CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200600057

A Model of the Chemical Bond Must Be Rooted in Quantum Mechanics, Provide Insight, and Possess Predictive Power

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Abstract: In this response to the preceding paper by Bader, we show that the core arguments and statements presented in the latter are flawed. We argue that it is insufficient for a model of the chemical bond to be rooted in quantum mechanics. A good model must in addition provide insight and possess predictive power. Our molecular orbital (MO) model of the chemical bond, in particular, the associated energy–decomposition approach satisfies all these conditions. On the other hand, Atoms-in-Molecules (AIM) theory is only rooted in quantum mechanics as far as its mathematical framework is concerned. The physical status of its central concepts is not so clear. In particular, "bond paths" and "bond critical points" are once more confirmed not to be indicators of a stabilizing interaction. Moreover, AIM theory lacks any predictive power. We also address specific questions raised in the preceding paper. Finally, interpreting chemical bonding implies choosing a perspective on this phenomenon. That there are many perspectives is a matter of fact and this is in no way unphysical. What is unscientific is to claim uniqueness and truth for one of these choices, namely AIM, and to dismiss on this ground all other approaches.

Keywords: atoms-in-molecules (AIM) theory • bond energy decomposition • bonding theory • density functional calculations • molecular orbital theory • steric repulsion

Introduction

Science is observation and experiment followed by appeal to theory and a return to experiment. This is also the first sentence of the preceding paper,[1] a rebuttal by Bader to an earlier article of ours in the same issue[2] in which we have falsified Bader's hypothesis that there would be H–H bonding in planar biphenyl.[3] With this statement we wholeheartedly agree (how could one disagree). But much of what follows in Bader's rebuttal[1] is flawed.

The present paper is a response in which we address the weaknesses in Bader's core arguments and statements, and in his theory of Atoms-in-Molecules (AIM).[4] To this end, we briefly review the characteristics of our own, quantitative molecular orbital (MO) model and the associated energy–decomposition approach (EDA) which are firmly rooted in physics.[5–7] This is then contrasted with AIM theory. In the course, we respond to some issues raised by Bader amongst which the He@adamantane inclusion complex[1,8] and the origin of the higher stability of phenanthrene compared to anthracene. We anticipate here that our bonding analyses and computational experiments falsify the hypotheses, derived from AIM, of the presence of He–C bonding in He@adamantane and H–H bonding as the origin of the higher stability of phenanthrene compared to anthracene. It is fair to stress, however, that we are not the first to recognize the flaws in AIM theory. For example, Haaland et al.,[8] Cioslowski et al.,[9] Frenking,[10] and, much earlier, Ruedenberg and Feinberg[11] preceded us in raising fundamental concerns about AIM theory.

Discussion

It is a necessary but, in our view, insufficient requirement for a model of the chemical bond that it is rooted in quantum mechanics and that it is able to correctly reproduce all observable quantities, in particular bond energy and molecu-

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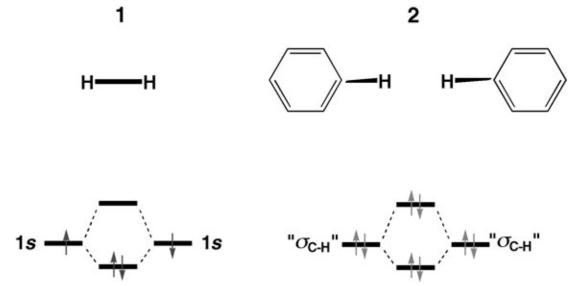
lar structure. A good model must, in addition, provide insight and possess predictive power: it should comprise concepts and quantities that enable one to understand *why*, for example, a particular bond is stronger or longer than another one. It is therefore essential that there is a transparent and causal relationship between the model's concepts and quantities (e.g., orbital overlap in our model) on one hand and the observables of interest (e.g., bond strength) on the other hand. In other words, the model should furnish really a bonding *mechanism* in terms of which the reader can think and argue about molecular structure and stability. The boost that chemistry can receive from such insight has been demonstrated by the work of Roald Hoffmann and his school.[12] Thus, the concepts and quantities of the model must be of such a nature that one can rationally and qualitatively predict the behavior of a molecular species in an experimentally or computationally yet unexplored situation, that is, without having to first carry out the measurement or high-level computer calculation that furnishes the quantitative answer.

The above considerations have led to the development of our approach, which has already previously been described in detail (see, for example, references [5,6,13], and also the methodological section of reference [2]). Here, we confine ourselves to a brief overview of the essential features of our methodology and MO model of the chemical bond. It is an asset of our approach that it focuses from the outset on the quantity of interest: the stabilization or bond energy $\Delta E_{\mathrm{AB}} = E_{AB} - E_A - E_B$ of a molecule AB relative to the separate molecular fragments A and B that are held together by the chemical bond. Thus, we directly examine the reaction of $A + B \rightarrow AB$ and it is completely in line with quantum mechanics to describe and understand this process in terms of going from the wavefunctions Ψ_{A} and Ψ_{B} of the fragments to the wavefunction Ψ_{AB} of the overall molecule. The reference wavefunction Ψ^0 that we invoke is mathematically and physically well defined: it is the antisymmetrized and renormalized product of Ψ_{A} and Ψ_{B} and it reveals how the Pauli principle acts as Ψ_{A} and Ψ_{B} begin to overlap. In practice, this approach has proven to provide a profound understanding of molecular structure and reactivity (see references [5,6,13,14] and references cited therein).

Does the fact that our quantitative MO method is rooted in quantum mechanics and possesses predictive power imply that it is a unique approach? No, of course not. Interpreting chemical bonding is indeed inherently connected with choosing a perspective on this phenomenon. This can be done in many ways, for example, with our MO approach,[5,6] valence bond theory,[15] and natural bond orbital (NBO) theory,[16] or by inspecting the topology of the electron density as is done in AIM theory.[4] In contrast to what Bader states,[1] there is nothing unscientific or unphysical if different perspectives or models exist and compete for providing the best way of understanding the observable nature. AIM theory is no exception; it is just one of the choices one can make for looking at the chemical bond. Also, as recently stressed by Frenking,[10] the choice to focus on the electron density does *not* imply that AIM theory is more solidly rooted in quantum physics than models proceeding from the wavefunction. Yet, AIM theory is not to be blamed for evolving from such choices of perspective, although it is somewhat unfortunate that even the very heart of the method, namely, the partitioning of molecules into atoms using zero-flux surfaces, is arbitrary and can even not be straightforwardly generalized to a relativistic formulation of quantum mechanics.[9] The main problem is however the unclear physical meaning and concomitant misinterpretation of topological concepts within AIM theory and the inability of this method to provide insight.

Failures of AIM theory in practice: The fact that there is no straightforward relationship between AIM concepts such as "bond path" and "bond critical point" on one hand and the question if the contact between two molecular fragments or atoms is stabilizing or destabilizing leads in practice to awkward failures. A point in case is the conclusion derived from AIM theory that the H–H contacts in both molecular hydrogen (see **1** in Scheme 1) and in a complex of two molecules, R–H···H–R, pointing towards each other with their C–H bonds are of the same nature and that they are both bonding (see, for example, reference [1]). The H–H bond in H_2 is indeed bonding, by $-155.3\ \mathrm{kcal\,mol^{-1}}$ at the equilibrium distance of 0.749 Å, as computed at BP86/TZ2P. But a completely different situation occurs for R–H···H–R, which we will make more concrete by taking, for example, two benzene molecules as shown in **2** of Scheme 1. Here, the interaction is strongly repulsive over a wide range of H–H distances. At the equilibrium bond distance of 0.749 Å in H_2, for example, the H–H interaction in **2** destabilizes this benzene complex heavily, by $+58.4\ \mathrm{kcal\,mol^{-1}}$ (in planar biphenyl, the repulsion between opposing *ortho*-hydrogen atoms is much less due to the larger H–H distance of 1.935 Å).



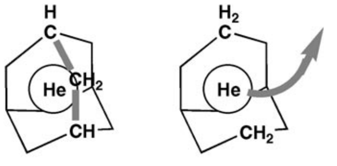
Scheme 1. H–H bonding in H_2 (**1**) and H–H repulsion between C–H bonds (**2**).

This is not just a gradual difference: these two H–H interactions differ in nature. And in a MO approach, this does not come as a surprise (see Scheme 1): In H_2, the H–H interaction is constituted by an electron-pair bond between the singly occupied 1s AOs of the two hydrogen atoms (see **1**). On the other hand, in the benzene complex, there is Pauli repulsion (or two-orbital–four-electron repulsion) between the closed-shell benzene by MOs that have amplitude on the opposing C−H bonds, that is, the MOs with σ_{C-H} character (see **2**); there is no electron-pair bond and no sufficient donor–acceptor bonding that could surmount the Pauli repulsion between the C−H bonds. What remains are weak dispersion forces at large intermolecular distances. In the case of solid methane, mentioned in the preceding paper by Bader,[1] these weak interactions break under atmospheric pressure already at −182.5 °C, the melting point of methane. The MO model provides a simple and transparent picture through which the situation can be understood on a qualitative, mechanistic level. At the same time, we can also compute the quantitative result of the bonding features, the molecular structure and stability, consistently within one and the same MO approach.

AIM, at variance, fails to diagnose the different nature of the H−H interaction in **1** and **2**. The picture emerging from AIM is in fact quite confusing. Apart from the fact that it is anyway difficult to predict the strength of a bond on the basis of the topology of the electron density of the constituting fragments, the electron densities of both **1** and **2** show a bond path with a bond critical point. In AIM, this is supposed to indicate bonding in **1** and, erroneously, also in **2**. In fact, two charge densities that are brought into contact such that they overlap will in most cases show an AIM "bond path" and an AIM "bond critical point", independent of the question whether this contact is stabilizing or destabilizing the overall system relative to the separate molecular fragments. It is therefore incorrect to conceive the occurrence of "bond paths" and "bond critical points" as indicators for bonding.

We anticipate the counter argument that **2** is not an equilibrium structure and thus the AIM concepts of bond path and bond critical point cannot be applied in the usual manner. But such an argument would not be cogent. One can apply a counterforce that hinders two C−H bonds to separate and, in this way, turn this geometrical configuration into a stationary point or an equilibrium structure, despite the intrinsic H−H repulsion. A nice example of such a stationary point is provided by planar biphenyl in which the C−C bond between the phenyl moieties forces opposing *ortho*-hydrogen atoms together. The computations and analyses show how the C−C bond elongates and how the opposing C^{ortho}–H^{ortho} bonds bend away from each other as biphenyl is brought from its twisted equilibrium conformation to the planar conformation, which for any given C−C distance yields the strongest H^{ortho}–H^{ortho} repulsion. This is discussed in much detail in our paper on biphenyl, earlier in this issue.

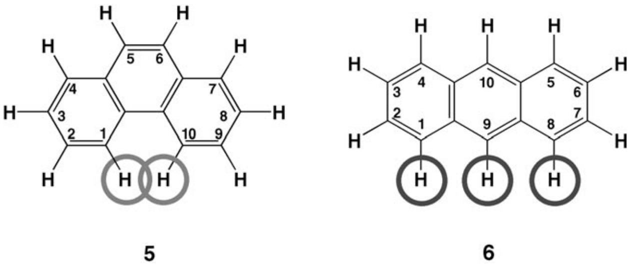
Another example is the inclusion complex of He in adamantane (**3** in Scheme 2). As pointed out by Haaland et al.,[8] **3** is strongly destabilized relative to separate He + adamantane. Nevertheless, AIM theory yields He−C "bond path" with "bond critical points" and, therefore, erroneously diagnoses He−C bonding. Here, we provide further evidence for the absence of He−C bonding through a numerical experiment. We have opened the adamantane cage by removing one of its "bars", the bold C-C-C unit in **3**. This was done by taking away the central methylene unit followed by saturating the resulting open valences at each of the two outer CH units with a H atom; all other geometry parameters of **3** were kept frozen. Thereafter, the resulting structure **4** was allowed to geometrically relax. What we observed was no He−C bonding. Instead, the He atom was directly expelled (bold arrow in **4**). Apparently, the He atom is trapped by the cage structure, not because of He−C bonding but, in contrary, because He-C repulsion prevents it to escape. The Feynmann force exerted on the He atom in the inclusion complex **3** at the equilibrium geometry is zero, not because of the absence of He−C repulsion but because of the mutual cancellation of the four counteracting He−C repulsive contacts. Thus, the fact that Feymann forces acting on the atoms in this equilibrium structure are zero does not imply the presence of a He−C bonding interaction.[11] It is therefore incorrect to interpret "bond paths" and "bond critical points" as indicators of bonding.



3 **4**

Scheme 2. He, caught in adamantane (**3**), is pushed out if the cage is opened (**4**).

Finally, we address the phenanthrene issue raised by Bader in the preceding paper.[1] Phenanthrene (**5**) is known to be more stable than the isomeric anthracene (**6**), see Scheme 3. Indeed, we find that **5** is 4.2 kcal mol^{-1} more stable than **6**, computed at BP86/TZ2P. According to Bader,[1,3] this is due to a stabilizing H−H interaction between hydrogen atoms H_1 and H_{10} which, in the bay region of **5**, come into close proximity. In **6**, there are no such short H−H contacts and thus, according to Bader, no stabilizing H−H bonding. These conclusions are based on AIM analyses that yield H−H "bond paths" and "bond critical points" for **5** but not for **6**.



5 **6**

Scheme 3. Phenanthrene (left) and anthracene (right).

But again, AIM theory fails. We have carried out an extensive and very detailed MO analysis and bond energy decomposition for both **5** and **6**. The key finding of our analyses is that in phenanthrene there is H–H Pauli repulsion, *not* H–H bonding. Phenanthrene is more stable than anthracene because of a more stabilizing interaction in the π-electron system and *despite* H–H repulsion. We have confirmed this with an independent numerical experiment: we have removed H_1 and H_{10} from phenanthrene (**5**) and, for comparison, H_1 and H_8 from anthracene (**6**). The resulting biradicals [**5**–2H] and [**6**–2H] have triplet ground states and are again isomers. If, as diagnosed by Bader's AIM analyses, the close H_1–H_{10} contact in **5** is stabilizing and, thus, the reason why **5** is more stable than **6**, then [**5**–2H] should have lost this stabilization and it should be closer in energy to [**6**–2H]. However, we find the opposite: the stabilization of the angular tribenzenoid relative to the linear one *increases* from 4.2 $kcal mol^{-1}$ for **5** and **6** to 5.4 $kcal mol^{-1}$ for [**5**–2H] and [**6**–2H]. There is really no H–H bonding in phenanthrene. The full results of these investigations will be published elsewhere.

Conclusion

A good model of the chemical bond should not only be rooted in quantum mechanics, it must also provide insight and possess predictive power. Our MO model of the chemical bond, in particular, the associated energy–decomposition approach satisfies all these conditions. On the other hand, AIM theory is only rooted in quantum mechanics as far as its mathematical framework is concerned. The physical status of its central concepts is not so clear. In particular, the interpretation of the concepts of "bond path" and "bond critical point" as indicators of a stabilizing interactions is flawed. Moreover, AIM theory does not provide a mechanistic insight into chemical bonding and lacks any predictive power. We have shown how this leads to confusion and erroneous conclusions in several examples. This further consolidates earlier studies[8–11] in which severe flaws in AIM theory were identified.

We admit that interpreting chemical bonding implies choosing a perspective on this phenomenon. That there are many perspectives is a matter of fact and this is in no way unphysical. It is unscientific, however, to claim uniqueness and truth for one of these choices, namely AIM, and to dismiss on this ground all other approaches.

Acknowledgements

We thank the Departament d'Universitats, Recerca i Societat de la Informació (DURSI) of the Generalitat de Catalunya and the Netherlands organization for Scientific research (NWO-CW), the Spanish MEC (Project number CTQ2005–08797-C02–01/BQU), and the European Union (TMR program) for financial support. Excellent service by the Stichting Academisch Rekencentrum Amsterdam (SARA) and the Centre de Supercomputació de Catalunya (CESCA) is gratefully acknowledged. We also thank Professors J. Cioslowski and W. H. E. Schwarz for helpful discussions.

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Received: January 16, 2006