

Is the decrease of the total electron energy density a covalence indicator in hydrogen and halogen bonds?

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Abstract In this work, halogen bonding (XB) and hydrogen bonding (HB) complexes were studied with the aim of analyzing the variation of the total electronic energy density $H(r_b)$ with the interaction strengthening. The calculations were performed at the MP2/6-311++G (2d,2p) level of approximation. To explain the nature of such interactions, the atoms in molecules theory (AIM) in conjunction with reduced variational space self-consistent field (RVS) energy decomposition analysis were carried out. Based on the local virial theorem, an equation to decompose the total electronic energy density $H(r_b)$ in two energy densities, $(-G(r_b))$ and $1/4\nabla^2\rho(r_b)$, was derived. These energy densities were linked with the RVS interaction energy components. Through the connection between both decomposition schemes, it was possible to conclude that the decrease in $H(r_b)$ with the interaction strengthening observed in the HB as well as the XB complexes, is mainly due to the increase in the attractive electrostatic part of the interaction energy and in lesser extent to the increase in its covalent character, as is commonly considered.

Keywords AIM · Energy decomposition · Hydrogen/halogen bonds · RVS · Total electron energy density

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Introduction

Hydrogen bonding (HB) and halogen bonding (XB) are two of the most important weak interactions playing a key role in chemistry, physics, and biology [1, 2]. A relevant topic, which is still open to discussion, is about the electrostatic/covalent nature of these interactions. The nature of HBs in particular is often subject of discussion. The XB is less familiar than the hydrogen bond, but it is similar to the latter in several respects [2]. Originally, the HB was considered an electrostatic interaction, as is shown by the previous definitions of hydrogen bond which stated that HB could be formed only when the hydrogen atom is placed between the most electronegative atoms [3]. It has been gradually recognized that other types of energetic contributions like the charge transference and dispersion energies are also relevant to HB formation. In the 1990s Gilli et al. [4] established, through their electrostatic-covalent hydrogen bond model (ECHBM), that the weak HBs are electrostatic in nature but they become increasingly covalent with the increase of strength, whereas very strong HBs are essentially *three-center-four-electron* covalent bonds. In a recent review about the nature of HBs, Grabowski [5] has pointed out that there is abundant evidence that covalency is attributed to hydrogen bond as a kind of interaction, and not only to short and strong interactions. According to the author, the covalency is the driving force of hydrogen bond determining its characteristics. Most of the recent evidence supporting this point of view arises from the topological parameters derived from Bader's charge density analysis.

The quantum theory of atoms in molecules (QTAIM) by professor Bader [6] provides the characteristics at the bond critical point (BCP) of the interaction. Particularly, the Laplacian of the electronic charge density at this point ($\nabla^2\rho(r_b)$) provides information about the nature of the interaction [7]. For shared interactions like covalent bonds, the Laplacian of

electron density is negative because there is a concentration of electron density within the atom-atom region. For the interactions between closed-shell systems like hydrogen and halogen bonds, there is a depletion of electron charge within the atom-atom region and hence the Laplacian is positive.

The local statement of the virial theorem (Eq. 1) relates a property of the charge density, as its Laplacian, with the local kinetic energy density ($G(r_b)$) and the local potential energy density ($V(r_b)$).

$$\frac{1}{4} \nabla^2 \rho(r_b) = 2G(r_b) + V(r_b) \quad (1)$$

Because $G(r_b) > 0$ and $V(r_b) < 0$, the modulus of the potential energy outweighs two times the kinetic energy, in those space regions with electronic charge concentration, i.e., where $\nabla^2 \rho(r_b) < 0$.

Moreover, the local electronic energy density at the interaction BCP is given by

$$H(r_b) = G(r_b) + V(r_b). \quad (2)$$

From Eqs. 1 and 2 one can see that for regions with electronic charge concentration where $|V(r_b)| > 2 G(r_b)$, the local electronic energy density will also be negative. Therefore, a negative value of $H(r_b)$ is often interpreted as a consequence of the charge density accumulation at the interaction BCP. Thus, for covalent bonds, both $H(r_b)$ and $\nabla^2 \rho(r_b)$ are negative quantities. There is an interesting situation in the case that the potential energy is the dominant density at the interaction BCP, despite the fact that $|V(r_b)| < 2 G(r_b)$. In such situation $\nabla^2 \rho(r_b)$ would be positive whereas $H(r_b)$ would still be negative. Some authors claim that this last case corresponds to the partial covalency of the interaction [8–12]. Moreover, when the kinetic energy is the dominant density, both $H(r_b)$ and $\nabla^2 \rho(r_b)$ are positive quantities. This is the case with non covalent interactions.

Based on this classification of interactions, Grabowski et al. [13] grouped a set of 34 complexes representing different types of interactions, in covalent ($\nabla^2 \rho(r_b) < 0$ and $H(r_b) < 0$), partially covalent ($\nabla^2 \rho(r_b) > 0$ and $H(r_b) < 0$) and non covalent ($\nabla^2 \rho(r_b) > 0$ and $H(r_b) > 0$) interactions. They found that the covalency of the interaction increases with the shortening of the proton-acceptor distance $d(H \cdots Y)$. In conjunction with the QTAIM analysis, they performed an energy decomposition analysis (EDA) on the same set of complexes, finding that the ratio $E_{\text{DEL}}/E_{\text{EL}}$ between the delocalization and electrostatic interaction energy components, also increases with the shortening of the $H \cdots Y$ distance. Since the delocalization interaction energy (or charge transfer) is usually attributed to the covalency of interaction [14], the increase of $E_{\text{DEL}}/E_{\text{EL}}$ ratio with the shortening of $d(H \cdots Y)$ indicates an increase in the covalency with the shortening of the proton-acceptor distance, in agreement with the QTAIM results.

However, recently Ramirez et al. [15] performed structural studies of the water pentamer finding that higher $\rho(r_b)$ values lead to stronger HBs and similarly, higher positive values for $\nabla^2 \rho(r_b)$, that is, more ionic and less covalent character of the hydrogen bonds also lead to more stable structures. This study demonstrates that electrostatic forces in the form of dipole–dipole interactions are the major contributors to the stabilization of the water pentamer.

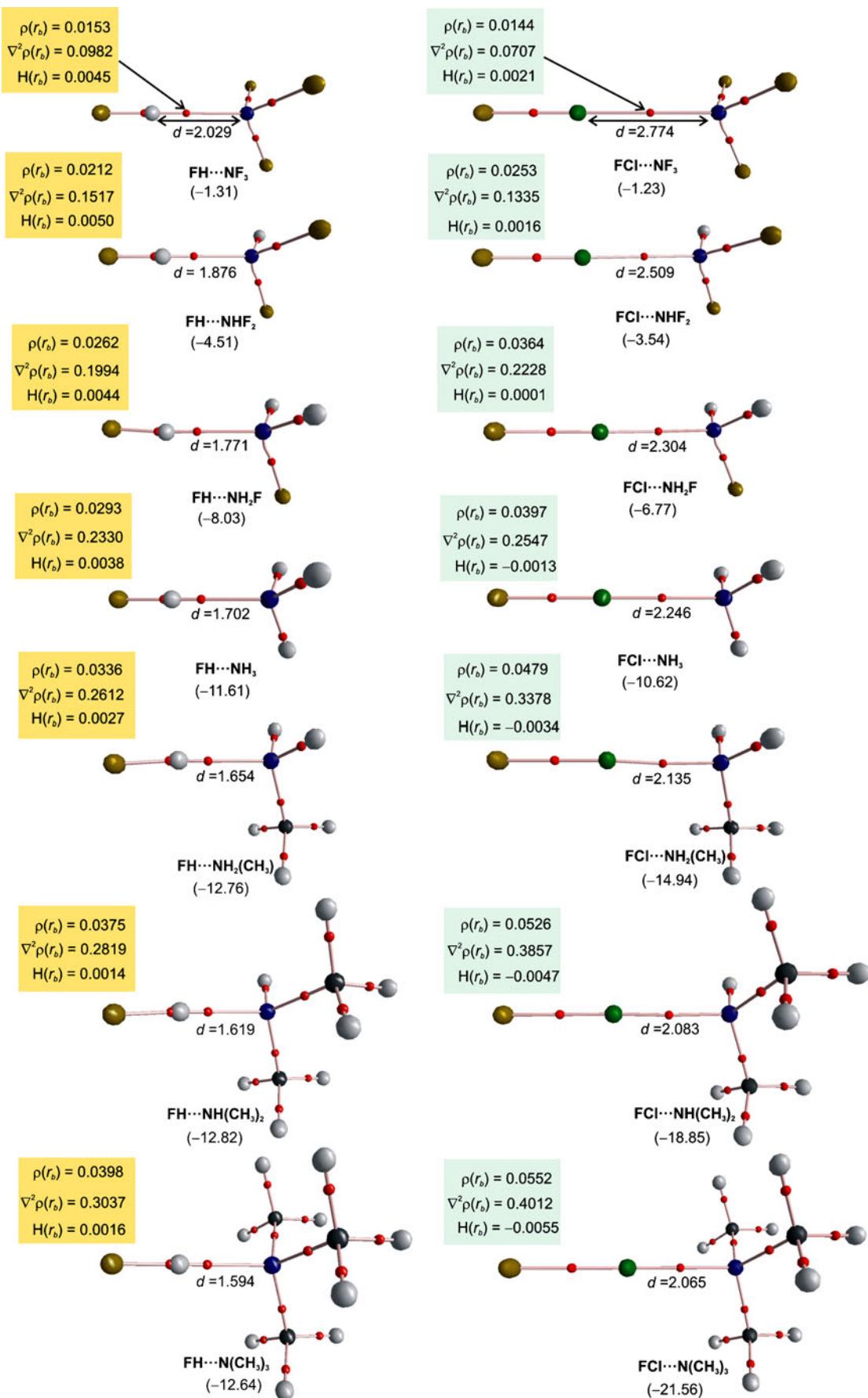
The interrelationship between the QTAIM topological parameters and the interaction energy components, is one of the most interesting aspects of Grabowski's research about the nature of the interactions, since it is intended to link the physics of electrons at a point (i.e., the intermolecular BCP) provided by the topological parameters with the physics of the electrons at the hydrogen (or halogen) bond, exploited by the interaction energy components.

On the basis of this background, we have previously proposed a local scheme to decompose the total electronic energy density at the interaction BCP ($H(r_b)$) in two components, $1/4 \nabla^2 \rho(r_b)$ and $(-G(r_b))$ linked with the interaction energy components that account for the covalency and the electrostatics of HB, respectively [16]. By applying the proposed decomposition scheme to a set of hydrogen bonding complexes, it was found that the decrease of $H(r_b)$ toward negative values, as the interaction strengthens, is due to the increase in the electrostatic contribution to the total interaction energy. These results dispute the belief that the negativity of $H(r_b)$ is related with the covalency of interactions.

In this work the proposed decomposition of $H(r_b)$ is applied to a set of complexes of the type $F-X \cdots NY_m H_{(3-m)}$ with $m=1-3$, $Y = -F$ or $-CH_3$ and $X = H$ or Cl for the HB or XB complexes, respectively (see Fig. 1), with the aim of extending the previous analysis to halogen bonding complexes.

From the present results it was possible to conclude that the decrease of total energy density at BCP, could be considered as an indicator of the strengthening or stabilization of the interaction in the same way that the total interaction energy is an indicator of the complex stabilization. A negative value of $H(r_b)$ (or its trend toward negative values) is not necessarily associated with covalency or electrostatics; but its components, $1/4 \nabla^2 \rho(r_b)$ and $(-G(r_b))$ are the ones which provide information about the nature of the interaction.

Fig. 1 Molecular graphs for the complexes $F-X \cdots NY_m H_{(3-m)}$ with $m=1-3$, $Y = -F$ or $-CH_3$ and $X = H$ or Cl , for the HB or XB complexes, respectively. The big circles correspond to attractors or nuclear critical points (3,−3), attributed to nuclei; the lines connecting the nuclei are the bond paths, and the small circles on them are the bond critical points or (3,−1) critical points. The interaction energy (in kcal mol^{-1}) calculated at the $\text{MP2}/6-311++G(2d,2p)$ level of theory is indicated in brackets. Also, the $\rho(r_b)$, $\nabla^2 \rho(r_b)$ and $H(r_b)$ values at the intermolecular BCP (in atomic units, au.) and the intermolecular distance (d , in Å), are shown



As was pointed out above, most of the recent evidence about the covalency of interactions is based on the QTAIM classification of interactions, i.e., according to the sign of $\nabla^2\rho(r_b)$ and $H(r_b)$. Therefore, if the negativity of $H(r_b)$ is not related to covalency as has been previously stated by several authors, then the concept of “covalency of the hydrogen bond” should be reviewed.

Computational details

The HB and XB complexes were optimized at the MP2/6–311++G(2d,2p) level of calculation. The harmonic vibrational frequencies were calculated with analytic second derivatives at the same level, which confirmed that the structures were minima. The interaction energy was calculated as the difference between the total energy of the complexes and the sum of the isolated monomers energies, at the same theory level. The counterpoise (CP) correction [17] was implemented in order to ensure that complexes and monomers were being computed with a consistent basis set. All these electronic structure calculations were performed with the Gaussian 03 suite of programs [18].

The calculations of local topological properties of the electron charge density at the interaction BCP as well as the display of the molecular graphs were performed with the AIM2000 package [19] with the electron density obtained at the B3LYP/6–311++G(d,p) level of theory.

The interaction energy component analysis was carried out with the reduced variational space self-consistent field energy decomposition scheme (RVS) [20] implemented in the GAMESS quantum chemistry package [21].

$$E_{\text{es}} + E_{\text{ex}} + E_{\text{pl}} + E_{\text{ct}} + E_{\text{res}} = E_{\text{RVS}} \quad (3)$$

In this energy decomposition analysis ΔE_{RVS} represents the total interaction energy, calculated at a RHF/6–311++G(2d,2p) level, without considering the deformation energy of the monomers. E_{es} is the electrostatic energy describing the Coulomb interaction between the charge distributions of undistorted monomers, E_{ex} is the exchange-repulsion energy due to the Pauli's exclusion principle, E_{pl} is the polarization term that describes the Coulomb interaction between the charge distributions of the distorted monomers and E_{ct} corresponds to the charge transfer term between the monomers. Finally, E_{res} represents the difference between the sum of the energy components and the ΔE_{RVS} . It must be small for a valid RVS analysis.

Results and discussion

The results and discussion section is organized as follows: first, the variation of $H(r_b)$ with the interaction strengthening in a set of the HB and XB complexes is analyzed according to the current meaning of $H(r_b)$ as a descriptor of the

covalency of the interactions. Then, an equation to decompose $H(r_b)$ in two energy densities, $(-G(r_b))$ and $1/4\nabla^2\rho(r_b)$, was derived. Next, the RVS interaction energy components were grouped in two terms, $(E_{\text{es}} + E_{\text{pl}})$ and $(E_{\text{ex}} + E_{\text{ct}})$, related with the electrostatic and covalent part of the total RVS interaction energy (ΔE_{RVS}), respectively. After that, the energy density components $(-G(r_b))$ and $1/4\nabla^2\rho(r_b)$ were related with the energy terms $(E_{\text{es}} + E_{\text{pl}})$ and $(E_{\text{ex}} + E_{\text{ct}})$ respectively, by analyzing the behavior of these parameters with the interaction strengthening in the HB and XB complexes. Finally, the nature of the variation of $H(r_b)$ with the interaction strengthening was established through the analysis of the variation of its components $(-G(r_b))$, $1/4\nabla^2\rho(r_b)$.

Variation of $H(r_b)$ with the interaction strengthening in the set of HB and XB complexes. Interpretation according to the current meaning of $H(r_b)$

One of the key properties of the system selected for this study resides in the fact that the binding properties at $\text{H}/\text{Cl}\bullet\bullet\text{N}$ bond can be strongly modulated by substituting hydrogen atoms attached to ammonia nitrogen by fluorine atoms or methyl groups. Figure 1 shows the molecular graphs for the hydrogen and halogen bonding complexes analyzed in this work. The interaction energy and the intermolecular distance calculated at the MP2/6–311++G(2d,2p) level of theory are shown. Also, the values of local topological properties at the intermolecular BCP are included in it. As can be seen in Fig. 1, in general the interaction energy becomes more negative going from the tri-fluorinated (top) to the tri-methylated complexes (bottom), on both HB and XB complexes. In the same way, the electronic charge density value at the intermolecular BCP ($\rho(r_b)$) increases and the intermolecular distance (d) decreases.

According to the $H(r_b)$ based classification of the interactions, all the HB complexes and the fluorinated XB complexes are closed shell or non covalent complexes, since both $H(r_b)$ and $\nabla^2\rho(r_b)$ are positive; whereas the remaining XB complexes are partially covalent interactions, with $\nabla^2\rho(r_b)>0$, but $H(r_b)<0$.

More about the nature of the interactions can be inquired if the topological parameters are analyzed as a function of the interaction strengthening (i.e., with increasing $\rho(r_b)$ or decreasing intermolecular distance). As can be observed in Fig. 1, in XB complexes the $H(r_b)$ value decreases with increasing $\rho(r_b)$, ranging from positive $H(r_b)$ values in the fluorinated XB complexes to negative values in the methylated ones. In the HB complexes, $H(r_b)$ also decreases with increasing $\rho(r_b)$, except that it does not reach negative values.

Therefore, if the negativity of $H(r_b)$ is attributed to covalency, as argued by some authors [5, 10, 11, 13, 14], then its trend toward negative values with increasing $\rho(r_b)$ observed

in XB as well as HB complexes, might be interpreted as indicative of the tendency toward covalency of these bonds with the interaction strengthening.

Decomposition of local electronic energy density

Reordering Eq. 1, we can write another equation in which two alternative expressions for the local electronic energy density $H(r_b)$, are shown.

$$\frac{1}{4} \nabla^2 \rho(r_b) + (-G(r_b)) = G(r_b) + V(r_b) = H(r_b) \quad (4)$$

The second member of Eq. 4 is the usual form to decompose $H(r_b)$, same as in Eq. 2, whereas in the first member the total electronic energy density at the BCP is decomposed in two different energy densities contributions, $1/4\nabla^2\rho(r_b)$ and $(-G(r_b))$.

In Fig. 2, the variations of $1/4\nabla^2\rho(r_b)$, $(-G(r_b))$ and $H(r_b)$ are represented as a function of the $\text{Cl}\cdots\text{N}$ halogen bond distance in the set of XB complexes studied here.

This figure shows that the term $1/4\nabla^2\rho(r_b)$ increases with the decrease in the $\text{Cl}\cdots\text{N}$ distance, or in other words, with the increase in the strength of the interaction. In the same way, $(-G(r_b))$ increases in magnitude and $H(r_b)$ slowly diminishes, ranging from positive to negative values with the decrease in the $\text{N}\cdots\text{Cl}$ distance.

Similar correlations between the energy densities and the $\text{H}\cdots\text{N}$ distance were found for the HB complexes (data not shown).

Interaction energy terms

Going back to Eq. 3, the electrostatic (E_{es}) and the polarization (E_{pl}) components of the interaction energy account

for the Coulomb interaction between the charge distributions of undistorted and distorted monomers, respectively [22]. Therefore they can be grouped in a single “electrostatic” term, $(E_{\text{es}} + E_{\text{pl}})$ [16].

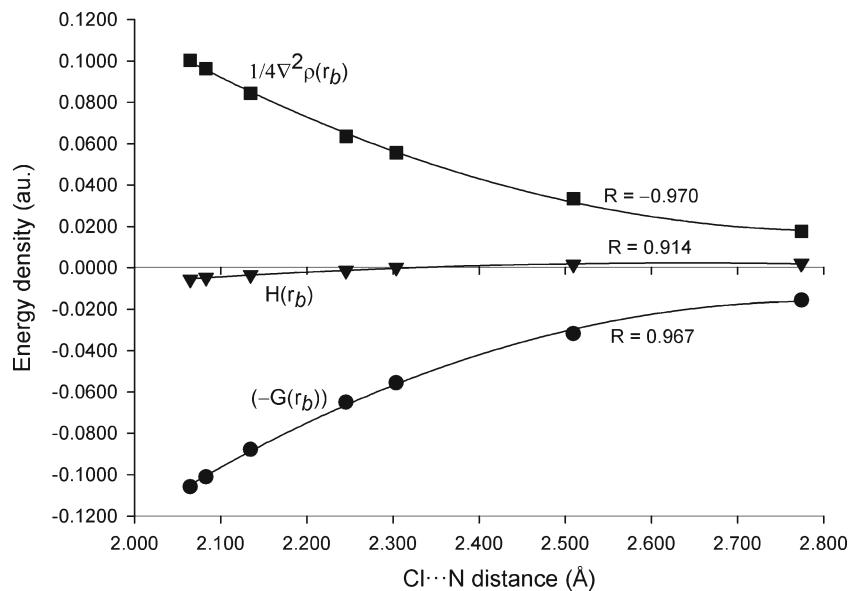
Moreover, there is another important reason, from the chemical point of view, for grouping the components E_{es} and E_{pl} into a single term. These components are obtained by neglecting the differential overlap between the atomic orbitals from different monomers, while in the calculation of the remaining components, i.e., the exchange repulsion E_{ex} and charge transfer E_{ct} components, the intermolecular differential overlap between the atomic orbitals is allowed [23]. Therefore, these last two components can also be grouped in another single term, $(E_{\text{ex}} + E_{\text{ct}})$, that takes into account the *sharing* of electrons between the monomers and hence it is useful to evaluate the *covalent character* of the interaction (i.e., the interaction will have more or less covalent character depending on the magnitude of E_{ct} relative to E_{ex}). Data of the individual interaction energy components as a function of $\rho(r_b)$ are included as supporting information for HB and XB complexes.

In the following section the energy densities from Eq. 4 are linked with the terms $(E_{\text{es}} + E_{\text{pl}})$ and $(E_{\text{ex}} + E_{\text{ct}})$ of the interaction energy which have well defined chemical meaning, as explained above.

Relationship between the local energy densities and the interaction energy terms

The Laplacian of $\rho(r_b)$ describes the balance between the charge transference (E_{ct} component) and the requirement of the Pauli exclusion principle (E_{ex} component) at the interaction BCP [6]. Therefore, the $(E_{\text{ex}} + E_{\text{ct}})$ term qualitatively describe the behavior of the $1/4\nabla^2\rho(r_b)$ energy density for

Fig. 2 Variation of $1/4\nabla^2\rho(r_b)$, $(-G(r_b))$ and $H(r_b)$ energy densities as a function of $\text{Cl}\cdots\text{N}$ halogen bond distance in the set of XB complexes. The correlation coefficients R are included



closed shell interactions (a more/less positive value of $1/4\nabla^2\rho(r_b)$ is associated with a more/less positive $(E_{\text{ex}} + E_{\text{ct}})$ sum).

Moreover, the total electronic energy density evaluated at intermolecular BCP represents the total energy density in the proposed decomposition (Eq. 4) whereas ΔE_{RVS} is the total interaction energy in the RVS decomposition scheme (Eq. 3). Thus, $H(r_b)$ and ΔE_{RVS} are conceptually related since both represent total quantities. Next, it will be shown that apart from the mentioned conceptual relations, quantitative relations between both decomposition schemes can be found.

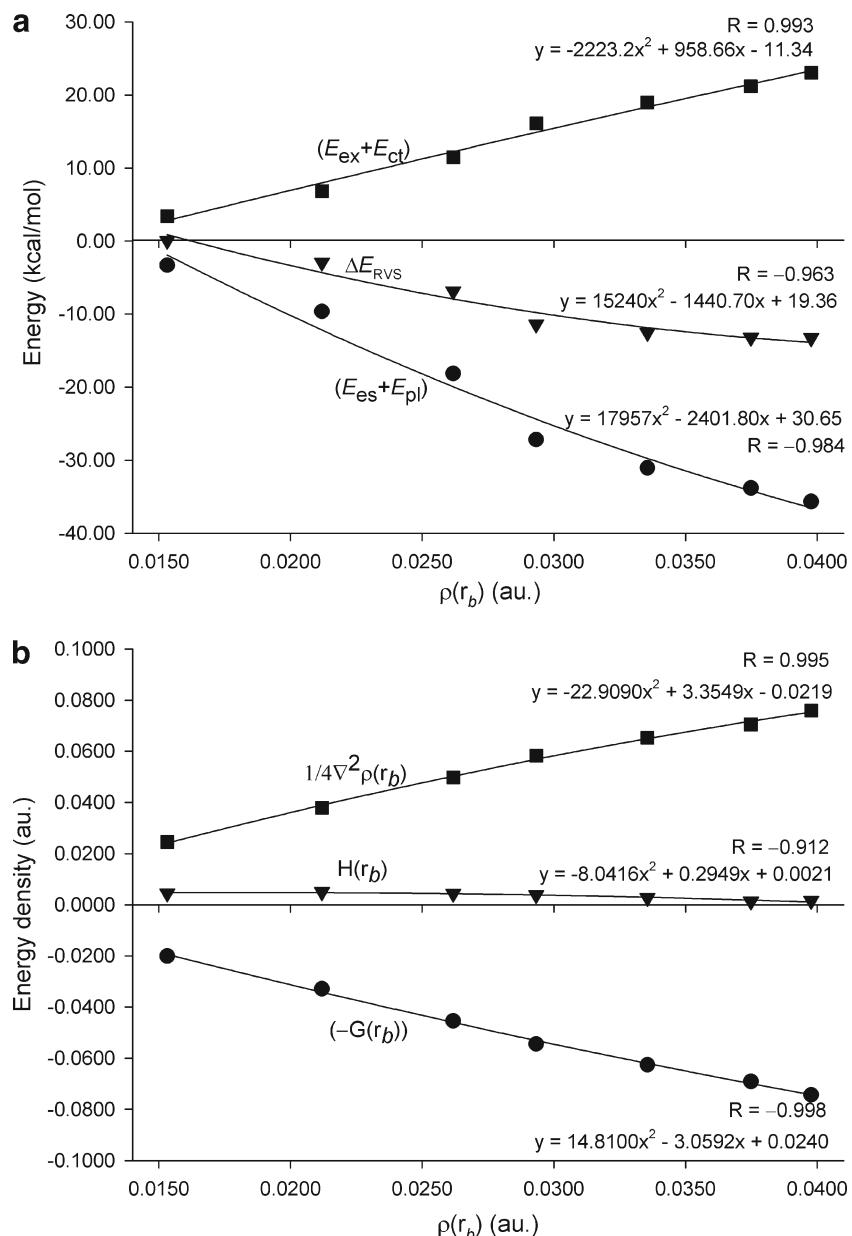
In Fig. 3a and b, the energetic terms $(E_{\text{es}} + E_{\text{pl}})$, $(E_{\text{ex}} + E_{\text{ct}})$ and ΔE_{RVS} , and the local energy densities $(-G(r_b))$, $1/4\nabla^2\rho(r_b)$ and $H(r_b)$ respectively, are represented as a

function of the $\rho(r_b)$ value for the set of HB complexes analyzed in the present work.

In these figures, a similar behavior between $1/4\nabla^2\rho(r_b)$ and the term $(E_{\text{ex}} + E_{\text{ct}})$ as a function of $\rho(r_b)$, can be observed. Both quantities show a smooth increase with the increase of $\rho(r_b)$. In addition, a similar tendency of variation can be observed between $(-G(r_b))$ and the electrostatic term $(E_{\text{es}} + E_{\text{pl}})$ with $\rho(r_b)$.

Moreover, as can be seen from Fig. 3a and b, ΔE_{RVS} as well as $H(r_b)$ decrease with increasing $\rho(r_b)$, although the variation of $H(r_b)$ is less pronounced than the variation of ΔE_{RVS} . In Fig. 4a and b, the variations of the energy terms and energy densities as a function of the $\rho(r_b)$ value in the XB complexes, are represented. The comparison of the correlation coefficients in Figs. 4b and 2 show that the

Fig. 3 Variation of $(E_{\text{es}} + E_{\text{pl}})$, $(E_{\text{ex}} + E_{\text{ct}})$ and ΔE_{RVS} energy terms (a), and $(-G(r_b))$, $1/4\nabla^2\rho(r_b)$ and $H(r_b)$ energy densities (b) with $\rho(r_b)$, for the HB complexes. The correlation coefficients R and the equations of the regressions are included



correlation of the $(-G(r_b))$, $1/4\nabla^2\rho(r_b)$ and $H(r_b)$ energy densities with $\rho(r_b)$ is even better than the correlation of these energy densities with the $\text{Cl}\cdots\text{N}$ distance. As in the HB complexes, the energy terms $(E_{\text{es}} + E_{\text{pl}})$, $(E_{\text{ex}} + E_{\text{ct}})$ and ΔE_{RVS} show similar behavior with $\rho(r_b)$ as the energy densities $(-G(r_b))$, $1/4\nabla^2\rho(r_b)$ and $H(r_b)$, respectively.

Beyond the qualitative connections described between the energy densities and the interaction energy terms in Fig. 5a and b the correlations of the energy densities $(-G(r_b))$ and $1/4\nabla^2\rho(r_b)$ with the interaction energy terms $(E_{\text{es}} + E_{\text{pl}})$ and $(E_{\text{ex}} + E_{\text{ct}})$ for XB complexes are shown. Similar correlations were found for HB complexes (data not shown).

As indicated in Fig. 5a a strong linear correlation between $(-G(r_b))$ and $(E_{\text{es}} + E_{\text{pl}})$ is observed. Similarly a nearly ideal

linear correlation was found between the energy density $1/4\nabla^2\rho(r_b)$ and the interaction energy term $(E_{\text{ex}} + E_{\text{ct}})$ as is shown in Fig. 5b.

Nature of $H(r_b)$ variation with the interaction strengthening

As can be seen in Fig. 3a and b, the decrease in ΔE_{RVS} with increasing $\rho(r_b)$ is due to a higher increase in magnitude of the negative term $(E_{\text{es}} + E_{\text{pl}})$, relative to the increase in the positive term $(E_{\text{ex}} + E_{\text{ct}})$. The $(E_{\text{es}} + E_{\text{pl}})$ term was previously related with the “pure electrostatic part” of the interaction, whereas the $(E_{\text{ex}} + E_{\text{ct}})$ term accounts for its “covalent character”. Therefore, the driving force for the HB and XB strengthening is the increase in the electrostatic forces and not the increase in its “covalency”. It can be seen

Fig. 4 Variation of $(E_{\text{es}} + E_{\text{pl}})$, $(E_{\text{ex}} + E_{\text{ct}})$ and ΔE_{RVS} energy terms (a), and $(-G(r_b))$, $1/4\nabla^2\rho(r_b)$ and $H(r_b)$ energy densities (b) with $\rho(r_b)$, for the set of XB complexes. The correlation coefficients R and the equations of the regressions are included

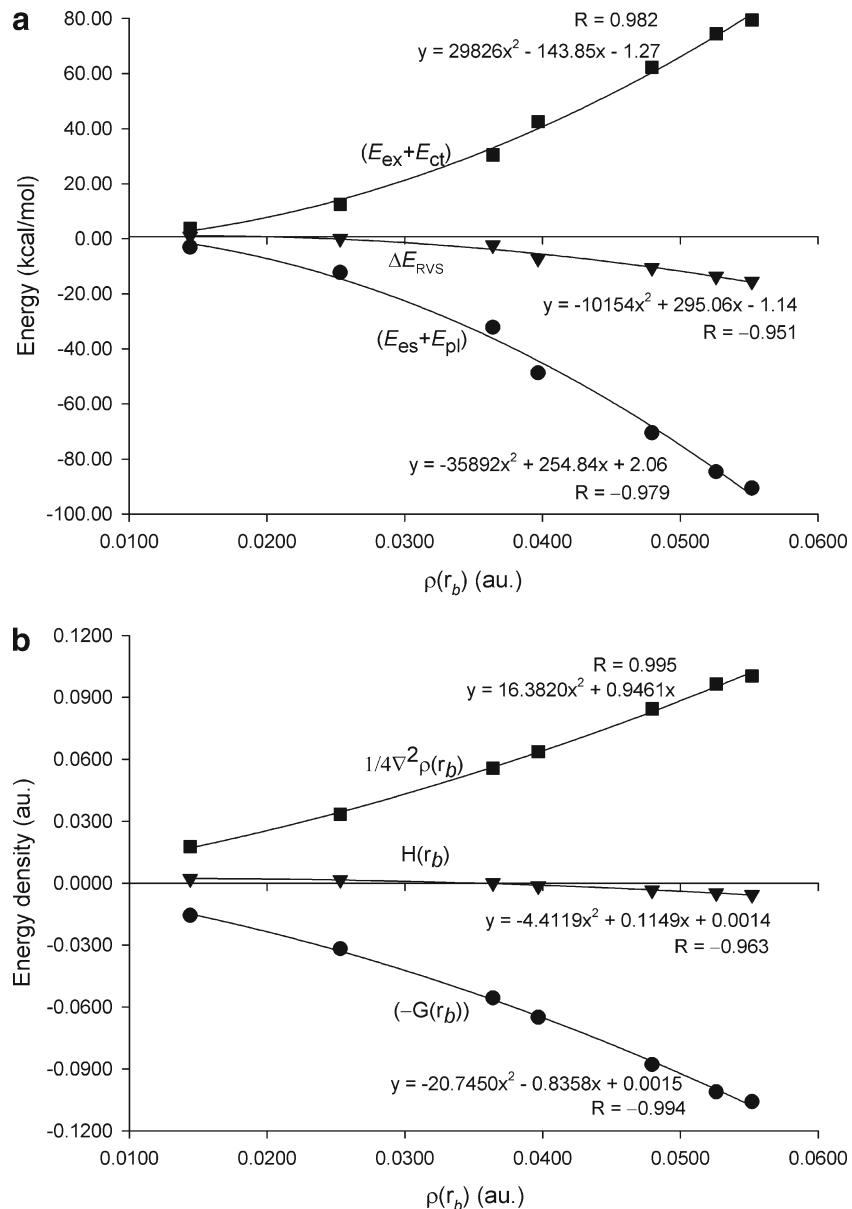
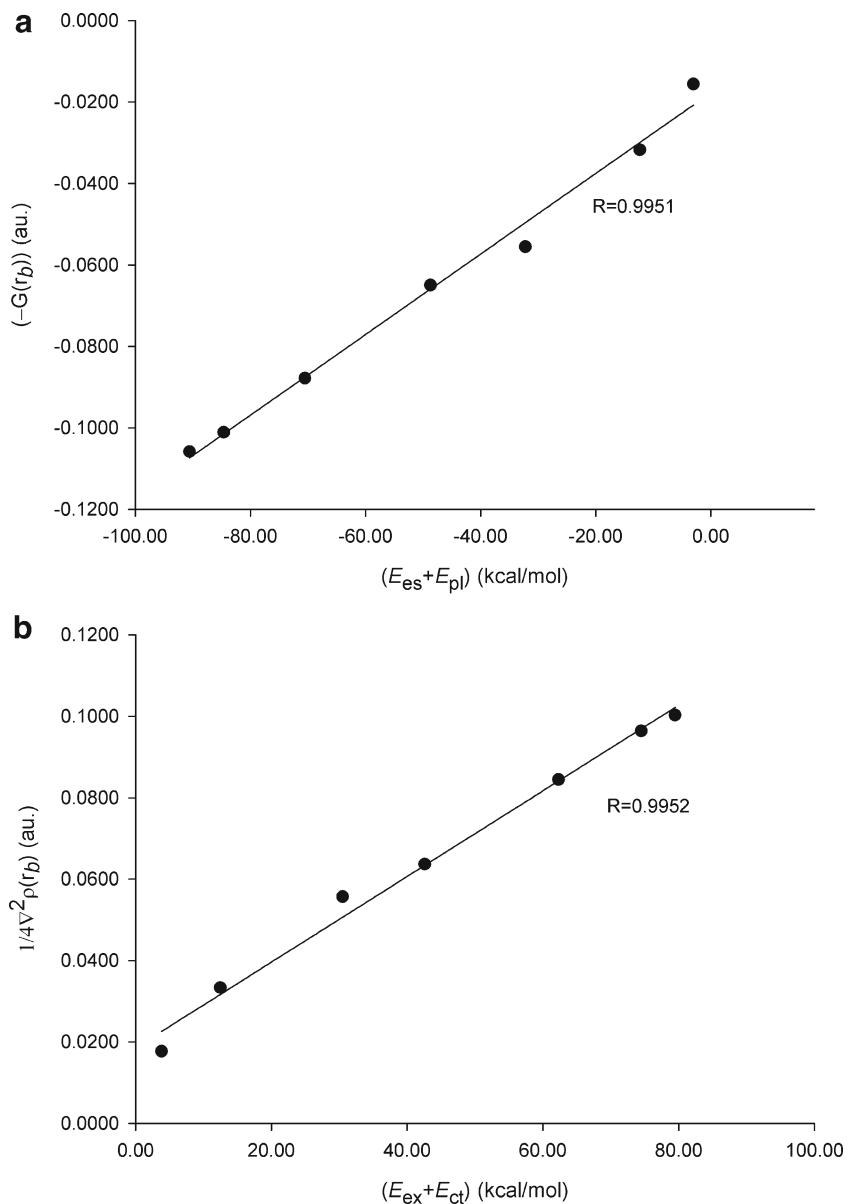


Fig. 5 Linear correlations between the energy density ($-G(r_b)$) and the interaction energy term ($E_{\text{es}} + E_{\text{pl}}$) (a) and between $1/4\nabla^2\rho(r_b)$ and the term ($E_{\text{ex}} + E_{\text{ct}}$) (b). The correlation coefficients R of the regressions are included



from the supporting information graphics (Figs. S1 and S2) that the E_{ct} component also helps to strengthen the HB and XB complexes since it becomes more negative with increasing $\rho(r_b)$ values. However, E_{ct} increases more slowly than E_{es} in magnitude as the interaction strengthens. Furthermore, if both components E_{es} and E_{pl} are considered together in the electrostatic ($E_{\text{es}} + E_{\text{pl}}$) term the increase of the electrostatic contribution of the interaction energy as the HB and XB interaction strengthen is even more pronounced when compared with the E_{ct} component. Therefore, the main driving force for the HB and XB strengthening is the increase in the electrostatic forces and in a lesser extent the increase in its “covalency”.

Moreover, as has already been mentioned in the previous section, the total electronic energy density $H(r_b)$ follows a similar trend as the total RVS interaction energy (ΔE_{RVS})

(see Figs. 3a, b and 4a, b). Thus, the decrease of $H(r_b)$ with increasing $\rho(r_b)$ could be considered as an indicator of the strengthening or stabilization of the interaction, in the same way that the decrease in ΔE_{RVS} is an indicator of the complex stabilization. A negative value of $H(r_b)$ (or its trend toward negative values) is not necessarily associated with covalency or electrostatics, but its components $1/4\nabla^2\rho(r_b)$ and $(-G(r_b))$ are the ones which provide information about the nature of the interaction.

Furthermore, Figs. 3b and 4b show that the decrease in $H(r_b)$ with increasing $\rho(r_b)$ is due to the higher increase in magnitude of the negative component $(-G(r_b))$, relative to the increase of the positive component $1/4\nabla^2\rho(r_b)$. The energy density $(-G(r_b))$ was previously related with the electrostatic term ($E_{\text{es}} + E_{\text{pl}}$). Therefore, the decrease of $H(r_b)$ with the interaction strengthening is mainly a consequence of the

increase in the attractive electrostatic part of the interaction energy rather than the increase in its covalent character, as is commonly considered to be the case.

Conclusions

In this work, an energetic analysis based on the local virial theorem from AIM theory in conjunction with RVS decomposition analysis were carried out on XB and HB complexes to look into the meaning of the decrease in $H(r_b)$ with the interaction strengthening.

The proposed decomposition scheme of $H(r_b)$ in two energy densities $-G(r_b)$ and $(1/4\nabla^2\rho(r_b))$, studied before in HB complexes, has been tested for the first time in a set of XB complexes. These energy densities were related with the RVS interaction energy terms that account for the electrostatics and the covalent character of the interaction, respectively.

Quadratic relationships were established between $\rho(r_b)$ and the local energy densities $-G(r_b)$, $1/4\nabla^2\rho(r_b)$ and $H(r_b)$ at the BCP. Similarly, quadratic relationships between the RVS interaction energy terms ΔE_{RVS} , $(E_{\text{ex}} + E_{\text{cl}})$ and $(E_{\text{es}} + E_{\text{pl}})$ and $\rho(r_b)$ were also established for HB and XB complexes.

Moreover, it was found that the decrease of the total electronic energy density at the BCP with increasing $\rho(r_b)$, could be considered as an indicator of the interaction strengthening or interaction stabilization in the same way as the decrease in the total interaction energy is an indicator of the complex stabilization.

In addition, through the connection between both decomposition schemes, we conclude that the decrease in $H(r_b)$ with the interaction strengthening observed in the HB as well as the XB complexes studied here, is mainly due to the increase in the attractive electrostatic part of the interaction energy and in lesser extent to the increase in its covalent character, as is commonly considered to be the case.

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References

- Jeffrey GA, Saenger W (1991) Hydrogen bonding in biological structures. Springer, Heidelberg
- Legon AC (2010) The halogen bond: an interim perspective. *Phys Chem Chem Phys* 12:7736–7747. doi:[10.1039/C002129F](https://doi.org/10.1039/C002129F)
- Pauling L (1960) The nature of the chemical bond. Cornell University Press, Ithaca
- Gilli G, Gilli P (2000) Towards an unified hydrogen-bond theory. *J Mol Struct* 552:1–15. doi:[10.1016/S0022-2860\(00\)00454-3](https://doi.org/10.1016/S0022-2860(00)00454-3)
- Grabowski SJ (2011) What is the covalency of hydrogen bonding? *Chem Rev* 111:2597–2625. doi:[10.1021/cr800346f](https://doi.org/10.1021/cr800346f)
- Bader R (1990) Atoms in molecules: a quantum theory. Oxford University Press, USA
- Bader RFW, Essen H (1984) The characterization of atomic interactions. *J Chem Phys* 80:1943–1960. doi:[10.1063/1.446956](https://doi.org/10.1063/1.446956)
- Jenkins S, Morrison I (2000) The chemical character of the intermolecular bonds of seven phases of ice as revealed by ab initio calculation of electron densities. *Chem Phys Lett* 317:97–102. doi:[10.1016/S0009-2614\(99\)01306-8](https://doi.org/10.1016/S0009-2614(99)01306-8)
- Arnold WD, Oldfield E (2000) The chemical nature of hydrogen bonding in proteins via NMR: J-couplings, chemical shifts, and AIM theory. *J Am Chem Soc* 122:12835–12841. doi:[10.1021/ja0025705](https://doi.org/10.1021/ja0025705)
- Espinosa E, Alkorta I, Elguero J, Molins E (2002) From weak to strong interactions: a comprehensive analysis of the topological and energetic properties of the electron density distribution involving X–H...F–Y systems. *J Chem Phys* 117:5529–5542. doi:[10.1063/1.1501133](https://doi.org/10.1063/1.1501133)
- Pakiari AH, Eskandari K (2006) The chemical nature of very strong hydrogen bonds in some categories of compounds. *J Mol Struct (THEOCHEM)* 759:51–60. doi:[10.1016/j.theochem.2005.10.040](https://doi.org/10.1016/j.theochem.2005.10.040)
- David J, Guerra D, Restrepo A (2012) Structure, stability and bonding in the ${}^1\text{Au}_{10}$ clusters. *Chem Phys Lett* 539–540:64–69. doi:[10.1016/j.cplett.2012.04.030](https://doi.org/10.1016/j.cplett.2012.04.030)
- Grabowski SJ, Sokalski WA, Dyguda E, Leszczyński J (2006) Quantitative classification of covalent and noncovalent H-bonds. *J Phys Chem B* 110:6444–6446. doi:[10.1021/jp0600817](https://doi.org/10.1021/jp0600817)
- Grabowski SJ, Sokalski WA, Leszczyński J (2006) The possible covalent nature of N–H...O hydrogen bonds in formamide dimer and related systems: an ab initio study. *J Phys Chem A* 110:4772–4779. doi:[10.1021/jp0556131](https://doi.org/10.1021/jp0556131)
- Ramírez F, Hadad CZ, Guerra D, David J, Restrepo A (2011) Structural studies of the water pentamer. *Chem Phys Lett* 507(4–6):229–233. doi:[10.1016/j.cplett.2011.03.084](https://doi.org/10.1016/j.cplett.2011.03.084)
- Angelina EL, Peruchena NM (2011) Strength and nature of hydrogen bonding interactions in mono- and di-hydrated formamide complexes. *J Phys Chem A* 115:4701–4710. doi:[10.1021/jp1105168](https://doi.org/10.1021/jp1105168)
- Boys SF, Bernardi F (1970) The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors. *Mol Phys* 19:553–566. doi:[10.1080/00268977000101561](https://doi.org/10.1080/00268977000101561)
- Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JA TV Jr, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazayev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski G, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko GA, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA (2004) Gaussian 03, revision D01. Gaussian Inc, Wallingford

19. Blieger-König F, Schönbohn J (2002) AIM2000 Program Package, version 20, chemical adviser by RFW Bader. Büro für Innovative Software Streibel Biegler-König, Germany
20. Stevens WJ, Fink WH (1987) Frozen fragment reduced variational space analysis of hydrogen bonding interactions. Application to the water dimer. *Chem Phys Lett* 139:15–22. doi:[10.1016/0009-2614\(87\)80143-4](https://doi.org/10.1016/0009-2614(87)80143-4)
21. Schmidt MW, Baldrige KK, Boatz JA, Elbert ST, Gordon MS, Jensen JH, Koseki S, Matsunaga N, Nguyen KA, Su S, Windus TL, Dupuis M, Montgomery JA (1993) General atomic and molecular electronic structure system. *J Comput Chem* 14:1347–1363. doi:[10.1002/jcc.540141112](https://doi.org/10.1002/jcc.540141112)
22. Morokuma K (1977) Why do molecules interact? The origin of electron donor-acceptor complexes, hydrogen bonding and proton affinity. *Acc Chem Res* 10:294–300. doi:[10.1021/ar50116a004](https://doi.org/10.1021/ar50116a004)
23. Morokuma K, Kitaura K (1981) Energy decomposition analysis of molecular interactions. In: Politzer P, Truhlar DG (eds) Chemical applications of atomic and molecular electronic potentials. Plenum, New York, pp 215–242