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REGULAR ARTICLE

Investigating sigma bonds in an electric field from the Pauling's perspective: the behavior of Cl–X and H–X (X = C, Si) bonds

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Abstract In the general framework concerning the description and the rationalization of the behavior (weakening/strengthening) of a bond of a polyatomic molecular system under the experience of an electric field, we have considered the sigma bonds Cl–X and H–X (where $X = $ C, Si). The Pauling's perspective for chemical bonding is adopted, and the corresponding ionic structures, responsible for the behavior of a considered bond inside the electric field, are examined by means of a recently developed poly electron population analysis. The CH_3Cl, SiH_3Cl, CH_4 and SiH_4 molecules are considered as model sigma systems, and the changes of their bonds induced by the electric field are investigated by means of full geometry optimizations in both HF and MP2 levels. The changes in the weights of the ionic structures are calculated in the basis of interatomically nonorthogonal natural hybrid orbitals, which are necessary to describe the ionic structures of sigma bonds. The correlation of these changes with the bond length variations is investigated, and the observed computational tendencies can be summarized in the following rule, concerning the behavior of a sigma heteronuclear Charge–Shift or covalent/Charge–Shift bond, or in general a sigma bond with non-negligible polarity: 'if the electric field decreases (or increases) the difference of the weights of the two principal ionic structures, then the bond length decreases (or increases, respectively)'.

Keywords Population analysis · Natural orbitals · Density operators · Electric field · Charge–Shift bonds

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1 Introduction

The control of chemical reactions by means of an electric field [1, 2], and in general the chemical reactivity in the presence of such a type of external stimulus [1–3] is a new challenge for Chemistry and in particular for Quantum Chemistry. The electric field is also used to control the behavior of some Technomimetic [4, 5] systems and other molecular devices developed in the framework of Molecular Electronics [6–8]. In order to confront with various chemical problems emerging from this new area, it is necessary to be able to rationalize, and even to predict (in a qualitative framework), the impact of an applied field on the bonds of a molecular system, namely to know which bonds are lengthened (and weakened) or shortened (and strengthened). Contributing to this general purpose, in the present work we consider some sigma non-symmetric (heteronuclear) bonds, since symmetric (homonuclear) ones show the same tendencies with respect to a positive or a negative longitudinal field orientation, and, in general, non-symmetric bonds are by far more frequent in various molecular devices. The considered bonds are the Cl–X and H–X bonds (where $X = $ C, Si) of some model sigma molecules, namely the CH_3Cl, SiH_3Cl, CH_4 and SiH_4.

Usually, bond dipoles, i.e. local dipoles, corresponding to polar chemical bonds of a polyatomic system, are viewed from a perspective issued from the traditional one-electron population analysis, that is, from the different values of atomic charges obtained by this type of analysis of the usually delocalized molecular orbital (MO) wave functions. In the framework of this one-electron standpoint, the role of the localized MOs in the formation of bond dipoles is also well investigated [9]. By applying an electric field on a polyatomic molecular system, certain bonds exhibit local bond dipoles which are favorable, while simultaneously other are (necessarily) unfavorable to the orientation of this external stimulus. In this context, the arising fundamental problem is to be able to predict which bonds are weakened or strengthened under the experience of the electric field. In this paper, we propose to regard to the local bond dipoles of the concerned sigma bonds from the traditional Pauling's valence bond (VB) perspective, shown in Fig. 1, i.e. from the coexistence of two ionic structures, $A^+B^- \leftrightarrow A^-B^+$, with different weights.

The role of Pauling's ionic structures in the stability of a chemical bond is well established [10–14], and their energetic contributions are examined by means of a valence-bond (VB) theory appropriate to investigate and analyze the Charge–Shift (CS) bonding [10–14]. It is worth to underline the fact that even for non-polar bonds, the ionic structures play a crucial role [10–14], conditioning the whole behavior of the bond; for example, a typical CS bond, as the F–F, cannot be appropriately described without its ionic components [12]. Since an external electric field acts essentially on the ionic structures, their role must be also decisive for the behavior of a chemical bond (even for a non-polar bond) inside the field [15, 16]; this is the basic idea, in which the present work is based. VB investigations inside an electric field are scarce [17–19], despite the fact that the Pauling structures as well as the Linnett-like ones, used to describe versatile bonding (beyond the usual two-electron bonding) by means of Increased Valence theory [20–23], can provide useful and chemically meaningful description for the effects induced by the electric field [17]. Localized VB-like bonding schemes, in atomic or bond orbitals can be obtained by means of Natural Resonance Theory [24, 25], and other well elaborated appropriate methods [26–35]. All these methods as well as the pure VB methodologies provide information concerning the whole electronic assembly of a molecule, while the local electronic structures of a target bond, belonging to a polyatomic molecular system, can be investigated by means of the poly electron population analysis (PEPA) [36, 37]. This methodology provides the possibility to 'place under the microscope' a bond, or, in general, a functional group, and examine the behavior of its electrons inside the given molecular system. This type of analysis of MO wave functions, obtained in a homogeneous electric field, is used in the present work to investigate the behavior of Pauling's ionic structures, shown in Fig. 1, by the impact of this external stimulus. The use of natural (in the Löwdin sense) orbitals developed within the natural bond orbital (NBO) [38–40] methodology, offers a solid background for chemically meaningful one-electron functions, which can be used in PEPA investigations.

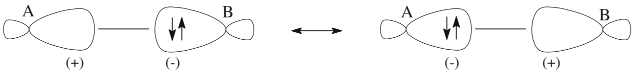

Fig. 1 The Pauling's ionic structures of a target two-electron two-center bond belonging in a polyatomic system

The Pauling's ionic structures of a target A–B bond (shown in Fig. 1), belonging in a poly atomic system, can be considered as local electronic events [36, 37] occurring in the valence orbitals of the component atoms A and B. For example, structure A^+B^- can be viewed as an electronic event defined from the simultaneous presence of two electrons (i.e. an electron pair) in B and two electron-holes (i.e. a pair of holes) in A, while the remaining electrons can reside anywhere else. The two electron distributions, examined in the absence of the electric field from the electron pair population analysis, provide pertinent chemical information and new insight for chemical bonding [41–48]. Inside an electric field, the structural changes induced by this external stimulus are investigated from MO calculations of various levels [49–52], and the changes of bond lengths are examined thoroughly by referring to the changes of the electronic density in the framework of methods based on the analysis of one-electron distributions [49, 51, 52]. In the present work, going beyond one and two electron population analysis schemes, we examine the simultaneous presence of two electrons and two holes by means of the recently developed efficient hole-expansion methodology [36]. Since the examination of the ionic structures of the considered sigma bonds inside an electric field is not explored from neither VB nor MO calculations, we have considered the aforementioned simple molecules as model sigma systems.

2 Calculating the weights of ionic structures in hybrid orbitals

In genuine chemical knowledge, the two-electron sigma Cl–X bond in H_3X–Cl (where $X =$ C, Si) molecules can be described in the basis of two valence hybrid orbitals μ and ν, namely a (model) sp hybrid in Cl and a (model) sp^3 hybrid in X atom. To gain access to an elementary ionic structure, such as the $\mu(\uparrow\downarrow)\nu(+)$ within a VB-like perspective, one must overcome some conceptual and computational difficulties. The first difficulty arises from the employment of usual non-minimal basis sets which are necessary to achieve reliable variational calculations providing MO wave functions. In most of the available SCF-AOs basis sets one cannot easily distinguish which of the basis orbitals are the valence (e.g. $2p$ for C, or $3p$ for Cl) and which are the Rydberg ones, and mainly one cannot know a priori in which extent each diffuse orbital of the adopted basis set contributes to the valence orbitals. Another difficulty arises from the fact that to access to one ionic structure $\mu(\uparrow\downarrow)\nu(+)$ between a hybrid μ (of an atom

A) and a hybrid v (of an atom B), one has to consider various structures of the type $\mu'(\uparrow\downarrow)v'(+)$, $\mu'(\uparrow\downarrow)v''(+)$, $\mu''(\uparrow\downarrow)v''(+)$ etc. (where μ', μ'' and v' , v'' are the non-hybrid valence AOs of atoms A and B, respectively). The above difficulties can be avoided using natural (in the Löwdin sense) orbitals having the appropriate hybridization, as this is imposed from the used geometry. A such a type of orbitals are the natural hybrid orbitals (NHOs) or the pre-natural hybrid orbitals (PNHOs) which can be obtained in the framework of NBO methodology [38–40]; the NHOs are orthogonal, while the PNHOs are interatomically nonorthogonal and intratomically orthogonal. These natural orbitals show remarkable stability with the extension of the SCF-AOs basis set, and provide a good basis for chemically meaningful interpretations of advanced quantum calculations. In the present work we preferred the use of PNHOs because we wish to obtain a VB-like local information, and the interatomic nonorthogonality underlies basic VB concepts and in general the VB perspective for chemical bonding.

The calculation of the weights of the ionic structures of a target bond, belonging to a polyatomic molecule, is achieved by means of PEPA methodology, which starts from a conventional (delocalized) MO wave function, $\Psi(\mathrm{MO})$. Initially, this wave function must be transformed to a new equivalent one, $\Psi'(\mathrm{MO})$, expressed in the basis of PNHOs. The NBO program does not provide the MOs in this basis, and for this reason the required transformations are achieved by solving a linear system of equations in a quite similar manner that is used to express $\Psi(\mathrm{MO})$ in the basis of NBOs [53, 54] and NAOs [55]. The orbitals of the PNHO basis set can be clearly distinguished to valence hybrid orbitals and Rydberg ones, and the necessary matrix providing the PNHOs in the basis of the SCF-AOs, is obtained from the NBO program [40]. Taking into account the fact that the PNHO basis set span the complete SCF-AO set, any type of projection can be avoided, and thus, the new $\Psi'(\mathrm{MO})$ satisfies the following relation:

$$\Psi(\mathrm{MO}) = \Psi'(\mathrm{MO}) \tag{1}$$

Applying Moffitt's theorem [56–58], $\Psi'(\mathrm{MO})$ can be expressed as a linear combination of totally local Slater determinants, $|K|$, which involve only orbitals of the PNHO basis set:

$$|\Psi'(\mathrm{MO})\rangle = \sum_K T_K|K\rangle \tag{2}$$

The calculation of the expansion coefficients, T_K, can be made by means of Moffitt's theorem, because it holds for both orthogonal and nonorthogonal one-electron basis sets. Due to the fact that we are working in the basis of single Slater determinants, $|K|$, the calculation of each T_K is independent on the subset of $|K|$ that is needed (see below) to obtain the weight of a local structure. From Eqs. 1 and 2 we obtain:

$$|\Psi(\mathrm{MO})\rangle = \sum_K T_K|K\rangle \tag{3}$$

If the initial wave function, $\Psi(\mathrm{MO})$, is calculated within an electric field, then expression (Eq. 3) provides the local description of the considered molecule under the experience of this external stimulus.

A structure $[\mu(\uparrow\downarrow)v(+)]$ is composed (by definition) of two electrons in orbital μ and two electron-holes (of α and β spin) in v. To obtain the corresponding two-electron-two-hole weights, $P_{2;2}\ (\mu,\ \bar{\mu};\ v,\ \bar{v}) = \boldsymbol{W}[\mu(\uparrow\downarrow)v(+)]$, we use the Coulson-Chirgwin definition of weights [59], $W(K)$, of determinantal wave functions:

$$W(K) = T_K^2\langle K|K\rangle + T_K \sum_{K' \neq K} T_{K'}\langle K|K'\rangle \tag{4}$$

The sums of the above $W(K)$ of well selected Slater determinants, $|K|$, provide occupation numbers within Mulliken partition. For example, they can provide the usual one-electron populations [60] or other higher order Mulliken populations [61–64] on the basis of PEPA. In this framework, the weights of the ionic structures examined in the present work are calculated [35, 36] by means of the following relation

$$\boldsymbol{W}[\mu(\uparrow\downarrow)v(+)] = \sum_{K(\neq v,\bar{v})}^{(\mu,\bar{\mu})} W(K) \tag{5}$$

where $\sum_{K(\neq v,\bar{v})}^{(\mu,\bar{\mu})}$ represents a summation over Slater determinants which involve spin-orbitals μ and $\bar{\mu}$, while simultaneously v and $\bar{v}$ are absent. It is worth noticing that the weights (Eq. 5) in a basis of orthogonal orbitals equal to the expectation values of generalized poly electron density operators, $\langle \sum_K T_K K|\mathrm{a}_\mu^+\,\mathrm{a}_{\bar{\mu}}^+\,\mathrm{a}_v\,\mathrm{a}_{\bar{v}}\,\mathrm{a}_{\bar{v}}^+\,\mathrm{a}_v^+\,\mathrm{a}_{\bar{\mu}}\,\mathrm{a}_\mu|\sum_K T_K K\rangle$, in which they can be reduced when $\langle K|K'\rangle = \delta_{K,K'}$ (and $W(K) = T_K^2$). The Coulson-Chirgwin weights are also widely (and almost exclusively) used to calculate the weights of VB spin-eigenfunctions; in this framework, the calculated weights in the basis of (interatomically) nonorthogonal PNHOs are consistent with those of VB weights.

It is worth noticing that for computational facility, the weights $\mathbf{W}[\mu(\uparrow\downarrow)v(+)]$ can be calculated by means of the following relation

$$W[\mu(\uparrow\downarrow)v(+)] = \sum_{K(\neq v,\bar{v})}^{(\mu,\bar{\mu})} T_K\langle\Psi(\mathrm{MO})|K\rangle \tag{6}$$

The above relation is totally equivalent to Eq. 5, from which it can be obtained straightforwardly using relations 3 and 4. For a better computational efficiency relation 6 can be employed [37, 65] in the framework of the mixed local-non-local formalism [66] of Slater determinants, and also to derive the relations in which is based the efficient hole-expansion methodology [36].

3 Results and discussion

3.1 Calculations

The initial wave functions, Ψ(MO), are obtained by means of GAMESS program [67], which permits the calculation of MO wave functions under the experience of an uniform static electric field [68]. Our basic investigations are performed using field strengths in the range of 0.0–0.02 au. Even though the principal conclusions can be drawn within this range, we extended our calculations for higher strengths (up to 0.04 au) in order to confirm the behavior and the (assumed) important role of the ionic structures, and mainly to check if the change of the weights of these structures is continuous and coherent within the proposed analysis. High field strengths are also frequently used and their effects on various chemical systems are reported [69–74]. For a given field strength and a given field orientation (see Fig. 2), full geometry optimizations (without any restriction) are performed in both HF and MP2 level of theory. The SCF-AO basis sets are the 6-31G* sets included in GAMESS program; we used these basis sets because our purpose is not to calculate polarisabilities [75, 76], which require very large and well adapted basis sets, but geometry changes and poly electron populations for closed shell systems, for which this quality of basis sets provides reliable results [15, 16].

The results of the full geometry optimizations of the aforementioned molecules of Fig. 2 are presented in Figs. 3, 4, 5, and 6, for both HF and MP2 levels; the slopes of the presented curves, and thus, the variations of lengths of the considered bonds are quite similar in these approximation levels. Consequently, the changes induced by the experience of the electric field in these closed shell systems can be described in either HF or MP2 level. For this reason, the investigation by means of PEPA of the initial Ψ(MO) under an electric field, is performed by the optimized geometry and the corresponding wave functions obtained in HF level for each field strength. Although the atomic populations are not the same in HF and MP2 levels, the changes of electron density with respect to the electric field for the considered closed shell systems are very similar. Consequently, a rationalization of the observed effects, based on the changes of electron density, must be the same for these two calculation levels.

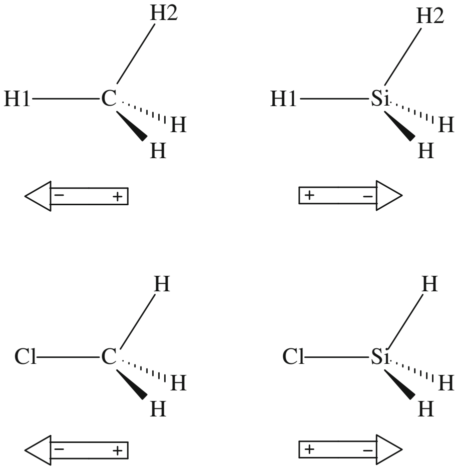

Fig. 2 Atom numbering, and definition of the positive field orientation, as this one which favors the bond polarity, $\Delta q = q_A - q_B$, obtained from the one-electron charges of H1–C, H1–Si, Cl–C and Cl–Si bonds of CH_4, SiH_4, CH_3Cl and SiH_3Cl, respectively

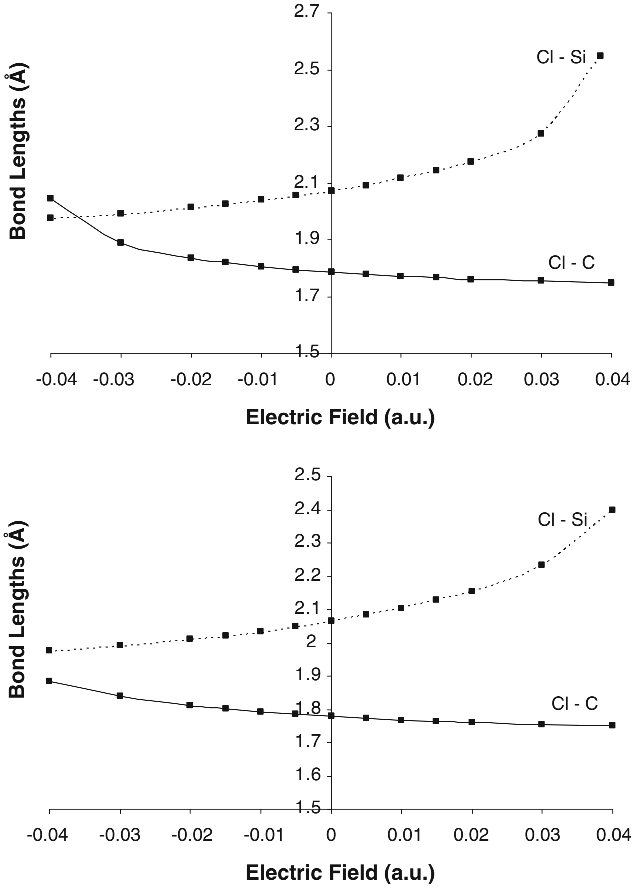

Fig. 3 Variations of lengths of Cl–C bond of CH_3Cl, and Cl–Si bond of SiH_3Cl, with respect to the electric field strength. *Up side* HF level. *Down side* MP2 level

Concerning the local bond dipoles of polyatomic molecules [9], the sign of the bond polarity is usually defined by the difference $\Delta q = q_A - q_B$ of the one electron charges (q_A and q_B) of atoms A and B. Although any definition of the external field direction would have some arbitrariness, in the present work this is chosen to be parallel to a given chemical bond A–B (for example, for H_3XCl molecules, this is parallel to the direction of the

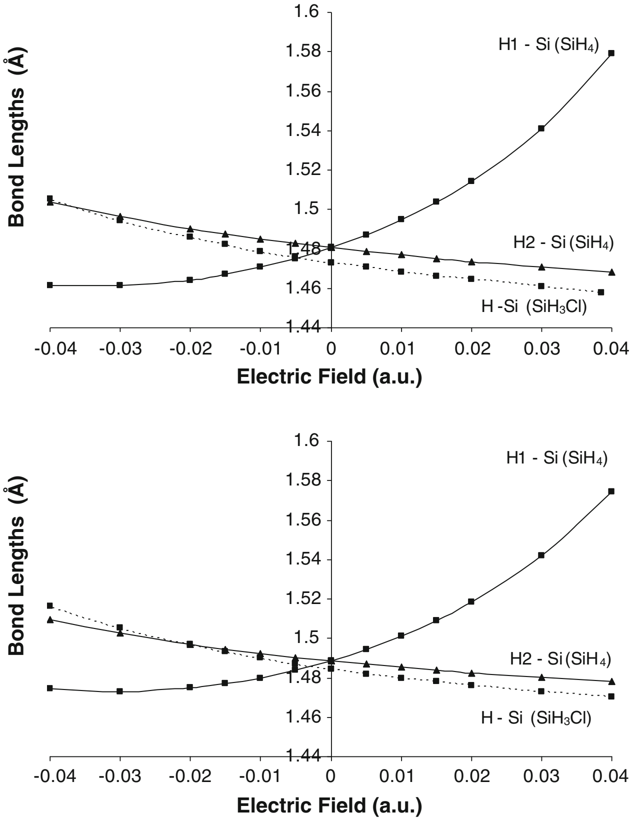

Fig. 4 Variations of lengths of H1–Si and H2–Si bonds of SiH_4, and H–Si bonds of SiH_3Cl, with respect to the electric field strength. *Up side* HF level. *Down side* MP2 level

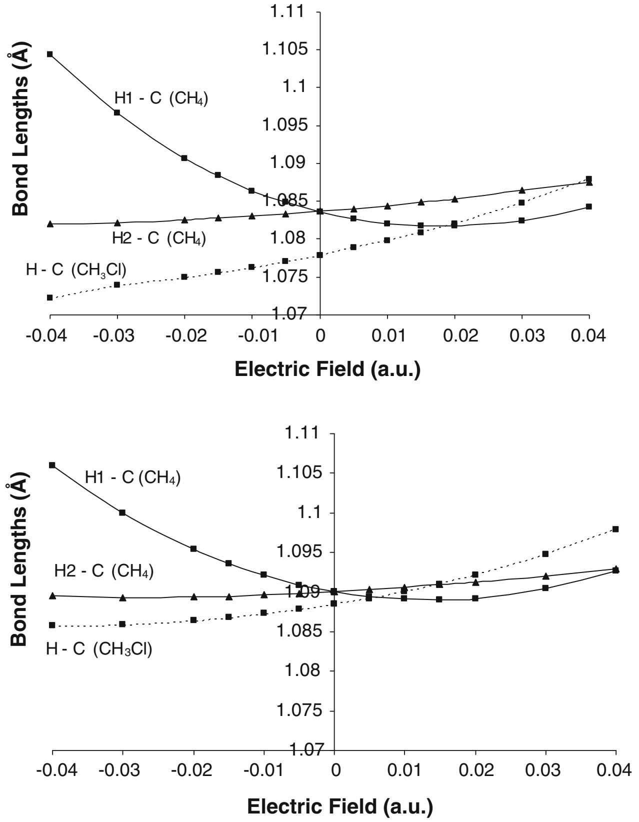

Fig. 5 Variations of lengths of H1–C and H2–C bonds of CH_4 and H–C bonds of CH_3Cl, with respect to the electric field strength. *Up side* HF level. *Down side* MP2 level

Cl–X bond); the positive electric field is defined as the orientation of the field that favors the existing bond polarity, Δq, issued from the one-electron population analysis [49] (i.e. the field orientation which is opposite to this of the A–B bond). For example, the one-electron charges issued from Löwdin/Mulliken/natural populations concerning the Cl–C bond are

$$\mathrm{Cl}: -0.074/-0.109/-0.100, \mathrm{C}: -0.456/0.536/-0.597,$$

and for the Cl–Si bond

$$\mathrm{Cl}: -0.195/-0.328/-0.446, \mathrm{Si}: 0.232/0.583/1.090,$$

and, thus, the positive field orientations are those shown in Fig. 2 (one can note the opposite positive orientations for Cl–C and Cl–Si bonds).

3.2 The Cl–Si and Cl–C bonds

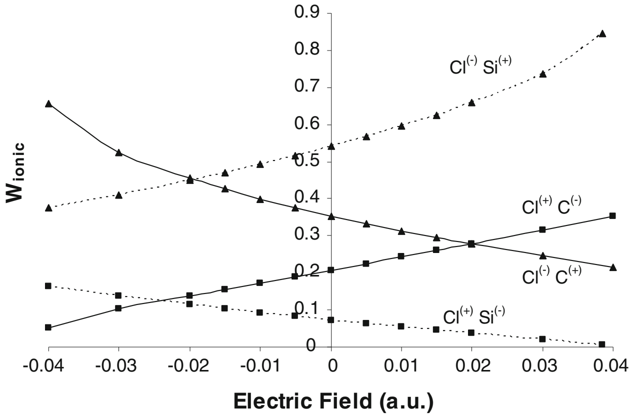

Fig. 6 Variations of ionic structures weights for the Cl–C bond of CH_3Cl, and the Cl–Si bond of SiH_3Cl, in the basis of hybrid orbitals (PNHOs), with respect to the electric field strength

The Cl–Si bond has a net CS character, while the Cl–C is a covalent (heteronuclear) bond with some CS character [10], and both show a significant polarity. Extending the full geometry optimization calculations beyond the electric field strengths, F, presented in Fig. 3, we have found a minimum for the Cl–C bond length in $F \approx 0.055$ au, and for Cl–Si in $F \approx -0.08$au, that is

$$|F_{\min}|_{\mathrm{Cl-C}} < |F_{\min}|_{\mathrm{Cl-Si}} \tag{7}$$

For SiH_3Cl, no convergence in the full geometry optimization process can be achieved for $F > 0.0385$ au.

The main difference in the behavior of these two sigma bonds is that the length of the Cl–Si bond is more sensitive than that of the Cl–C inside the electric field; for example, the variations $\Delta l/|\Delta F|$ from $F = 0.0$ au to $F = |0.03|$ au are 6.76 and 3.49 for Cl–Si and Cl–C bond, respectively. In general, the slopes with which the corresponding bond lengths decrease (in $F < 0$ for Cl–Si, and $F > 0$ for Cl–C) or increase (in $F > 0$ for Cl–Si and $F < 0$ for Cl–C) are greater for the bond Cl–Si.

The weights of the covalent structures, $\mathrm{Cl}^{\uparrow}\mathrm{X}^{\downarrow}$ (where $X = \mathrm{C}$ and Si), are essentially invariant with the electric field strength, in contrast with the weights of the ionic structures, $\mathrm{Cl}^{-}\mathrm{X}^{+}$ and $\mathrm{Cl}^{+}\mathrm{X}^{-}$, which vary significantly. By adopting the Pauling's perspective, the understanding and the rationalization of the changes of the bond lengths can be done by examining the behavior of these structures under the experience of the electric field. In Table 1 we present the weights of the ionic structures in the absence of the electric field, obtained in the present work in comparison with those reported by other authors [10], and in Fig. 6 we show the variations of these weights with respect to the electric field strength.

The positive electric field ($F > 0$) favors the major ionic structure, $\mathrm{Cl}^{-}\mathrm{Si}^{+}$, but not (as expected) the minor one, $\mathrm{Cl}^{+}\mathrm{Si}^{-}$; consequently, at $F > 0$ the weight of the former must increase while that of the latter must decrease, as revealed by the results presented in Fig. 6. The same trends hold for $\mathrm{Cl}^{-}\mathrm{C}^{+}$ and $\mathrm{Cl}^{+}\mathrm{C}^{-}$ in $F < 0$. In general, the difference, ΔI, of the weights of the two ionic structures of the Cl–X sigma bond

$$\Delta I(\mathrm{X}) = W[\mathrm{Cl}^{-}\mathrm{X}^{+}] - W[\mathrm{Cl}^{+}\mathrm{X}^{-}] \tag{8}$$

provides a measure of the electron density flow along the Cl–X bond, with respect to the field. As ΔI increases with the field strength, the electron density moves in the direction X → Cl, i.e. away from the bonding region of the Cl–X bond. In this framework, and based on the variations of ionic structure of Cl–Si bond (shown in Fig. 6), we expect that for $F > 0$ the electric field must weaken and, thus, elongate this bond [49]; this trend is verified from the full geometry optimizations presented in Fig. 3. As far as the Cl–C bond is concerned, we remind the fact that the definition of the positive field orientation, based as usually in one-electron populations [49], leads to opposite positive fields for Cl–Si and Cl–C bonds. In this framework, the increase of ΔI(C) in Cl–C bond occurs in $F < 0$, and can correctly describe the flow of electron density in the direction C → Cl, which must cause both weakening and elongation of Cl–C bond, in agreement with the results presented in Fig. 3.

Table 1 The weights of ionic structures of $\mathrm{CH_3Cl}$ and $\mathrm{SiH_3Cl}$ in the absence of the electric field obtained (A) in the present work, and (B) in reference [10]

Ionic structure	Weights	
	(A)	(B)
$\mathrm{Cl}^{-}\mathrm{C}^{+}$	0.3532	0.262
$\mathrm{Cl}^{+}\mathrm{C}^{-}$	0.2076	0.116
$\mathrm{Cl}^{-}\mathrm{Si}^{+}$	0.5409	0.436
$\mathrm{Cl}^{+}\mathrm{Si}^{-}$	0.0726	−0.030

The above analysis is based on arguments concerning the electron density obtained in HF level. Although the electron correlation diminishes systematically the weights of ionic structures, the differences of these weights obtained in HF and correlated levels are clearly smaller for heteronuclear polar than for homonuclear bonds [77], particularly when the SCF-AO basis set is non-minimal. The comparison of the weights of ionic structures in HF and a correlated (VB) level, given in Table 1, provides the same conceptual pictures. One must also underline that, due to the fact that the diminution of the weights of ionic structures in a correlated level is systematic, one can expect that the differences, ΔI, of these weights (in which our analysis is based) must be similar for HF and correlated levels, as this can be confirmed by the results presented in Table 1.

From Fig. 6 it follows (in accord with intuition) that ΔI decreases for a field strength increasing from zero to negative values for Cl–Si bond, and positive values for Cl–C. The decrease of ΔI in both Cl–X bonds shows that the flow of electron density must be in the direction Cl → X. In general, in the considered Cl–X bonds, the effects emerging from the electron density flow toward the X atom, and the appearance of a minimum in the bond lengths, can be rationalized by similar arguments presented in reference [49], concerning an analogous flow in the direction H → C occurring in the H–C bond of $\mathrm{CH_4}$ (which present also a minimum in its length). The flow of electron density toward the X atom starts (in $F = 0$) from an electronic distribution in which the larger part of the density is closer to Cl than the X atom. As the field strength increases from zero (in negative values for Cl–Si, or positive for Cl–C), the electron density moves toward the bonding region, and provokes the strengthening [49] (initially) and, thus, the shortening of this bond. However, if the field strength increases further, it is possible that in higher field strengths the electron density is moved away from the bonding region (toward the X atom), such as the bond weakens [49] and elongates. These effects explain the appearance of a minimum in the lengths of both the Cl–C and the Cl–Si bonds.

The smaller value of $|F_{\mathrm{min}}|$ for Cl–C bond and the smaller slope of its bond length changes can be attributed to the fact that the ionic structure $\mathrm{Cl}^{-}\mathrm{C}^{+}$ varies slower than

$Cl^{-}Si^{+}$, and mainly to a basic feature characterizing these two different types of bonds in the absence of an electric field, namely the important difference of ΔI (see Table 1) in $F = 0$:

$$\Delta I(\mathrm{C}) \ll \Delta I(\mathrm{Si}) \qquad (9)$$

Introducing an electric field, although both ΔI(C) and ΔI(Si) are significantly modified, the above inequality is not inverted: the difference ΔI(C) in a given field, F, remains always clearly smaller than ΔI(Si) in the corresponding opposite field, $-F$. Based on inequality (Eq. 9), and also taking into account the fact that the increasing of the field strength (in negative values for Cl–Si and positive for Cl–C) has the consequence of diminishing the ΔI of both bonds, one can conclude that the flow of the electronic density in the direction Cl → X, and away from the bonding region of Cl–X, must be achieved in smaller field strengths for Cl–C than for Cl–Si bond; therefore the Cl–C bond achieves its minimum length in smaller strengths with smaller slope.

Although, in general, the trends in the electron density change along the bond direction could be also obtained from one-electron populations in orbital or coordinate spaces, the investigation of the considered sigma bonds from the Pauling's perspective (Fig. 1) implies the examination of the weights of the ionic resonance structures. In this framework, the various results presented in Figs. 3 and 6 can be summarized in a simple rule allowing us to predict the behavior of a sigma heteronuclear CS or covalent–CS bond, or, in general, a sigma bond with non-negligible polarity, under the experience of an electric field. For a given bond of this type and a given field orientation, we examine the variations that are caused by the electric field to the difference, ΔI, of the weights of the two ionic structures involved in this bond: 'if the field decreases (or, increases) the ΔI, we conclude that the bond length decreases (or, increases, respectively)'. It is worth noticing that this rule assumes the knowledge of the ionic structure that is the more important outside the electric field, for which the traditional one-electron atomic charges could introduce confusions in some cases. For example, in CH_3Cl, structure $Cl^{-}C^{+}$ is more important than $Cl^{+}C^{-}$, although the one-electron charge of Cl is smaller than that of C (see also Sect. 3.1), showing an opposite bond polarity.

3.3 The H–Si bonds

The H1–Si bond of SiH_4, is clearly a polar bond, $H1^{\delta-}Si^{\delta+}$. The variations of the two ionic structures, corresponding to the bond length variations of Fig. 4, are presented in Fig. 7. In a positive electric field orientation, the flow of electron density of the H1–Si bond is in the Si → H1 direction, and is correctly ascribed by the simultaneous decrease of the weight of the minor ionic structure $H1^{+}Si^{-}$ and the increase of that of the main ionic structure $H1^{-}Si^{+}$; the opposite flow in negative field orientation is also correctly described by the corresponding changes of the weights of the same ionic structures.

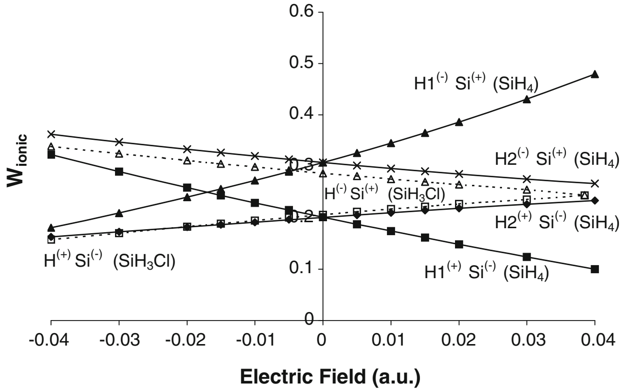

Fig. 7 Variations of ionic structures weights for H1–Si and H2–Si bonds of SiH_4 and H–Si bonds of SiH_3Cl, in the basis of hybrid orbitals (PNHOs), with respect to the electric field strength

Figure 4 shows that in a negative field orientation, a minimum appears for the H1–Si bond length in $F \approx -0.03$ au. This can be understood by means of similar arguments presented in Sect. 3.2, or in reference [49]: the flow of the electron density according to the scheme, H1 → Si, initially reinforces the bond (moving the electrons toward the bonding region), but in stronger field strengths the same flow weakens the bond (moving the electrons away from this region). Based on these arguments one can also explain why the corresponding minimum in the Cl–Si bond length appears in a field clearly stronger ($F \approx -0.08$ au) than this one concerning the H1–Si bond: due to the greater electronegativity of Cl (with respect to H atom of H1–Si), a higher field strength is necessary to move the electron density away from this atom, toward the Si atom.

The H2–Si bond length of SiH_4 varies slower than that of H1–Si, and in an opposite direction. This behavior can be understood straightforwardly by means of arguments based on the field component analysis [16], shown in Fig. 8, in which the bonds of the given molecular system inside the electric field are regarded from the Pauling's perspective. In this framework, the applied electric field, F, is analyzed in two components, one perpendicular and one parallel to the H2–Si bond of silane. The component perpendicular to this bond, F_P (see Fig. 8) has no important effects to both ionic structures $H2^{+}Si^{-}$ and $H2^{-}Si^{+}$, and only the (parallel) longitudinal one, F_L, is able to affect significantly the bond characteristics and, thus, its length.

In SiH_3Cl molecule, the behavior of the ionic structures of the H–Si bond (Fig. 7), as well as the variations of its

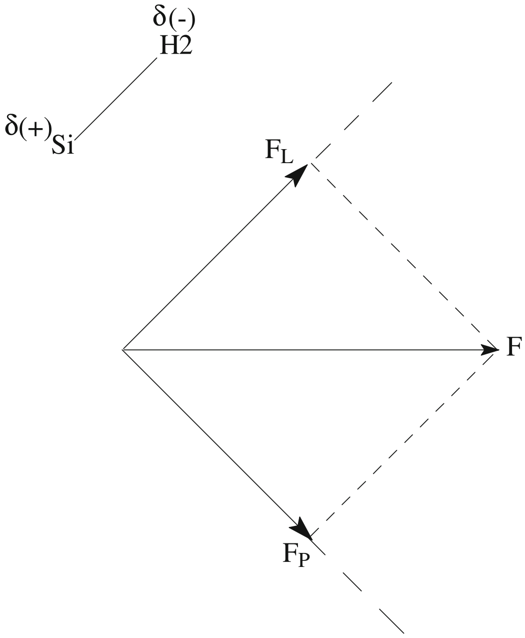

Fig. 8 Field component analysis of the applied electric field, *F*, in a direction defined by the H2–Si bond of SiH_4

length (Fig. 4) with respect to the electric field strength are quite similar to those of the H2–Si bond of SiH_4. These results confirm the fact that the behavior of these sigma bonds inside the electric field can be rationalized on the basis of the local picture of Pauling's resonance structures. It is worth noticing that in all field (relative) directions and orientations, the H–Si bonds in both SiH_4 and SiH_3Cl molecules follow the rule presented in Sect. 3.2.

3.4 The H–C bonds

The H–C bond lengths are thoroughly investigated in other work [49], and their behavior is classified according to the acidity of the H atom of these bonds. If the H has a non-negligible acidity, as for example in the HCN or HCCH molecules, the H–C bond length increases in $F > 0$ and decreases in $F < 0$. In terms of local ionic structures, these trends should be explained on the basis of the same arguments presented in previous sections, and in general they must follow the rule presented in Sect. 3.2; this is checked by performing additional calculations for the HCN molecule.

In the case of a low acidity of H atom, as for example, in CH_4 molecule, the H–C bond length decreases slowly in $F > 0$, presenting a minimum in $F \approx 0.02$ au, while increases in $F < 0$ (see Fig. 5). In Fig. 9, the variations of the weights of ionic structures, $H1^{+}C^{-}$ and $H1^{-}C^{+}$, of CH_4 show a flow of electron density in the direction H1 → C in $F > 0$ and C → H1 in $F < 0$. This is in total agreement with the flow assumed in reference [49] and, thus, the consequences of this effect can be understood by means of the same explanations. We remind that, according to the authors of this work, the electron density of H1–C bond, being closer to the H atom in CH_4 than in HCN or HCCH molecules, moves toward the bonding region of H1–C bond, as the field increases from $F = 0$ to $F > 0$, causing a strengthening and shortening (and thus a minimum in $F > 0$) only in CH_4 molecule. It is clear that the covalent H–C bond of CH_4, with a low H acidity, does not follow the rule presented in Sect. 3.2, which concerns more polar bonds.

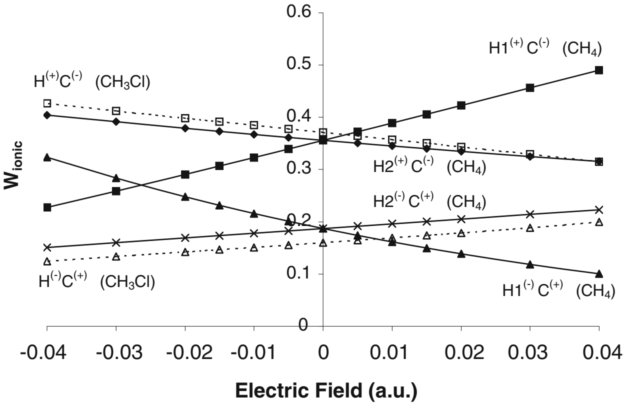

Fig. 9 Variations of ionic structures weights for H1–C and H2–C bonds of CH_4 and H–C bonds of CH_3Cl, in the basis of hybrid orbitals (PNHOs), with respect to the electric field strength

The changes in lengths of the bonds H2–C of CH_4 and H–C of CH_3Cl (see Fig. 5), as well as the behavior of the ionic structures $H2^{+}C^{-}$, $H2^{-}C^{+}$ (of CH_4) and $H^{+}C^{-}$, $H^{-}C^{+}$ (of CH_3Cl) (see Fig. 9), are quite similar, and in opposite direction with those of the H1–C of CH_4. These results support the local perspective provided by the Pauling's ionic resonance structures, in which the present work is based.

4 Conclusion

In the framework of the general purpose concerning the understanding and the rationalization (and even the qualitative prediction) of the changes induced by a given electric field to the bond lengths of a polyatomic molecular system, we investigated the Cl–X and H–X (where $X =$ C, Si) bonds under the experience of an electric field. These bonds belong to the class of non-symmetric sigma bonds, which are the most frequently accounted in polyatomic systems, and they show variable behavior with respect to the field direction and orientation.

The changes induced by an electric field in a π-system are controlled from the changes induced in the π-delocalization within various $\pi_{ij} \rightarrow \pi_{kl}{}^{*}$ intramolecular electron transfers [15], and can be rationalized by the corresponding changes of ionic π-bond structures [16]. In sigma systems, the electric field does not affect significantly the (clearly smaller) interbond delocalization, and the principal effects are controlled from local intrabond reorganizations. However, the descriptions emerging from traditional MO (or DFT) calculations provide clearly delocalized pictures in which the local specificities of sigma bonds are lost. In the framework of PEPA, one can place a bond 'under the microscope' and, thus, examine the behavior of various types of local structures, including the ionic ones. For the purposes of the present work we have extended our population analysis investigations to chemically meaningful hybrid (sigma) orbitals, such as the PNHOs introduced in the framework of NBO methodology.

The investigation of sigma bonds in an electric field from the Pauling's perspective implies the examination of the difference, ΔI, of the weights of their ionic resonance structures (Fig. 1), which are mainly affected from the experience of the electric field, and control the behavior of these bonds. Although the trends of changes of electron density along the bond direction could be also obtained from one-electron populations in both orbital and coordinate spaces, the use of ΔI is necessary to investigate the bonds from a VB-like viewpoint referring to the resonance of local structures. The obtained results for bond length changes in both HF and MP2 levels, and the presented rationalizations on the basis of ΔI, confirm that the behavior of a sigma bond inside an electric field can be understood and rationalized from the Pauling's perspective. In this framework, and in order to investigate a polyatomic sigma molecular system inside a given field direction and orientation, one can examine the behavior of the two ionic structures of its bonds. In the case of a sigma (heteronuclear) Charge–Shift or a covalent/Charge–Shift bond, or in general a sigma bond with non-negligible polarity, our results can be summarized to the following rule: 'if the field decreases (or, increases) the difference of the weights of the two ionic structures, then the bond length decreases (or, increases, respectively)'. This rule concerns all bonds considered in this work, except a covalent H–C bond having a non-acidic H atom (e.g. in CH_4 molecule). In general, it seems that this type of covalent bonds necessitates a topological population analysis [51, 52] in order to elucidate the fine details of electron density changes due to the electric field.

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