding force between two atoms is due to the electron density accumulated between the two nuclei.

Page 145, column 3: We argue that, because the atomic charges in BF_3 suggest a stronger interatomic charge interaction in BF_3 than in LiF, while at the same time the density at the bond critical point increases from LiF to BF_3, we must conclude that both the ionic character and the covalent character of the A–F bond increases from LiF to BF_3. This conclusion contradicts the commonly held view that increasing covalent character is accompanied by decreasing ionic character and vice versa. This view is exemplified by the common description of bond polarity in terms of resonance structures such as H–F and $H^+ F^-$, which assumes that as covalent character increases ionic character decreases, and vice versa. However, we do not agree with this view, although Frenking appears to think that we do, as it is not consistent with the evidence from the electron density that clearly indicates that both covalent character and ionic character increase from LiF to BF_3 in so far as covalent character is measured by the electron density at the bond critical point and ionic character is measured by the atomic charges. Thus, it is as clear to us, as it is to Frenking, that the ionic and covalent contributions may both increase, although we disagree with Frenking that this is also clear to all other chemists. To describe our argument as a "con", thus implying that we have deliberately tried to deceive the reader, is completely unjustified and unscientific.

Page 146, column 1: We see nothing wrong with our laconic or terse statement that "the reasons for the large bond angles in $N(CF_3)_3$ and $N(SCF_3)_3$ are not clear". As we admit, the VSEPR theory cannot be expected to explain every feature of molecular structure. Perhaps Frenking or another reader of our book might be able to provide an explanation. In criticizing our discussion of the relative Lewis acid strengths of BF_3 and BCl_3, Frenking states that the fact that BF_3 is a weaker Lewis acid than BCl_3, despite the atomic charge of boron in BF_3 being larger than that of boron in BCl_3, cannot therefore be explained by the electron density, but he does not explain how he reaches this conclusion. We do not criticise the widely held p(π) back-donation explanation simply because it is expressed in terms of orbitals, but because, as we discuss in our book, there is no other evidence for it other than the short length of the B–F bond which can alternatively be accounted for by the large polarity of the B–F bond.

Page 146, column 2: We do not "praise AIM atomic charges as a basis for the nature of the chemical bond" as Frenking claims. They are simply one of the properties of a molecule related to the electron-density distribution that are useful in understanding bonding. Although he states earlier that the AIM theory "has become an important tool … for analyzing the bonding situation in molecules" he nevertheless criticizes the atomic charges, quoting the case of methane for which the atomic charges on hydrogen have a very small negative value of -0.04. In other words, the atomic charges in this molecule are very close to zero. However, his criticism of these charges amounts only to the subjective statement that "everybody who knows about the fundamental difference between the chemical behavior of protic and hydridic hydrogen will be startled by this". Perhaps they will be startled, but this is no evidence that these charges are incorrect. Essentially, the charge transfer is zero as expected, which indicates that CH_4, situated at the boundary between hydridic and protic behavior, shows neither type of behavior.

There follows a criticism of our discussion of the geometry of CF_3O^- in which Frenking states that "the authors fail to justify why they are using the radius of the carbonyl oxygen for the oxygen atom". But nowhere in our discussion do we use, or even mention, the radius of the carbonyl oxygen atom. In general, as we state elsewhere in the book, we do not find covalent (atomic) radii to be a useful concept. Frenking seems to have completely misunderstood our arguments, which can be simply summarized by the statement that Lewis structures may be used to *describe* the bonding in OCF_3^-, but they do not provide an explanation for the geometry which can be understood in terms of the LCP model independently of the Lewis structures used to describe the bonding. To describe our arguments as "deceptive" is both unjustified and unfair. We do not claim, as Frenking states, that the shorter bond in CO compared with CO_2 is consistent with the LCP model. It is clear to anyone that ligand packing is not relevant when there are only one or two ligands. We state only (p. 206) that "molecules in which the carbon is four-coordinated have longer CO bonds than in molecules in which the carbon is three-coordinated which in turn are longer than the bonds in CO_2 and CO". We make no comparison of the bond lengths in CO_2 and CO. Ligand packing places a restraint on the lengths of the bonds when they are close-packed, as in four- and three-coordinated molecules, but this restraint is absent in both CO_2 and CO.

Page 146, column 3: In our discussion of the description of the bonding in SF_6, our aim was to show that the common representation of bond polarity using Lewis structures with ionic bonds is unnecessarily complicated. This type of description does, as we have mentioned before, consider formal charges to be real charges—it would be useless if it did not. To give a description consistent with the atomc charge on sulfur of $+3.55$ it would be necessary to include further structures with more than two ionic bonds as well as those written in accordance with the octet rule structures which give a charge of $+2.0$ on sulfur, thus further complicating the description. If we accept, as Lewis did, that the bonds are polar, and that a bond line can be used to describe a polar bond as well as a nonpolar bond, then the Lewis type structure with six-bond lines is a perfectly acceptable description, and there is no need to use a multitude of Lewis structures incorporating ionic bonds. Once again Frenking has not understood our arguments. We are perfectly aware that formal charges are not real charges, but in describing bond polarity in terms of Lewis structures formal charges are indeed taken to represent real charges, a point that does not seem to have been appreciated by Frenking.

Following this discussion he claims to have found data in the tables that contradict the VSEPR and LCP models. He gives only the example of the lengths of the equatorial bonds in SF_4 (154.5 pm) and in SF_2 (162.5 ppm) and claims that these are not in accordance with the LCP model, which he says predicts that the bonds in SF_4 should be longer than in SF_2. However, he ignores the bond-lengthening effect of the lone pairs, which must also be taken it account since SF_2 has two lone paris whereas SF_4 has only one.

Frenking claims that the reason why the lone electron pair in SeF_6^{2-}, IF_6^-, and XeF_6 "suddenly becomes inactive, although it plays an important role in the C_{4v} geometry of IF_5, remains unclear". In fact the lone pair does not suddenly become inactive in these molecules, but it is partially active giving the observed C_{3v} geometries. This, as we explain, is because the space occupied by the six ligands leaves insufficient space for a full lone pair, which therefore partially occupies the valence shell while remaining partially in the region immediately surrounding the core. In IF_5, which has only five ligands, there is plenty of space in the valence shell to accommodate the lone pair. This point has previously been thoroughly discussed in an article in this journal[9] and in a forthcoming article.[10]

We could quote several other examples where Frenking has misrepresented or misunderstood our arguments, but lack of space prevents discussion of them here.

In summary, we may say a) Frenking's detailed criticisms that are leveled mainly at the VSEPR and LCP models, based as they are on his lack of understanding and misinterpretation of our arguments are unjustified. These models are independent of both the wave function of the molecule and the electron density, although they receive support from the analysis of the electron density and from quantum mechanics. b) The question of whether or not the wave function or the electron density is the more fundamental is perhaps open to dispute, but in our opinion the electron density, which is an easily understandable property of a molecule and can be obtained directly from the wave function and by experiment, is much more useful for understanding chemical bonding and molecular geometry than is the wave function, which Frenking states "is too abstract and elusive for the human imagination to grasp". When Frenking refers to the wave function he must surely be referring to approximate orbital models based on the wave function and, as we show, in the case of ethylene for example, these are just descriptions of the bonding that in general are not unique and do not explain geometry. c) We believe that our book does indeed provide a useful introduction to models and theories of chemical bonding and geometry, in particular, to simple orbital models, the VSEPR model, the LCP model, and the AIM analysis of the electron density, which is presented at a level much more accessible to undergraduate students than Bader's original monograph.[7] Moreover, our book shows students that none of these models and theories are perfect, although they all have their uses.

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