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The nature of the chemical bond revisited. An energy partitioning analysis of diatomic molecules E_2 (E = N–Bi, F–I), CO and BF

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Abstract. The nature of the chemical bonds in the diatomic molecules E_2 (E = N−Bi, F−I), CO and BF has been studied with an energy partitioning analysis using gradient-corrected density functional theory calculations. The results make it possible to estimate quantitatively the strength of covalent and electrostatic attractions and the Pauli repulsion between the atoms. The data suggest that some traditional explanations regarding the strength of the molecules should be modified. The energy partitioning analysis shows that the chemical bonds in the group 15 diatomic molecules have significant electrostatic character, which increases from 30.1% in N_2 to 58.3% in Bi_2. The contribution of the electrostatic attraction to the binding interactions in Sb_2 and Bi_2 is larger than the covalent bonding. The strength of the π bonding in the triply bonded dinitrogen is less than that of the σ bonding. The calculations indicate that ΔE_π is between 32.2% (Bi_2) and 40.0% (P_2) of the total orbital interaction energy (ΔE_{orb}). The much stronger bond of N_2, as compared with the heavier group 15 E_2 homologues, is not caused by a particularly strong contribution by the π bonding, but rather by the relatively large σ interactions. The comparison of N_2 with isoelectronic CO shows that the electrostatic character in the heteroatomic molecule is slightly smaller (28.8%) than in the homoatomic molecule. The contribution of the π bonding in CO is larger (49.2%) than in N_2 (34.3%). The reason why CO has a stronger bond than N_2 is the significantly weaker Pauli repulsion in CO. The electrostatic character of the bonding in BF is slightly larger (32.0%) than in CO and N_2. BF has much weaker π-bonding contributions that provide only 11.2% of the covalent interactions, which is why BF has a much weaker bond than CO and N_2. The chemical bonds in the dihalogen molecules have much higher covalent than electrostatic character. The ΔE_{orb} term contributes between 74.4% (Br_2) and 79.7% (F_2) to the total attractive interactions. The relatively weak bond in F_2 comes from the rather large Pauli repulsion.

Keywords: Diatomic molecules – Energy partitioning analysis – Bonding analysis

Introduction

The nature of the chemical bond between two neutral atoms, such as between the hydrogen atoms in H_2, has been one of the great scientific puzzles since the time when it was found that the strong interatomic attraction in dihydrogen could not be explained using the classical laws of electrostatics. Calculations of the electrostatic interactions, ΔE_{elstat}, between two neutral hydrogen atoms at the equilibrium distance of H_2 give only a spurious attraction of $\Delta E_{elstat} = -1.4$ kcal/mol [1, 2], while the bond dissociation energy (BDE) of H_2 is $D_e = 109.5$ kcal/mol [3].[1] It was only after Schrödinger and Heisenberg introduced modern quantum theory [4] that a satisfactory explanation for the chemical bond could be given. In 1927 Heitler and London showed that the interatomic attraction in dihydrogen results mainly from the resonance interactions between the electrons, which are treated as waves [5]. This was the breakthrough that led to a new interpretation of the nature of the interatomic interactions in molecules, which in turn paved the way for the development of quantum chemical models of the chemical bond [6, 7].

The theoretical work by Heitler and London led to the dogma that nonpolar bonds are purely covalent,

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[1] The energy partitioning analysis (*EPA*) of H_2 using the same level of theory as in the present work gives a repulsive electrostatic contribution at the equilibrium distance. The calculated value is $\Delta E_{elstat} = 5.8$ kcal/mol

which is stated in many chemistry textbooks to this day. This statement is supported by the valence bond (VB) model of the chemical bond, which uses mesomeric forms for describing the electronic structure in molecules [6]. Ionic structures such as II and III in Fig. 1 become increasingly important when the bond *A–B* becomes more polar, while the neutral form, I, is the dominant structure for nonpolar bonds *A–A*. It seems intuitively reasonable that covalent bonding prevails in I, while electrostatic attraction is the dominant force in II and III. But intuition does not always lead to the right answer! It was shown in 1974 by Hirshfeld and Rzotkiewicz [8] and then in 1986 by Spackman and Maslen [1], who investigated 148 diatomic molecules, that the electrostatic attraction between two neutral atoms in most homonuclear diatomic molecules, A_2, and many heteronuclear diatomic molecules is very strong. It may even be stronger than the BDE! For example, the electrostatic attraction between two nitrogen atoms in the ^{4}S ground state at the equilibrium distance of N_2 was calculated as $\Delta E_{\mathrm{elstat}} = -330.7$ kcal/mol [1], which is clearly higher than the BDE $D_e = 228.4$ kcal/mol [3]. The electrostatic attraction between two neutral atoms becomes repulsive only at very short distances, which is one reason why in H_2, which has a very short bond length, $\Delta E_{\mathrm{elstat}}$ is so small. What is missing in the work by Hirshfeld and Rzotkiewicz [8] and by Spackman and Maslen [1] is an estimate of the strength of the covalent bonding. This could be the reason why their reports about the strong electrostatic attraction did not change the prevailing picture of the nature of the chemical bond in nonpolar molecules.

Another widely held belief regarding quantum chemical models concerns the strength of π bonds between elements of the second and higher octal rows of the periodic system. There are a ubiquitous number of stable compounds of elements of the first octal row that have double and triple bonds, whereas molecules that have multiple bonds between heavier main-group elements are much less stable, unless they are protected by bulky substituents [9]. Textbooks of general and inorganic chemistry explain the intrinsically lower stability of the latter compounds by the weakness of the π bond between heavier elements.

We challenge both the previous dogmas regarding the nature of the chemical bond by giving a quantitative estimate of the electrostatic and covalent contributions to the chemical bond and the σ and π components of the latter interactions. In the following, we present an analysis of the interatomic interactions in the homonuclear diatomic molecules E_2 (E = N–Bi, F–I) and in the heteronuclear species CO and BF using an energy partitioning scheme that has been shown to give quantitative insights into chemical bonds of different classes of compounds [10, 11].

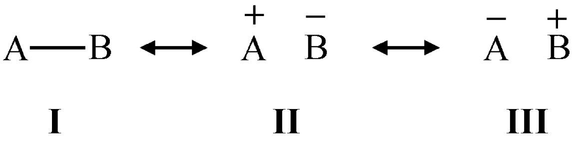

Fig. 1. Schematic representation of neutral (*I*) and ionic (*II*, *III*) resonance forms of a diatomic molecule *AB*

Methods

The bond lengths of the diatomic molecules were optimized at the nonlocal density functional theory level using the revised PBE exchange functional proposed by Hammer, Hansen and Norskov [12] in conjunction with the correlation functional of Perdew, Burke and Ernzerhof (RPBE) [13]. Uncontracted Slater-type orbitals (STOs) were employed as basis functions for the self-consistent-field (SCF) calculations [14]. The basis sets have triple-ζ quality augmented by one set of d-type polarization functions. This level of theory is denoted RPBE/TZP. An auxiliary set of s, p, d, f and g STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle [15]. Scalar relativistic effects were considered using the zero-order regular approximation [16]. The calculations were carried out with the program package ADF(2.3) [17, 18].

The interatomic interactions were analyzed by means of an energy decomposition scheme that was developed independently by Morokuma [19] and by Ziegler and Rauk [20]. The focus of the bonding analysis is the instantaneous interaction energy ΔE_{int} of the *A–B* bond, which is the energy difference between the molecule and the atoms in the electronic reference state; in this work this is always the electronic ground state. The interaction energy can be divided into three main components:

$$\Delta E_{\mathrm{int}} = \Delta E_{\mathrm{elstat}} + \Delta E_{\mathrm{Pauli}} + \Delta E_{\mathrm{orb}} \qquad (1)$$

$\Delta E_{\mathrm{elstat}}$ gives the electrostatic interaction energy between the promolecule *AB*, which is the juxtaposition of the free atoms at the equilibrium distance of the diatomic molecule, and the energy of the two atoms. The second term in Eq. (1), $\Delta E_{\mathrm{Pauli}}$, refers to the repulsive interactions between the atoms, which are caused by the fact that two electrons with the same spin cannot occupy the same region in space. $\Delta E_{\mathrm{Pauli}}$ is calculated by enforcing the Kohn–Sham determinant of the promolecule *AB* to obey the Pauli principle by antisymmetrization and renormalization. The stabilizing orbital interaction term, ΔE_{orb}, is calculated in the final step of the energy decomposition analysis when the Kohn–Sham orbitals relax to their optimal form. This term can be further partitioned into contributions by orbitals having σ, π, δ, etc. symmetry. The interaction energy, ΔE_{int}, of the diatomic molecules gives directly (by definition with opposite sign) the BDE $-D_e$. Further details of the EPA can be found in the literature [18].

Results and discussion

The EPA results of the diatomic group 15 molecules N_2–Bi_2 are given in Table 1. For the purpose of this study it is helpful to analyze the calculated data for dinitrogen in more detail. The calculated interaction energy of $\Delta E_{\mathrm{int}} = -232.2$ kcal/mol for N_2 gives a theoretical BDE $D_0 = 228.8$ kcal/mol, after correction for the contribution of zero-point vibrational energy, which is in excellent agreement with the experimental value $D_0 = 225.0$ kcal/mol [3]. The breakdown of ΔE_{int} into the three energy terms, as in Eq. (1), shows that the largest contribution comes from the Pauli repulsion, $\Delta E_{\mathrm{Pauli}} = 794.8$ kcal/mol. The attractive orbital term $\Delta E_{\mathrm{orb}} = -721.9$ kcal/mol is slightly smaller than the Pauli repulsion. However, the classical Coulomb attraction

Table 1. Energy partitioning analysis of the *E*–*E* bond for *E* = N–Bi. Energy values are given in kilo calories per mole. Bond lengths are given in angstroms. The symmetry point group is $D_{\infty h}$

	N_2	P_2	As_2	Sb_2	Bi_2
ΔE_{int}	−232.2	−109.2	−80.6	−54.4	−48.4
ΔE_{Pauli}	791.7	299.3	247.9	182.3	168.1
ΔE_{elstat}	−308.5(30.1%)	−175.8(43.0%)	−160.5(48.9%)	−131.5(55.6%)	−126.3(58.3%)
ΔE_{orb}	−715.4(69.9%)	−232.7(57.0%)	−168.0(51.1%)	−105.2(44.4%)	−90.3(41.7%)
ΔE_{σ}	−470.0(65.7%)	−140.1(60.0%)	−105.1(62.6%)	−69.9(66.4%)	−61.2(67.8%)
ΔE_{π}	−245.4(34.3%)	−92.6(40.0%)	−62.9(37.4%)	−35.3(35.6%)	−29.1(32.2%)
Overlap σ	0.18	0.30	0.32	0.34	0.34
Overlap π	0.37	0.30	0.28	0.24	0.24
E–*E* bond length[a]	1.105 (1.09768)[b]	1.935 (1.8931)[b]	2.161 (2.103)[b]	2.579 (2.48)[c]	2.728 (2.660)[b]
D_e	−232.2	−109.2	−80.6	−54.4	−48.4
D_0[a]	−228.8 (−225.0)[b]	−108.1 (−116.1)[b]	−80.0 (−91.3)[b]	−54.0(71.3)[b]	−48.1 (−47.0)[b]

[a] Experimental results are given in parentheses

[b] Bond lengths and D_0 values from Ref. [3]

[c] Bond length from Ref. [21]

between the two nitrogen atoms in the ^4S electronic ground state is also rather large. The calculated value $\Delta E_{elstat} = -310.6$ kcal/mol is clearly higher than the BDE $D_e = 232.2$ kcal/mol. This is in agreement with the previous work of Spackman and Maslen [1]. Following our suggestion to use the ratio of ΔE_{elstat} and ΔE_{orb} as a classification of the chemical bond [10, 11], the N–N bond in N_2 is 30.1% electrostatic and 69.9% covalent.

The three-step mechanism of the EPA suggests the following scenario for the bond formation. Two neutral nitrogen atoms in the ^4S ground state at the equilibrium distance of N_2 attract each other electrostatically with $\Delta E_{elstat} = -310.6$ kcal/mol. The curves of ΔE_{elstat}, ΔE_{Pauli} and ΔE_{orb} as a function of the N–N interatomic distances are shown in Fig. 2. The energy minimum of ΔE_{elstat} is at around 0.85 Å, with a well depth of around 450 kcal/mol. If the interatomic interactions in N_2 were to follow the laws of classical electrostatic forces, the N–N bond would be much shorter and the BDE much higher than experimentally observed. The energy curves in Fig. 2 use two different scales in order to demonstrate that the quantum theoretical forces ΔE_{Pauli} and ΔE_{orb} are stronger than ΔE_{elstat} over the whole range of the internuclear distance. The contributions by the Pauli repulsion and attractive orbital interactions nearly cancel at N–N distances of 1.2 Å or greater; however, the Pauli repulsion becomes dominant at shorter bond lengths.

The actual bond length and BDE of N_2 are determined by quantum theoretical effects. This statement sounds trivial and superfluous 76 years after the paper by Heitler and London [5] but a critical inspection of present chemistry textbooks [22] shows that the teaching of the chemical bond is still heavily influenced by thinking in terms of classical laws of physics. The quantum chemical contributions can be divided into two different quantities: ΔE_{Pauli} and ΔE_{orb}. Table 1 shows that the interatomic repulsion, ΔE_{Pauli}, between electrons in N_2 having the same spin is much higher than the electrostatic attraction between the nitrogen atoms. It is the attractive orbital term ΔE_{orb} which then leads to the calculated net attraction $D_e = 232.2$ kcal/mol. It is arbitrary, of course, to begin with the ΔE_{elstat} term and then to point out that the ΔE_{orb} term yields the overall bonding. Both terms are important for the interatomic attraction which yields chemical bonding. Therefore, we criticize the suggestion that ΔE_{elstat} and ΔE_{Pauli} should be added together to obtain a term called ΔE_{steric} [23]. The latter expression has nothing to do with the model of repulsive interactions between bulky substituents, which are mainly determined by ΔE_{Pauli}. The arbitrary addition of ΔE_{elstat} and ΔE_{Pauli} would lead to the deceptive result that only the covalent term ΔE_{orb} is responsible for the chemical bond in N_2. Of course, it would be equally arbitrary to add ΔE_{Pauli} and ΔE_{orb}, which nearly cancel each other at N distances of 1.2 Å or greater. Even if the equilibrium distance of N_2, by coincidence, had a value where $-\Delta E_{Pauli} = \Delta E_{orb}$, i.e. the point where the ΔE_{int} and ΔE_{elstat} curves in Fig. 2 cross, it would be misleading to state that the bond is completely electrostatic.

There are two other points we wish to clarify in order to avoid misunderstanding of the EPA results. Firstly, the suggestion that the attractive interactions in N_2 are 30.1% electrostatic and 69.9% covalent should not be used to support the idea that covalent bonding comes from the accumulation of electronic charge in the bonding region. The covalent bond is not an electrostatic phenomenon! The charge accumulation in the interatomic region is the result of chemical bonding but not its driving force. This has been shown in the ground breaking work by Ruedenberg [24], which revealed that the kinetic energy rather than the potential energy of the electrons plays the pivotal role in the formation of a covalent bond. For a more didactical approach to his results and enlightening discussions of Ruedenberg's work, see the papers by Kutzelnigg [25] and Rioux [22]. What we are trying to point out is that classical electrostatic attraction is an important component in chemical bonding, even in nonpolar bonds, without which molecules such as N_2 in the electronic ground state would not exist. Dihydrogen is perhaps the only molecule that has a chemical bond that is purely covalent [8].

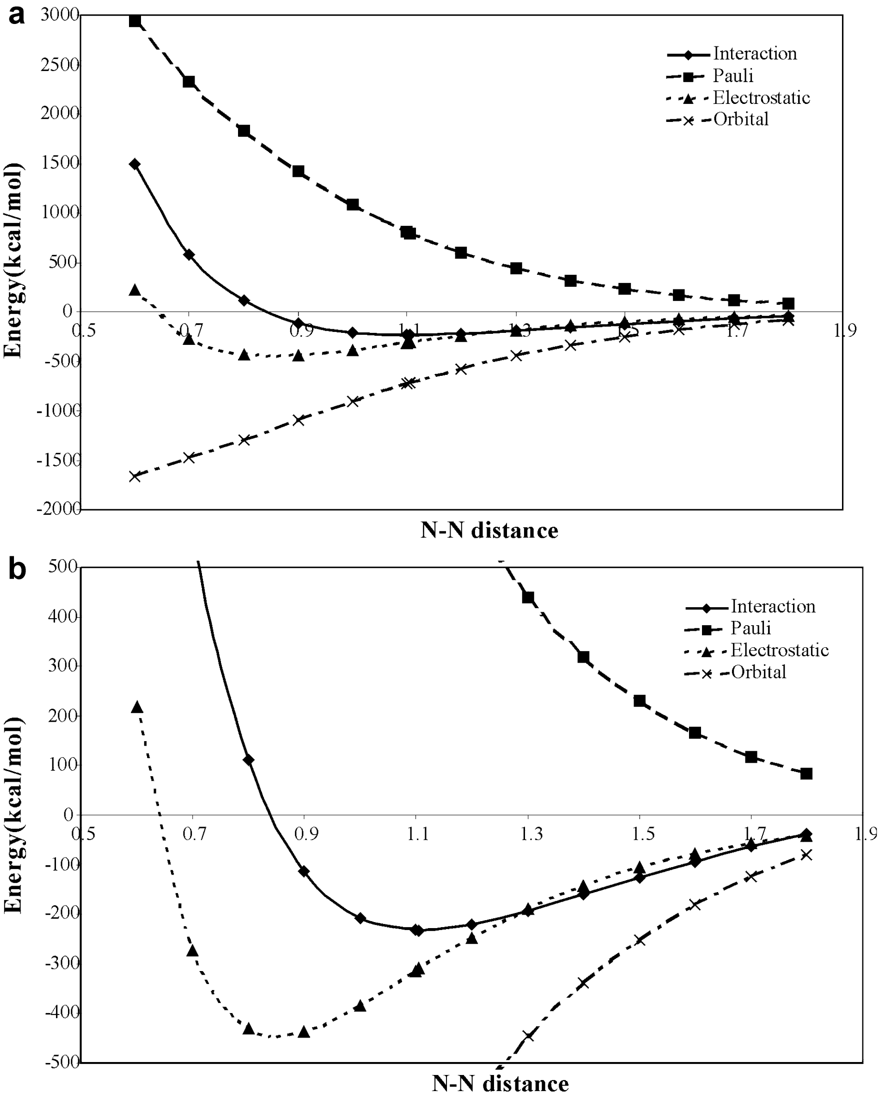

Fig. 2. Energy contributions to the bonding in N_2 as a function of N–N interatomic distance: **a** small scale, **b** large scale

Secondly, we want to emphasize that the calculated contributions by ΔE_{elstat} must not be confused with the weight of ionic resonance structures that are used to describe the bonding situation of a molecule using VB theory. The definition of ΔE_{elstat} has nothing to do with the electrostatic component of the bonding interactions, which is associated with a "mesomeric" structure. In VB theory, the bonding between two atoms or fragments is described in terms of neutral resonance forms, which are identified with covalent bonding, and ionic resonance forms, which suggest electrostatic interactions. This intuitively pleasing model was used by Pauling in order to explain that heteroatomic molecules often have stronger bonds than isoelectronic homoatomic bonds [6]. We will discuss this model in the light of the EPA result for CO later.

Table 1 shows that, in N_2, 65.7% of the orbital term, ΔE_{orb}, comes from σ contributions and 34.3% comes from π bonding. This is in agreement with the general picture that σ bonds are stronger than π bonds. It has been argued, however, that the σ bonding in N_2 is rather weak and that it is much weaker than the π bonds [25, 26]. The reasoning was based on a comparison of the bond strength of the N–N single bond in N_2H_4 which was used for estimating the value of a σ(N–N) bond (38 kcal/mol) with the total BDE of N_2 yielding a value of 94 kcal/mol for one π(N–N) bond. The comparison is not justified for several reasons. Hydrazine has a much longer N–N bond (1.449 Å) than N_2 (1.0977 Å), which means that the σ bonds in the two molecules are quite different. It has been shown by us that the weak N–N bond of N_2H_4 is mainly caused by the large Pauli repulsion between the nitrogen lone-pair electrons and that the strength of the σ orbital interactions is actually rather high (−225.9 kcal/mol) [2]. The dissociation energy of a bond is not a good measure for the strength of σ and π orbital interactions because electrostatic attraction and Pauli repulsion have a large influence on the BDE. The calculated values of ΔE_{σ} and ΔE_{π} which are given in Table 1 are much better estimates of the strength of σ and π orbital interactions.

Table 1 also gives the EPA results for the heavier homologues P_2–Bi_2. The bonds become weaker when the atoms become heavier. The calculated D_0 values are in good agreement with the experimental values except for Sb_2. The EPA results indicate that the electrostatic character of the *E*–*E* bond increases from N_2 ($\Delta E_{\mathrm{elstat}} = 30.1\%$) to Bi_2 ($\Delta E_{\mathrm{elstat}} = 58.3\%$). Thus, the chemical bonds in Sb_2 and Bi_2 are more electrostatic than covalent although the bonds are nonpolar. There is a decrease in the absolute values of $\Delta E_{\mathrm{elstat}}$ but the decrease is less than the decrease in ΔE_{orb}.

Table 1 shows that the relative contribution of the π orbitals to the ΔE_{orb} term increases from N_2 ($\Delta \mathrm{E}_{\pi} = 34.3\%$) to P_2 ($\Delta E_{\pi} = 40.0\%$) but then it decreases slightly in As_2 ($\Delta E_{\pi} = 37.4\%$), Sb_2 ($\Delta E_{\pi} = 35.6\%$) and Bi_2 ($\Delta E_{\pi} = 32.2\%$). It is experimentally known that molecules with multiple bonds between main-group elements of period 3 and higher are much less stable than compounds that contain multiply bonded elements of the first octal row of the periodic system, unless they are sterically protected [9]. This is often explained by the putatively weak π bond between heavier main-group elements. The data in Table 1 show that this explanation is not justified. The percentage contributions by ΔE_{π} to the orbital interactions in P_2, As_2 and Sb_2 are even slightly higher than in N_2 and the ΔE_{π} value of Bi_2 is only slightly less than in dinitrogen. The high reactivity and thus low stability of molecules with sterically unprotected multiple bonds between heavy main-group elements comes from the relatively small total BDE compared with the multiple bond between elements of the first octal row. Table 1 shows that the value of ΔE_{int} ($-D_{\mathrm{e}}$) of N_2 is much higher than for the heavier group 15 molecules, E_2. A comparison between the calculated energy terms of N_2 and the heavier homologues E_2 shows that the orbital interactions are much more important in the former molecule, as a result of the large $\Delta \mathrm{E}_{\sigma}$ value. The results of the EPA calculations thus indicate that the much stronger bond in N_2 as compared with the heavier E_2 homologues is not caused by a particularly strong contribution of the π bonding but rather by the large increase in the σ interactions.

Next we discuss the EPA results of the heteroatomic dimers CO and BF, which are shown in Table 2. CO is the most strongly bonded diatomic molecule that is known. The experimental BDE $D_0 = 255.7$ kcal/mol is higher than the BDE of N_2, $D_0 = 225.0$ kcal/mol. In chemistry textbooks the higher BDE of CO is explained by the larger weight of ionic resonance structures (Fig. 1). Since ionic resonance structures in VB theory are identified with electrostatic attraction, we can use the EPA results to check if the explanation is justified.

Table 2 shows that the theoretically predicted BDE of CO ($D_0 = 255.4$ kcal/mol) is in excellent agreement with experiment. The EPA calculation of CO was carried out in two different ways. CO has a $^1\Sigma^+$ ground state which dissociates into (^{3}P) C and (^{3}P) O, which are the atomic ground states. There are two different ways of combining the atoms with the electron configurations $1s^2 2s^2 2p^{\alpha} 2p^{\alpha} 2\mathrm{p}^0$ (^{3}P) carbon and $1s^2 2s^2 2p^2 2p^{\beta} 2p^{\beta}$ (^{3}P) oxygen yielding ($^1\Sigma^+$) CO. They are shown schematically in Fig. 3. The approach where the overall symmetry of the atomic configurations is the same as the point group of the CO molecule ($C_{\infty v}$) is displayed in Fig. 3a. This is the symmetry-adapted fragmentation procedure which leads to a donor–acceptor σ bond and two degenerate electron-sharing π bonds. The doubly occupied $2p^2$ orbital of oxygen and the empty $2p^0$ orbital of carbon have σ symmetry. The second approach, shown in Fig. 3b, has only C_{2v} symmetry for the atomic fragments. Here the doubly occupied $2p^2$ orbital of oxygen and the empty $2p^0$ orbital of carbon have π symmetry. The latter approach has one electron-sharing π-bond electron, one donor–acceptor π bond and an electron-sharing σ bond, as suggested by VB methods. Since the EPA calculation gives the contributions by orbitals having different symmetry it will be interesting to compare the strength of the electron-sharing and donor–acceptor σ and π bonds.

We discuss first the results of the symmetry-adapted fragmentation shown in Fig. 3a. The energy contributions to the calculated interaction energy ΔE_{int} ($-D_{\mathrm{e}}$)

Table 2. Energy partitioning analysis of the C–O and B–Fbonds. Energy values are given in kilo calories per mole. Bond lengths are given in angstroms. b_1 is the representation of bond formation, b_2 is the representation of donor–acceptor

	CO (optimized geometry $C_{\infty v}$)	CO (optimized geometry C_{2v})	CO (N_2 geometry)	BF (optimized geometry $C_{\infty v}$)	BF (N_2 geometry)
ΔE_{int}	−258.4	−258.4	−256.5	−180.8	−156.2
$\Delta E_{\mathrm{Pauli}}$	575.8	725.9	636.8	476.1	744.4
$\Delta E_{\mathrm{elstat}}$	−240.0(28.8%)	−291.1(29.6%)	−260.0(29.1%)	−210.5(32.0%)	−288.1(32.0%)
ΔE_{orb}	−594.2(71.2%)	−693.2(70.4%)	−633.3(70.9%)	−446.4(68.0%)	−612.6(68.0%)
ΔE_{σ}	−301.7(50.8%)	−464.7(67.0%)	−319.9(50.5%)	−396.4(88.8%)	−533.6(87.1%)
ΔE_{π}	−292.5(49.2%)	b_1 −143.8 (20.7%); b_2 −84.7(12.2%)	−313.4 (49.5%)	−50.0 (11.2%)	−79.0 (12.9%)
C–O bond length[a]	1.144 (1.128)[b]	1.144	1.105	1.285 (1.262)[b]	1.105
D_{e}	−258.4			−180.8	
D_0[a]	−255.4 (−255.7 ± 1)			−178.9 (179.9 ± 3)[c]	

[a] Experimental results are given in parentheses bond

[b] Bond lengths and D_0 values from Ref. [3]

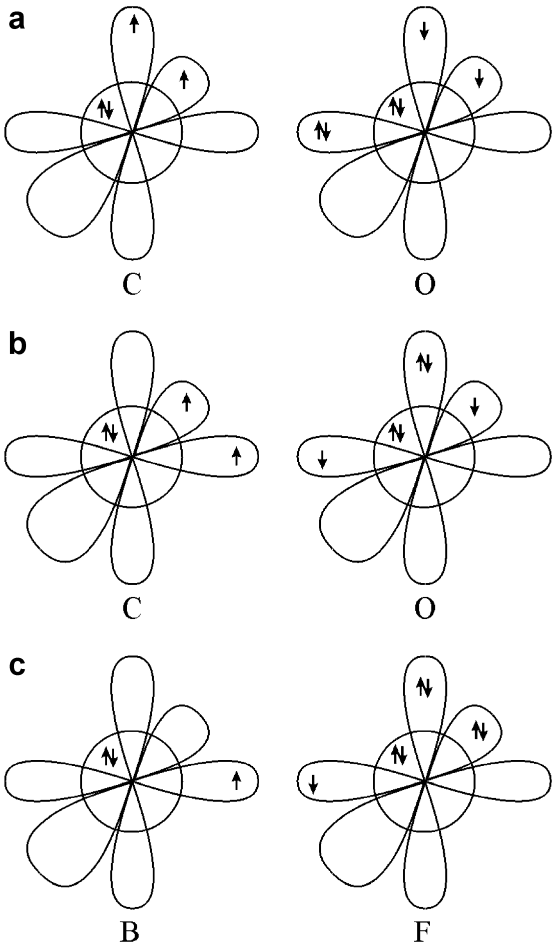

Fig. 3. Schematic diagram showing the different ways of combining the electron configurations for the energy partitioning analysis: **a** symmetry-adapted fragmentation procedure for CO, **b** C_{2v} symmetry approach for CO; **c** symmetry-adapted fragmentation procedure for BF

suggest that 71.2% come from the orbital term and only 28.8% come from the electrostatic attraction. The small relative contribution of the $\Delta E_{\mathrm{elstat}}$ term, which is even smaller than in N_2 (30.1%), is surprising considering the fact that CO is a polar molecule [27].[2] Even more surprising, but at the same time more revealing, are the absolute values of $\Delta E_{\mathrm{elstat}}$ and ΔE_{orb}. Table 2 shows that the attractive energy components $\Delta E_{\mathrm{elstat}}$ (-240.0 kcal/mol) and ΔE_{orb} (−594.2 kcal/mol) are both smaller in CO than in N_2. The EPA results indicate a paradoxical situation by saying that CO has a stronger bond than N_2 although the attraction between carbon and oxygen is less than between two nitrogen atoms. The main difference between the two molecules is the strength of the Pauli repulsion, which is much smaller in CO than in N_2.

Does the surprising EPA result of CO depend on the fragmentation pattern that has been chosen for the calculation? The answer is no! Table 2 shows that the EPA results of the calculation using the configuration pattern shown in Fig. 3b lead to the same conclusion although the numbers calculated are somewhat different. The latter data suggest slightly greater electrostatic character (29.6%) compared with the results of the symmetry-adapted arrangement of the atomic fragments. The absolute values of $\Delta E_{\mathrm{elstat}}$ (−291.1 kcal/mol) and ΔE_{orb} (−693.2 kcal/mol) are higher in the C_{2v} approach than in the $C_{\infty v}$ approach but they are still smaller than the attractive energy components of N_2. The larger value for the interaction energy ΔE_{int} of CO comes from the much smaller $\Delta E_{\mathrm{Pauli}}$ value. This holds for the C_{2v} approach as well as for the $C_{\infty v}$ approach.

Finally, we analyzed the interatomic interactions in CO at the bond length of N_2 (1.105 Å) using the $C_{\infty v}$ approach. Table 2 shows that the values of the attractive components $\Delta E_{\mathrm{elstat}}$ (−260.0 kcal/mol) and ΔE_{orb} (−633.3 kcal/mol) are larger at $r = 1.105$ Å than at the equilibrium bond length r(C–O) = 1.144 Å, but they are still smaller than the attractive interactions in N_2. Thus, the smaller value for $\Delta E_{\mathrm{Pauli}}$ for CO than for N_2 is not because the former molecule has a slightly longer bond. The reason why CO has a stronger bond than N_2 is the significantly weaker Pauli repulsion in CO! This result contradicts present bonding models in chemistry textbooks, but because it is based on a quantitative energy decomposition analysis rather than on hand-waving arguments it is physically meaningful and thus the correct explanation.

Table 2 also gives the EPA results of BF. The bonding analysis was carried out using the symmetry-adapted fragmentation approach shown in Figure 3c. The theoretically predicted BDE of BF ($D_0 = 178.9$ kcal/mol) agrees very well with the experimental value ($D_0 = 183 \pm 3$ kcal/mol). The calculated interaction energy $\Delta E_{\mathrm{int}} = -180.8$ kcal/mol is clearly less than what is found for N_2 and CO. Nevertheless, the bond strength is much higher compared with a typical B–F single bond and, thus, a significant contribution by π-orbital interactions could be expected. Table 2 shows that the Pauli repulsion in BF is much less ($\Delta E_{\mathrm{Pauli}} = 476.1$ kcal/mol) than in N_2 and CO. This comes from the B–F bond (1.285 Å), which is clearly longer than the N–N and C-O bonds. The EPA calculation of BF at the equilibrium distance of N_2 gives the much larger value $\Delta E_{\mathrm{Pauli}} =$ 744.4 kcal/mol, which is larger than in CO and nearly as large as in N_2 (Tables 1, 2).

The EPA data thus indicate that the weaker bond of BF comes from less interatomic attraction compared with N_2 and CO. The calculated value $\Delta E_{\mathrm{elstat}} =$ −210.5 kcal/mol is indeed lower than the values for the latter diatomic molecules. A much larger decrease, however, is found for the orbital interactions. The covalent contribution to the attractive interactions in BF

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[2] The overall polarity of CO given by the dipole moment is rather small (0.11 D) [28]. This comes from the topography of the electronic charge distribution. The highest occupied molecular orbital of CO is mainly a σ lone-pair orbital which has its largest extension at the carbon end. It has a strong influence on the dipole moment, which is a vector property. The polarity of the σ and π bonding orbitals is rather high

($\Delta E_{\mathrm{orb}} = -446.4$ kcal/mol) is much less than in N_2 and CO. Note that the relative contribution of ΔE_{orb} (68.0%) is only slightly less than in the latter molecules. The large decrease in the orbital interactions comes from the strength of the π orbitals, which provide only $\Delta E_{\pi} = -50.0$ kcal/mol (11.2%) to the ΔE_{orb} term. The crucial difference between the bond strength of BF compared with N_2 and CO is the π bond, which is rather weak in the former molecule but very strong in the latter two. A comparison of the results for the three diatomic molecules at the same interatomic distance $r = 1.105$ Å, which is the equilibrium distance of N_2, shows that, without the ΔE_{π} values, BF would have the strongest bond (Tables 1, 2). This is due to the large ΔE_{σ} value of BF.

The difference in strength of the electron-sharing and donor–acceptor σ and π bonds can also be analyzed using the data in Table 2. The results from analysis of CO in the C_{2v} symmetry give us a picture of the difference between electron-sharing and donor–acceptor π bonds. Donor–acceptor π bonds are substantially (59.1 kcal/mol) weaker than those obtained from the sharing of one electron from each atom. The value of the single donor–acceptor π bond in the C_{2v} symmetry calculation is approximately half of the total value for the two π donor–acceptor bonds in the $C_{\infty v}$ approach. The σ bond shows an even greater sensitivity to being donor–acceptor or electron-sharing, with the electron-sharing bonds being 163.0 kcal/mol stronger.

Finally, we discuss the EPA results for the dihalogens E_2 ($E = \mathrm{F{-}I}$) which are shown in Table 3. The calculated BDE values are in very good agreement with experimental data, except for F_2. The theoretical result $D_0 = 46.0$ kcal/mol is higher than the experimental value $D_0 = 36.9$ kcal/mol but theory and experiment agree that the BDE of F_2 is less than the BDE of Cl_2. This is usually explained by enhanced Pauli repulsion between the occupied $p(\pi)$ orbitals which is particularly strong in F_2 because it has the shortest bond of the dihalogens. The calculated and observed values of the interaction energies and the BDEs exhibit the trend $Cl_2 > Br_2 > F_2 > I_2$.

Table 3 shows that the values of $\Delta E_{\mathrm{Pauli}}$ and ΔE_{orb} increase monotonously from I_2 to F_2. The values of $\Delta E_{\mathrm{elstat}}$ also increase from I_2 to Cl_2, whereas the electrostatic attraction in F_2 is 5.9 kcal/mol weaker than in Cl_2. However, the sum of the attractive interactions $\Delta E_{\mathrm{elstat}} + \Delta E_{\mathrm{orb}}$ increases from Cl_2 to F_2 by 6.0 kcal/mol. Thus, the EPA calculations show that the lower value of the interaction energy in F_2 ($\Delta E_{\mathrm{int}} = -47.4$ kcal/mol) when compared with Cl_2 ($\Delta E_{\mathrm{int}} = -59.1$ kcal/mol) is indeed caused by the larger Pauli repulsion in the former compound ($\Delta E_{\mathrm{Pauli}} = 140.8$ kcal/mol) than in the latter molecule ($\Delta E_{\mathrm{Pauli}} = 123.2$ kcal/mol).

According to the EPA results, chemical bonding in dihalogens is mainly covalent but the electrostatic attraction is not negligible. The covalent contributions to the attractive interactions are between 75 and 80% (Table 3), which means that the dihalogen bonds are much more covalent than the dinitrogen bonds. The calculated values of ΔE_{σ} and ΔE_{π} indicate that the covalent bonding in the dihalogens comes, as expected, from the σ interactions. The small stabilization by the π orbitals is surprising at first sight because there are no empty π valence orbitals that could lead to covalent bonding. Closer investigation shows that the weak stabilization does not come from genuine orbital interactions but rather from the energy-lowering of the occupied π orbitals through the electrostatic field of the other halogen atom.

We calculated the values of $\Delta E_{\mathrm{elstat}}$, $\Delta E_{\mathrm{Pauli}}$ and ΔE_{orb} as a function of the F–F interatomic distance in F_2. A plot of the energy curves is displayed in Fig. 4. The equilibrium distance of F_2 occurs before the curves of ΔE_{int} and $\Delta E_{\mathrm{elstat}}$ cross. This does not mean that the electrostatic attraction between two fluorine atoms may not become strong at short distances. The electrostatic attraction has a minimum at around 0.77 Å, with a well depth of around 380 kcal/mol, which is shorter and less steep than for N_2 (Fig. 2) but still rather strong. The crucial difference between the interatomic interactions in N_2 and F_2 comes from the different strengths of the Pauli repulsion and orbital terms. A comparison of the $\Delta E_{\mathrm{Pauli}}$ and ΔE_{orb} values of N_2 and F_2 at $r = 1.30$ Å shows that the Pauli repulsion in N_2 is much stronger (440.0 kcal/mol) than in F_2 (258.4 kcal/mol) because the nitrogen orbitals are more diffuse than the fluorine orbitals. This is compensated, however, by the even

Table 3. Energy partitioning analysis of the E–E bond for $E = \mathrm{F{-}I}$. Energy values are given in kilo calories per mole. Bond lengths are given in angstroms. The symmetry point group is $D_{\infty h}$

	F_2	Cl_2	Br_2	I_2
ΔE_{int}	−47.4	−59.1	−47.8	−34.1
$\Delta E_{\mathrm{Pauli}}$	140.8	123.2	76.7	45.4
$\Delta E_{\mathrm{elstat}}$	−38.2 (20.3%)	−44.1 (24.2%)	−31.9 (25.6%)	−19.8 (24.9%)
ΔE_{orb}	−150.0 (79.7%)	−138.1 (75.8%)	−92.6 (74.4%)	−59.7 (75.1%)
ΔE_{σ}	−144.6 (96.4%)	−123.8 (89.6%)	−85.9 (92.8%)	−59.4 (99.5%)
ΔE_{π}	−5.4 (3.6%)	−14.3 (10.4%)	−6.7 (7.2%)	−0.3 (0.5%)
E–E bond length[a]	1.424 (1.412)[b]	2.037 (1.987)[b]	2.381 (2.281)[b]	2.860 (2.666)[b]
D_e	−47.4	−59.1	−47.8	−34.1
D_0[a]	−46.0 (−36.9)[b]	−58.3 (−57.2)[b]	−47.4 (−45.4)[b]	−33.8 (−35.6)[b]

[a] Experimental results are given in parentheses

[b] Bond lengths and D_0 values from Ref. [3]

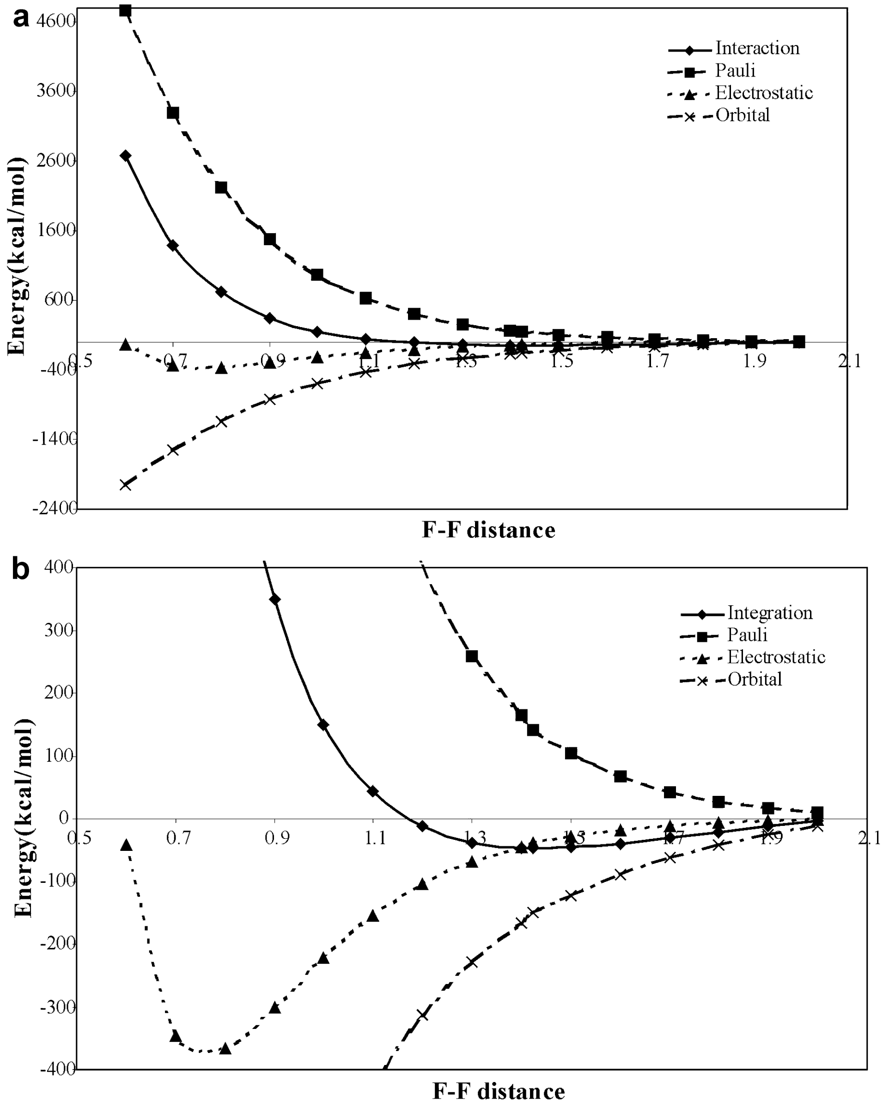

Fig. 4. Energy contributions to the bonding in F_2 as a function of F–F interatomic distance: **a** small scale, **b** large scale

stronger attractive orbital term in N_2 (−445.2 kcal/mol) than in F_2 (−227.9 kcal/mol). Thus, the net effect of $\Delta E_{\text{Pauli}}+\Delta E_{\text{orb}}$ for N_2 at $r=1.30$ Å is nearly zero and the electrostatic attraction therefore yields an N_2 bond shorter than $r=1.30$ Å. In F_2, however, the net effect of $\Delta E_{\text{Pauli}}+\Delta E_{\text{orb}}$ of F_2 at $r=1.30$ Å is repulsive with a strength of 30.5 kcal/mol. The equilibrium bond length of F_2 is therefore more than 1.30 Å.

Summary and conclusion

The results of the work can be summarized as follows.

1. The EPA suggests that the chemical bonds in the group 15 diatomic molecules E_2 have significant electrostatic character which increases from 30.1% in N_2 to 58.3% in Bi_2. The contribution of the electrostatic attraction to the binding interactions in Sb_2 and Bi_2 is larger than the covalent bonding. The strength of the π bonding in the triply bonded dinitrogens is less than that of the σ bonding. The calculations indicate that ΔE_π is between 32.2% (Bi_2) and 40.0% (P_2) of ΔE_{int}. The much stronger bond of N_2 compared with the heavier E_2 homologues is not caused by a particularly strong contribution by the π bonding, but rather by the relatively large σ interactions.
2. A comparison of N_2 with isoelectronic CO shows that the electrostatic character in the heteroatomic molecule is slightly smaller (28.8%) than in the homoatomic molecule. The contribution of the π bonding in CO is larger (49.2%) than in N_2 (34.3%). The reason for CO having a stronger bond than N_2 is the significantly weaker Pauli repulsion in CO. The electrostatic character of the bonding in BF is slightly larger (32.0%) than in CO and N_2. BF has much weaker π-bonding contributions that provide only 11.2% of the covalent interactions. This is the reason why BF has a much weaker bond than CO and N_2.
3. The chemical bonds in the dihalogen molecules have much higher covalent than electrostatic character. The ΔE_{orb} term contributes between 74.4% (Br_2) and 79.7% (F_2) to the total attractive interactions. The

relatively weak bond in F_2 comes from the rather large Pauli repulsion.

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References

1. Spackman MA, Maslen EN (1986) J Phys Chem 90:2020
2. Kovács A, Esterhuysen C, Frenking G (2003) Chem Eur J (submitted)
3. Huber KP, Herzberg G (1979) Molecular spectra and molecular structure IV. Constants of diatomic molecules. Van Nostrand Reinhold, New York
4. (a) Schrödinger E (1926) AnnPhys 79:361; (b) Heisenberg W (1927) Z Phys 43:172
5. Heitler W, London F (1927) Z Phys 44:455
6. Pauling L (1960) The nature of the chemical bond, 3rd edn. Cornell University Press, Ithaca, NY
7. Coulson CA (1952) Valence. Oxford University Press, Oxford
8. Hirshfeld FL, Rzotkiewicz S (1974) Mol Phys 27:1319
9. Power PP (1999) Chem Rev 99:3463
10. (a) Diefenbach A, Bickelhaupt FM, Frenking G (2000) J Am Chem Soc 122:6449; (b) Chen Y, Frenking G (2001) J Chem Soc Dalton Trans 434; (c) Lein M, Frunzke J, Timoshkin A, Frenking G (2001) Chem Eur J 7:4155; (d) Uddin J, Frenking G (2001) J Am Chem Soc 123:1683; (e) Doerr M, Frenking G (2002) Z Anorg Allg Chem 628:843; (f) Frenking G, Wichmann K, Fröhlich N, Grobe J, Golla W, Le Van D, Krebs B, Läge M (2002) Organometallics 21:2921; (g) Frunzke J, Lein M, Frenking G (2002) Organometallics 21:3351; (h) Loschen C, Voigt K, Frunzke J, Diefenbach A, Diedenhofen M, Frenking G (2002) Z Anorg Allg Chem 628:1294; (i) Rayón VM, Frenking G (2002) Chem Eur J 8:4693; (j) Cases M, Frenking G, Duran M, Solà M (2002) Organometallics 21:4182
11. Frenking G, Wichmann K, Fröhlich N, Loschen C, Lein M, Frunzke J, Rayón VM (2003) Coord Chem Rev 55:239–239
12. Hammer B, Hansen LB, Norskov JK (1999) Phys Rev B 59:7413
13. Perdew JP, Burke K, Ernzerhof M (1996) Phys Rev Lett 77:3865
14. Snijders JG, Baerends EJ, Vernooijs P (1982) At Nucl Data Tables 26:483
15. Krijn J, Baerends EJ (1984) Fit functions in the HFS method, internal report (in Dutch). Vrije Universiteit Amsterdam, Amsterdam
16. (a) Chang C, Pelissier M, Durand P (1986) Phys Scr 34:394; (b) Heully J-L, Lindgren I, Lindroth E, Lundquist S, Martensson-Pendrill A-M (1986) J Phys B 19:2799; (c) van Lenthe E, Baerends EJ, Snijders JG (1993) J Chem Phys 99:4597; (d) van Lenthe E, Baerends EJ, Snijders JG (1996) J Chem Phys 105:6505; (e) van Lenthe E, van Leeuwen R, Baerends EJ Snijders JG (1996) Int J Quantum Chem 57:281
17. Bickelhaupt FM, Baerends EJ (2000) In: Lipkowitz KB, Boyd DB (eds) Reviews of computational chemistry, vol 15. Wiley-VCH, New York, p 1
18. te Velde G, Bickelhaupt FM, Baerends EJ, van Gisbergen SJA, Fonseca Guerra C, Snijders JG, Ziegler T (2001) J Comput Chem 22:931
19. Morokuma K (1971) J Chem Phys 55:1236
20. Ziegler T, Rauk A (1977) Theor Chim Acta 46:1
21. Sontag H, Weber R (1982) J Mol Spectrosc 91:72
22. Rioux F (2003) Chem Educator 8:1
23. (a) Ziegler T, Tschinke V, Becke A (1987) J Am Chem Soc 109:1351; (b) Ziegler T, Tschinke V, Ursenbach C (1987) J Am Chem Soc 109:4825; (c) Li J, Schreckenbach G, Ziegler T (1995) J Am Chem Soc 117:486
24. Ruedenberg K (1962) Rev Mod Phys 34:326
25. Kutzelnigg W (1990) In: Maksic ZB (ed) Theoretical models of chemical bonding, vol 2. Springer, Berlin Heidelberg New York, p 1
26. (a) Kutzelnigg W (1984) Angew Chem 96:262; (b) Kutzelnigg W (1984) Angew Chem Int Ed Engl 23:272
27. Lupinetti AJ, Jonas V, Thiel W, Strauss SH, Frenking G (1999) Chem Eur J 5:2573
28. Muenter JS (1975) J Mol Spectrosc 55:490