Angewandte
Korrespondenz

Quantum-Chemical Calculations (1)

DOI: 10.1002/ange.201411374

No Need for a Re-examination of the Electrostatic Notation of the Hydrogen Bonding: A Comment

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chemical bonds · electrostatic interactions ·
hydrogen-bonded complexes · hydrogen bonds ·
quantum-chemical calculations

In a recent publication by Weinhold and Klein[1] (WK) the authors report about bonding analyses of doubly charged complexes $[A\text{-}HB]^{2\pm}$ using the natural bond orbital (NBO)[2] method. It is claimed that the interactions between the equally charged fragments $A^{\pm}\cdots HB^{\pm}$ are a manifestation of so-called „anti-electrostatic“ hydrogen-bond (AEHB) complexes, where the „short-range donor–acceptor covalency forces overcome the powerful long-range electrostatic opposition to be expected between ions of like charge“. WK suggest that „full recognition of the AEHB phenomenon should therefore prompt critical re-examination and reform of many aspects of current pedagogy[3] of H-bonding“. They further write that „AEHB complexes may finally put to rest the superficial quasi-classical conceptions of H-bonding and other resonance-type phenomena that have too long held sway in the molecular and supramolecular sciences“.

We critically re-examined the claimed resonance phenomena and the electrostatic forces in one example given by WK using a more precise quantum theoretical approach for estimating the dominant interactions in the „AEHB“ complexes. The chosen example is the dianion $[F\cdots HCO_3]^{2-}$ which exhibits a shallow minimum on the potential energy surface that is 50 $kcal\,mol^{-1}$ higher in energy than the separated fragments $F^- + HCO_3^-$. We took the optimized geometries at B3LYP/aug-cc-pVTZ of the equilibrium structure and the transition state for the dissociation from the work by WK. The structures are shown in Figure 1. The „AEHB“ complex $[F\cdots HCO_3]^{2-}$ has a F-H „bond“ length of 1.814 Å while the transition state has a slightly longer distance of 2.100 Å.

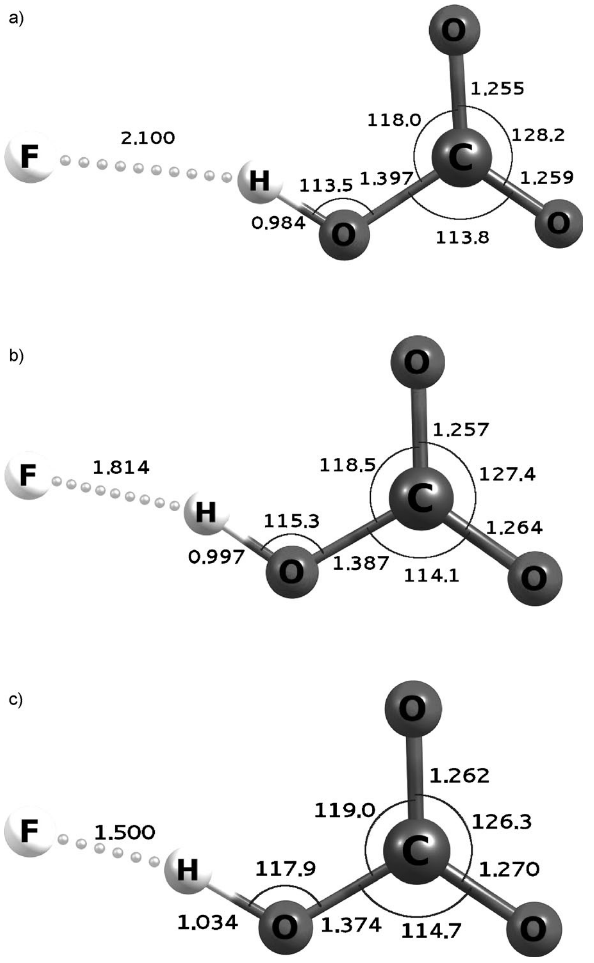

Figure 1. Calculated structures of $[F\cdots HCO_3]^{2-}$ at B3LYP/aug-cc-pVTZ. a) Transition state for formation of the „AEHB“ complex. b) Equilibrium structure. c) Optimized structure with fixed distance $R_{F\text{-}H} = 1.50$ Å. The coordinates for the structures shown in (a) and (b) were taken from WK.[1] Distances in Ångström, angles in degree.

It takes much chutzpah to use an energy-minimum structure with a well depth of 0.05(!) $kcal\,mol^{-1}$ at B3LYP/aug-cc-pVTZ (0.08 $kcal\,mol^{-1}$ at MP2/aug-cc-pVTZ)[1] as object for a bonding analysis with the NBO method. But it takes a still higher degree of flippancy when the electrostatic interactions between the fragments are estimated with a formula that was proven already in 1927[4] not to be suitable for calculating Coulombic forces between atoms at shorter region. WK write: „... for typical $R_{A\text{-}B}$ separations of main-group H-bonded complexes...the Coloumbic e^2/R potential barrier might be expected to range up to 100 $kcal\,mol^{-1}$ or

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201411374.

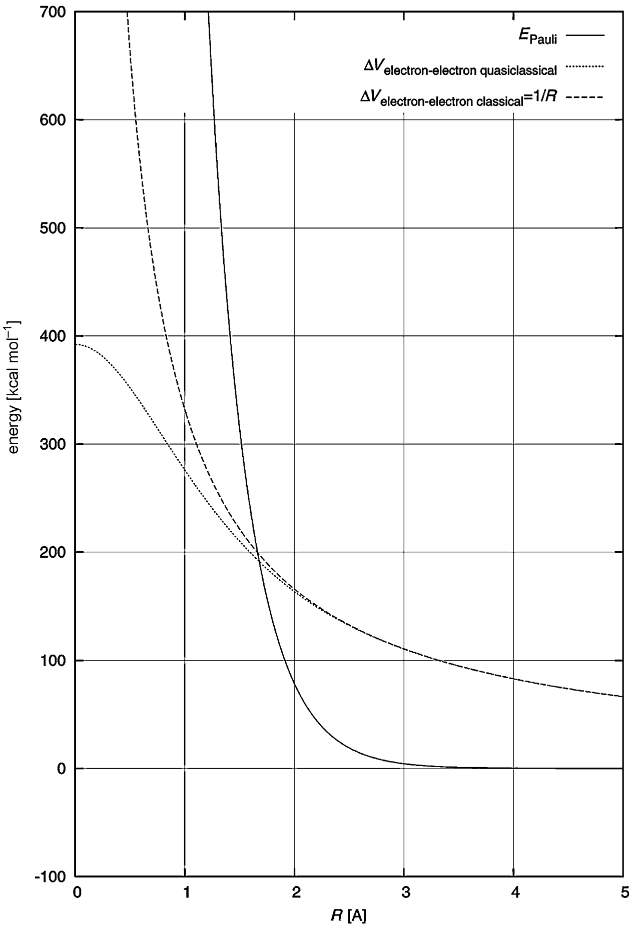

Figure 2. Calculated interaction energies between two charged particles as a function of their distance r_{12}. Repulsive interactions between two electrons calculated classically $\Delta E_{\text{elstat}}(\text{classical}) = q_1 x q_2 / r_{12}$ (dashed line); quasiclassical repulsion between two electrons in 1s orbitals $\Delta E_{\text{elstat}} = \int \rho_1 x \rho_2 / r_{12} d\tau_1 d\tau_2$ (dotted line); exchange repulsion between two electrons with the same spin in 1s orbitals ΔE_{Pauli} (solid line). The figure was reproduced with permission from Ref. [7].

more, well beyond the strength of even the strongest known H-bonds". But in regions where orbital overlap becomes important (and this is what is claimed for „AEHB" complexes by WK), the formula e^2/R, which is valid for point charges only, leads to grave errors. This becomes obvious from Figure 2 which shows the calculated curves for the interactions between two electrons as point charges $1/R$ (dashed line) and between two electrons in hydrogen 1s orbitals using the correct formula [Eq. (1); dotted line]

$$\Delta E_{\text{elstat}} = \int \rho_1 x \rho_2 / r_{12} \, d\tau_1 d\tau_2 \qquad (1).$$

With the onset of overlap, the latter curve clearly deviates from the former curve and approaches to a finite value at $R = 0$ while the repulsion between point charges becomes infinite. Using the classical formula $1/R$ for electrostatic interactions is a fundamental flaw in the study of WK!

We calculated the Coulombic forces between F^- and HCO_3^- at the equilibrium geometry and at the transition state using the electronic and nuclear charges of the two fragments rather than point charges. The calculations were performed using the B3LYP/aug-cc-pVTZ optimized geometries of WK[1] at B3LYP-D3/TZ2P+ with the program package ADF.[5] The latter calculation which uses Slater-type basis functions gives a well depth of 0.77 kcal mol^{-1}, somewhat larger than the B3LYP/aug-cc-pVTZ result of 0.05 kcal mol^{-1}. The difference between the two values is not relevant for the study. Table 1 shows the calculated data. The Coulombic repulsion at the transition state where $R_{\text{F-H}} = 2.100$ Å amounts to $\Delta E_{\text{Coul}} = 57.36$ kcal mol^{-1}. The equilibrium structure has a shorter distance $R_{\text{F-H}} = 1.814$ Å but the Coulombic repulsion ($\Delta E_{\text{Coul}} = 53.73$ kcal mol^{-1}) is weaker than at the transition state! Thus it appears that the formation of the „AEHB" complex $[F\cdots HCO_3]^{2-}$ is associated with a substantial decrease of the overall Coulombic forces which can be ascribed to a stabilizing electrostatic interaction that comes from the hydrogen bonding. It follows that the strength of the stabilizing Coulombic interactions of the hydrogen bonding at the equilibrium distance amounts to $\Delta\Delta E_{\text{Coul}} = -3.63$ kcal mol^{-1}. The counterintuitive contribution of quasi-classical[6] electrostatic bonding comes from the diffuse nature of the electronic charge that yields Coulombic interactions which exhibits a profoundly different behavior for interatomic interactions at short distances than what „is to be expected between ions of like charge". The shortening of the F-H distance does not only lead to stronger repulsion between the electronic charges. It also enhances the attraction between the nucleus of the fluorine atom and the electronic charge of HCO_3^-. The calculation of the Coulombic interactions between F^- and HCO_3^- using the correct formula shows that the increase of the nuclear–electron attraction at the equilibrium distance overcompensates the electron–electron repulsion. It is advisable to use quantum-chemical calculations rather than rough estimates based on invalid formulas for

Tabelle 1: Energy decomposition analysis at B3LYP/TZ2P+ of the equilibrium structure and transition state of $[F\cdots HCO_3]^{2-}$ which are reported in Ref. [1] and the structure with fixed distance $R_{\text{F-H}} = 1.5$ Å. The interacting fragments are F^- and CHO_3^-. Energy values in kcal mol^{-1} (TS = transition state; ES = equilibrium structure).

	TS	ES	Difference (ES–TS) $\Delta\Delta E$	$R_{\text{F-H}} = 1.5$ [Å]	Difference ($R_{\text{F-H}} = 1.5$ Å–TS) $\Delta\Delta E$
$R_{\text{F-H}}$	2.100	1.814		1.500	
ΔE_{Coul}	57.36	53.73	−3.63	42.15	−15.21
ΔE_{orb}	−11.10	−16.04	−4.94	−26.44	−15.34
ΔE_{Pauli}	4.24	10.58	6.34	29.64	25.40
ΔE_{Int}[a]	*50.50*	*48.27*	*−2.23*	*45.35*	*−5.15*
$\Delta E_{\text{Def.}}$	3.43	4.89	1.46	8.80	5.37
ΔE_{tot}[b]	*53.93*	*53.16*	*−0.77*	*54.15*	*0.22*

[a] $\Delta E_{\text{Int}} = \Delta E_{\text{Coul}} + \Delta E_{\text{orb}} + \Delta E_{\text{Pauli}}$. [b] $\Delta E_{\text{tot}} = \Delta E_{\text{Int}} + \Delta E_{\text{Def}}$.

assessing the strength of Coulombic interactions! A thorough discussion of the quasi-classical contributions to covalent bonding in conjunction with orbital interactions has been given in a paper by Krapp et al.[7]

We also calculated the contribution of the attractive orbital (covalent) interactions in $[F\cdots HCO_3]^{2-}$ which comes from the mixing of the occupied and vacant MOs of the fragments. Table 1 shows that the strength of the overall orbital interactions increases from $\Delta E_{orb} = -11.10$ kcal mol^{-1} at the transition state to $\Delta E_{orb} = -16.04$ kcal mol^{-1} at equilibrium. Thus, the formation of the hydrogen bonding is associated with a covalent contribution of $\Delta\Delta E_{orb} = -4.94$ kcal mol^{-1}. However, the mixing of the orbitals must also consider the interactions between electrons with the same spin which gives rise to exchange (Pauli) repulsion. Pauli repulsion is considered through antisymmetrization of the fragment MOs. Table 1 shows that the strength of the Pauli repulsion increases from $\Delta E_{Pauli} = 4.24$ kcal mol^{-1} at the transition state to $\Delta E_{Pauli} = 10.58$ kcal mol^{-1} at equilibrium which gives a net repulsion of $\Delta\Delta E_{Pauli} = 6.34$ kcal mol^{-1}. The sum of the differences of the three energy terms (Coulombic attraction, orbital interaction, Pauli repulsion) between the transition state and the equilibrium structure leads to an intrinsic interaction energy for the hydrogen bond of $\Delta\Delta E_{int} = -2.23$ kcal mol^{-1}. The associated deformation of the HCO_3^- fragment is $\Delta\Delta E_{Def} = 1.46$ kcal mol^{-1} which leads to the well depth of 0.77 kcal mol^{-1} (Table 1).

It is instructive to analyze the hydrogen bonding in $[F\cdots HCO_3]^{2-}$ at even shorter distances where according to WK the energy slowly increases with respect to the equilibrium structure. Table 1 shows the energy values for the complex where $R_{F\text{-}H} = 1.500$ Å which is the starting point of the relaxed scan energy curve that was reported by WK.[1] The geometry of the molecule is shown in Figure 1. The calculation shows that the Coulombic repulsion between F^- and HCO_3^- at the shorter distance $R_{F\text{-}H} = 1.500$ Å becomes still weaker ($\Delta E_{Coul} = 42.15$ kcal mol^{-1}) than at the transition state which has $R_{F\text{-}H} = 2.100$ Å ($\Delta E_{Coul} = 57.36$ kcal mol^{-1}). This can be explained with the strong attraction of the nucleus of F^- which comes closer to the electronic charge of HCO_3^-. The counterintuitive effect of atoms which have nuclei that are larger than hydrogen for Coulombic interactions at close distances has already been pointed out in 1974 by Hirshfeld and Rzotkiewicz[8a] and in 1986 by Spackman and Maslen.[8b] Table 1 shows that the orbital interactions ($\Delta E_{orb} = -26.44$ kcal mol^{-1}) and the Pauli repulsion ($\Delta E_{Pauli} = 29.64$ kcal mol^{-1}) are also larger than at longer distances. Interestingly, the overall net interaction energy at $R_{F\text{-}H} = 1.500$ Å with respect to the transition state is even more strongly attractive ($\Delta\Delta E_{int} = -5.15$ kcal mol^{-1}) than at the equilibrium structure ($\Delta\Delta E_{int} = -2.23$ kcal mol^{-1}). But the total energy increases at the shorter distance by 0.22 kcal mol^{-1} because the deformation energy of the HCO_3^- fragment ($\Delta\Delta E_{Def} = 5.37$ kcal mol^{-1}) overcompensates the stronger interaction energy.

The results of the energy decomposition analysis (EDA)[9] of the „AEHB“ complex which are presented here provide an alternative view of the interactions between the anions F^- and HCO_3^- in $[F\cdots HCO_3]^{2-}$ which is directly connected to the physical mechanism of the bond formation. The calculated energy terms are not observable, but they are mathematically unambiguously defined and can be interpreted in a physically meaningful way which is connected to concepts and models that are widely used in chemistry. The basic assumption of the EDA is the breakdown of a molecule into fragments which are then assembled in a well-defined procedure. A detailed discussion can be found in the literature.[7,10] The sum of the energy terms yields the experimentally observable bond dissociation energy which is a very important feature of the method. The underlying concept of the EDA method like any other energy partitioning method may become criticized for formal reasons. The great success in explaining experimental findings, particular for chemical bonding, molecular structures and energies, for many classes of main group compounds and transition-metal complexes are striking evidence for the usefulness of the method.[7,10c,11] Unlike in the paper by WK,[1] the Coulombic interactions are calculated with the correct formula for electronic charges rather than using hand-waiving arguments and a wrong equation. Furthermore, the calculated orbital interactions come directly from the relaxation of the fragment orbitals rather than from perturbation theory. Finally, the Pauli repulsion which is completely ignored by WK is calculated using proper antisymmetrization of the product wave function. The calculated numbers of the EDA terms are internally consistent and add up to the total interaction energy. In contrast, the NBO calculations of WK give an estimated strength of the donor–acceptor interaction in $[F\cdots HCO_3]^{2-}$ of 13.25 kcal mol^{-1} without that the connection to the well depth of 0.05 kcal mol^{-1} is explained.

The NBO approach is doubtlessly a helpful method to transfer the numerical results of a quantum-chemical calculation in a Lewis picture of chemical bonding. The simple usage and the often intuitively „correct“ results made it a widely used method. One should know, however, that NBO results do not come from straightforward mathematical steps but employ arbitrarily chosen weighting factors which yield biased data. The setup of the NBO algorithm comprises steps which were designed to give results that agree with the desired bonding picture of the authors and thus, they serve a self-fulfilling purpose.[12] More disturbing are recent attempts to use NBO calculations for analyzing the nature of the chemical bond. The NBO method has been developed with the goal to transform the calculated wave function into a set of MOs which can easily be interpreted in terms of Lewis structures. Other types of interatomic interactions such as Coulombic interactions which play an important role for chemical bonding are totally ignored.[13] It is therefore not surprising that NBO calculations always suggest orbital interactions for explaining chemical phenomena. Examples are the preference of the staggered conformation in ethane[14] and the nature of hydrogen bonding as discussed by WK.[1,15] The NBO method has been designed to explain a molecular structure in terms of Lewis picture. Problems arise whenever a molecule possesses an electronic structure which deviates from a classical description.

The physical nature of chemical bonding is quite complicated.[16] It is in most cases not necessary for a synthetic chemist to engage in elaborate quantum-chemical investigations. Standard calculations will usually provide sufficient information to classify a new compound and to design new experiments. The NBO method is often useful for such purpose, provided that the molecules can be well described with Lewis structures. The NBO method is useless for elucidating the nature of chemical bonding because it affords only information about orbital interactions in a biased way. The call for re-examination of the electrostatic nature of hydrogen bonding is unwarranted.

Eingegangen am 24. November 2014
Online veröffentlicht am 4. Februar 2015

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[12] For example, the standard NBO algorithm suppresses via artificial weighting factors the mixing of atomic orbitals (AOs) which are vacant in the ground state of an atom in the calculation of the MOs. The contribution of d AOs of heavier main group atoms in chemical bonding is disabled through the weighting factors but not by an unbiased diagonalization of the density matrix. Thus, the NBO method is unsuitable for disproving d AOs as main-group valence orbitals. The same situation holds true for the contribution of p AOs of transition metals to chemical bonding. NBO calculations have been used in the past to propose that the 18-electron rule for stable transition-metal complexes is invalid and should be replaced by a 12-electron role: C. R. Landis, T. K. Firman, D. M. Root, T. Cleveland, *J. Am. Chem. Soc.* **1998**, *120*, 1842–1854; The suggestion has been rejected by unbiased calculations which show that the transition metal p AOs are genuine valence orbitals: F. Maseras, K. Morokuma, *Chem. Phys. Lett.* **1992**, *195*, 500–504; C. A. Bayse, M. B. Hall, *J. Am. Chem. Soc.* **1999**, *121*, 1348–1358; A. Diefenbach, F. M. Bickelhaupt, G. Frenking, *J. Am. Chem. Soc.* **2000**, *122*, 6449–6458; For reviews see: G. Frenking, N. Fröhlich, *Chem. Rev.* **2000**, *100*, 717–774; G. Frenking in *The Chemical Bond. Chemical Bonding Across the Periodic Table* (Eds.: G. Frenking, S. Shaik), Wiley-VCH, Weinheim, **2014**, p. 175. For a recent example where the NBO method fails to describe the bonding situation in carbene complexes of coinage metals see: P. Jerabek, H. W. Roesky, G. Bertrand, G. Frenking, *J. Am. Chem. Soc.* **2014**, *136*, 17123–17135.

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