

# The physical origin of large covalent–ionic resonance energies in some two-electron bonds

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This study uses valence bond (VB) theory to analyze in detail the previously established finding that alongside the two classical bond families of covalent and ionic bonds, which describe the electron-pair bond, there exists a distinct class of charge-shift bonds (CS-bonds) in which the fluctuation of the electron pair density plays a dominant role. Such bonds are characterized by weak binding, or even a repulsive, covalent component, and by a large covalent–ionic resonance energy  $RE_{CS}$  that is responsible for the major part, or even for the totality, of the bonding energy. In the present work, the nature of CS-bonding and its fundamental mechanisms are analyzed in detail by means of a VB study of some typical homonuclear bonds (H–H, H<sub>3</sub>C–CH<sub>3</sub>, H<sub>2</sub>N–NH<sub>2</sub>, HO–OH, F–F, and Cl–Cl), ranging from classical-covalent to fully charge-shift bonds. It is shown that CS-bonding is characterized by a covalent dissociation curve with a shallow minimum situated at long interatomic distances, or even a fully repulsive covalent curve. As the atoms that are involved in the bond are taken from left to right or from bottom to top of the periodic table, the weakening effect of the adjacent bonds or lone pairs increases, while at the same time the reduced resonance integral, that couples the covalent and ionic forms, increases. As a consequence, the weakening of the covalent interaction is gradually compensated by a strengthening of CS-bonding. The large  $RE_{CS}$  quantity of CS-bonds is shown to be an outcome of the mechanism necessary to establish equilibrium and optimum bonding during bond formation. It is shown that the shrinkage of the orbitals in the covalent structure lowers the potential energy,  $V$ , but excessively raises the kinetic energy,  $T$ , thereby tipping the virial ratio off-balance. Subsequent addition of the ionic structures lowers  $T$  while having a lesser effect on  $V$ , thus restoring the requisite virial ratio ( $T/V = 1/2$ ). Generalizing to typically classical covalent bonds, like H–H or C–C bonds, the mechanism by which the virial ratio is obeyed during bond formation is primarily orbital shrinkage, and therefore the charge-shift resonance energy has only a small corrective effect. On the other hand, for bonds bearing adjacent lone pairs and/or involving electronegative atoms, like F–F or Cl–Cl, the formation of

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the bond corresponds to a large increase of kinetic energy, which must be compensated for by a large participation or covalent–ionic mixing.

## I Introduction

The first effective formulation of bonding in terms of the covalent–ionic classification, which is still being taught today, dates back to the famous 1916 paper of G. N. Lewis,<sup>1</sup> in which the concept of electron-pair bonding is introduced for the first time. The connection between this concept and quantum mechanics was subsequently established by Heitler and London,<sup>2</sup> who showed that bonding in H<sub>2</sub> originates in the quantum mechanical “resonance” interaction which is contributed as the two electrons are allowed to exchange their positions between the two atoms, thus defining the covalent interaction. For more general cases, the definitive quantum mechanical description of the two-electron bond was achieved when Pauling extended the Heitler–London description to a superposition of the covalent form and the two possible ionic forms of the bond, in proportions that vary according to the polarity of the bond.<sup>3</sup> In modern terms (using Slater determinants), the covalent–ionic superposition takes the form of  $\Psi_{\text{VB-3}}$  in eqn (1) and (2), for a two-electron bond that links together some atomic orbitals  $\chi_a$  and  $\chi_b$ .

$$\Psi_{\text{VB-3}} = C_1(|\dots \varphi\bar{\varphi} \dots \chi_a\bar{\chi}_b| - |\dots \varphi\bar{\varphi} \dots \bar{\chi}_a\chi_b|) + C_2|\dots \varphi\bar{\varphi} \dots \chi_b\bar{\chi}_b| + C_3|\dots \varphi\bar{\varphi} \dots \chi_a\bar{\chi}_a| \quad (1)$$

where  $\varphi$  represents the set of orbitals, if any, which are not involved in the bond under study (*e.g.*, adjacent bonds or lone pairs). The first term in the wavefunction represents the purely covalent interaction, and the two others characterize the ionic components, so that eqn (1) can be re-expressed as in eqn (2)

$$\Psi_{\text{VB-3}} = C_1\Psi_{\text{A}\bullet\text{-}\bullet\text{B}} + C_2\Psi_{\text{A}^+\text{B}^-} + C_3\Psi_{\text{A}^-\text{B}^+} \quad (2)$$

It should be noted that, although the concept of covalent–ionic superposition appears most clearly in valence bond (VB) theory, it is also present, albeit in a hidden form, in a wavefunction of molecular orbital (MO) type, since it is well known<sup>4</sup> that an MO treatment followed by complete configuration interaction is equivalent to the VB-based covalent–ionic scheme of Pauling. Moreover, it should also be noted that the simple wavefunction shown in eqn (1) is in fact an accurate one, since it accounts for the bonding energy of any two-electron bond, provided an accurate VB computational method is used.<sup>5</sup>

Since the covalent–ionic superposition (eqn (1) and (2)) scheme accounts for the totality of the bonding energy while the purely covalent interaction does not, it is clear that adding the ionic terms corresponds to a covalent–ionic resonance energy (RE) component of the bonding. Just how large is this resonance energy is the question that concerns us here.

In Pauling's days, for lack of accurate *ab initio* VB methods, some simplifying assumptions were made, namely that (i) the covalent–ionic RE is proportional to the electronegativity difference between the bonded atoms, and (ii) the covalent–ionic RE is negligible in homopolar bonds.<sup>6</sup> Curiously enough, the latter assumption maintained the status of an unverified working hypothesis over several decades. This lack of verification/falsification of the hypothesis is attributed to the inability of MO-based methods, or of VB methods dealing with semi-delocalized orbitals (*e.g.* generalized valence bond or spin-coupled methods) to quantify covalent-ionic REs. The first verifications came with the advent of accurate VB methods dealing with strictly localized atomic orbitals.<sup>7–9</sup> They revealed that alongside the traditional category of homopolar bonds in which the ionic component plays a minor role (*e.g.* H–H, C–H, C–C bonds . . .), there exists a specific category of bonds in which the major phenomenon responsible for the bonding energy is neither the covalent

interaction nor the ionic electrostatic stabilization, but rather the resonance stabilization brought by the covalent–ionic mixing. As this covalent–ionic resonance is characterized by a fluctuation of the electronic density, such bonds have been termed “charge-shift bonds” (CS bonds).

Charge-shift bonding has been characterized in some homopolar bonds (*e.g.* F–F, HO–OH, *etc.*) as well as in some polar bonds (*e.g.* Si–Cl, C–Cl, H–F, *etc.*).<sup>7–9</sup> Atoms or fragments that are prone to CS bonding are compact electronegative and/or lone-pair-rich species, albeit with significant electronegativity. It has been characterized not only *via ab initio* VB calculations, but also through ELF/DFT calculations; the latter calculations demonstrated that such bonds manifest themselves by a depleted population with a large variance and negative covariance.<sup>8</sup> Far from being merely an academic concept, CS bonding has some experimental manifestations, among which negative or weakly positive bonding electron densities<sup>8</sup> and, more importantly, some effects on reactivity. Thus, the reason why the halogen exchange reactions,  $H + XH' \rightarrow HX + H'$  ( $X = \text{halogen}$ ), have systematically larger barriers than the hydrogen exchange reactions,  $X + HX' \rightarrow XH + X'$ , was shown to be due to the increasing CS character of the H–X bond in the series  $X = \text{I, Br, Cl, F}$ . The barrier difference culminates for  $X = \text{F}$ , with a hefty barrier of 42 kcal mol<sup>−1</sup> for the fluorine transfer reaction, compared with only 18 kcal mol<sup>−1</sup> for the hydrogen abstraction reaction. This difference was shown to derive from the CS character of the H–F bond.<sup>9</sup>

Now that the CS-bonding concept is firmly established, by means of accurate VB calculations and by independent ELF/DFT calculations, it is timely to try to understand the nature of the fundamental mechanism by which this type of bond can be established in some molecules and not in others. For this purpose, this paper is aimed at studying in detail all the aspects of bond formation in a series of molecules that each display a range of bonding features: H<sub>2</sub>, and C<sub>2</sub>H<sub>6</sub> as members of the classical family of covalent bonds, Cl<sub>2</sub> as a bond exhibiting significant CS character, and the series N<sub>2</sub>H<sub>4</sub>, H<sub>2</sub>O<sub>2</sub> and F<sub>2</sub> as molecules exhibiting increasing CS character from left to right of the periodic table.

## II Theoretical

The wavefunction that describes the bond between atomic orbitals  $\chi_a$  and  $\chi_b$  is expressed in eqn (1), which can also be rewritten as eqn (2). While some VB methods allow for the use of semi-delocalized orbitals, here all the orbitals are kept strictly localized on a single atom or fragment, so as to keep the distinction between covalent and ionic bonds perfectly clear. The  $\varphi$  orbitals that are adjacent to the  $\chi_a$ – $\chi_b$  bond, *e.g.* the lone pairs in F<sub>2</sub> or the orbitals of the C–H bonds in C<sub>2</sub>H<sub>6</sub>, are kept doubly occupied in the three VB structures. The valence bond calculations are performed at two levels: valence-bond-self consistent field (VBSCF)<sup>10</sup> and breathing-orbital valence bond (BOVB).<sup>5,11</sup>

At the VBSCF level, the coefficients C<sub>1</sub>–C<sub>3</sub> of eqn (1) and (2) and all the orbitals are optimized simultaneously. This computational level ensures left–right correlation in the  $\chi_a$ – $\chi_b$  bond, but lacks dynamic correlation. In the BOVB method, the structural coefficients and orbitals of the VB structures are also optimized simultaneously, but now dynamic correlation is introduced by allowing the orbitals to assume sizes and shapes that are different for the different structures. This specific feature has rendered the method capable of yielding realistic bonding energies while keeping the compactness and interpretability of the simple VBSCF wavefunction.<sup>5</sup>

The BOVB method has a few levels, which differ in sophistication hierarchy. At the most basic level, referred to as L-BOVB, all the orbitals, including the inactive set  $\varphi$ , are kept strictly localized, and the ionic components  $\Psi_{A+B^-}$  and  $\Psi_{A-B^+}$  are described as simple closed-shell VB functions. This simple level, which makes repetitive calculations an easy task, is sufficient for yielding reasonable dissociation curves in the series H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, N<sub>2</sub>H<sub>4</sub>, H<sub>2</sub>O<sub>2</sub>. We emphasize that this simple level, that

has been chosen here for the sake of simplicity, yields less accurate bonding energies and equilibrium bond lengths than higher BOVB levels,<sup>5,8</sup> but provides the same trends for the resonance energies. For F<sub>2</sub> and Cl<sub>2</sub>, which are the sites of strong repulsions between lone pairs and for which calculations of virial ratios are performed, a more sophisticated level has been deemed necessary. This level is characterized by two improvements relative to the basic level: (i) the active doubly occupied orbitals of an ionic structures are split into two singlet-coupled singly-occupied orbitals, so as to bring some radial correlation to the active electrons; (ii) the  $\pi$  lone pairs are allowed to be delocalized on the three fragments. This does not change the physical meaning of the VB structures, but allows some flexibility in the interactions between lone pairs. We refer to this level as  $\pi$ -SD-BOVB. This level is slightly different from the full SD-BOVB level (more complicated to use<sup>5</sup>), in which the s lone pairs are also allowed to be delocalized. For comparative purposes, F<sub>2</sub> has been calculated at both the L-BOVB and  $\pi$ -SD-BOVB levels. On the other hand, Cl<sub>2</sub> has been calculated at the  $\pi$ -SD-BOVB level alone. Previous calculations performed at the full SD-BOVB level<sup>8</sup> may differ slightly from those reported here.

All calculations were performed in the standard 6-31G(d) basis set, with the exception of the H<sub>2</sub> molecule which is calculated in the 6-31G(d,p) basis set, so that all the active orbitals  $\chi_a$  and  $\chi_b$  are calculated in basis sets of double-zeta + polarization quality. In the H<sub>2</sub> case, VB structures corresponding to the  $\pi$  bonding of H<sub>2</sub> are added. Previous experience has shown us that such VB structures are not negligible in diatomic molecules such as H<sub>2</sub>, Li<sub>2</sub>, *etc.*, in which  $\sigma^2 \rightarrow \pi^2$  transitions are possible (of course this should not be considered as  $\pi$ -bonding but as angular correlation correction). The geometry optimizations were performed at the Møller–Plesset perturbational level (MP2) in the MO framework. In order to generate entire dissociation energy curves, a series of geometry optimizations was carried out at fixed inter-fragment distances for all molecules.

The weights of the VB structures are determined by use of the Coulson–Chirgwin<sup>12</sup> formula, eqn (3), which is the equivalent of a Mulliken population analysis in VB theory:

$$W_i = C_i^2 + \sum_{j \neq i} C_i C_j \langle \Psi_i | \Psi_j \rangle; \quad (\Psi_i, \Psi_j : \text{covalent or ionic structures, eqn (2)}) \quad (3)$$

The charge-shift resonance energy, RE<sub>CS</sub>, is defined in eqn (4) as the energy difference between the covalent structure  $\Psi_{A \bullet \bullet B}$  and the full wavefunction  $\Psi_{VB-3}$  of eqn (2), at the equilibrium geometry of the latter ( $R_{\text{eq}}^{\text{VB-3}}$ ):

$$\text{RE}_{\text{CS}} = E(\Psi_{A \bullet \bullet B}) - E(\Psi_{\text{VB-3}}) \quad (4)$$

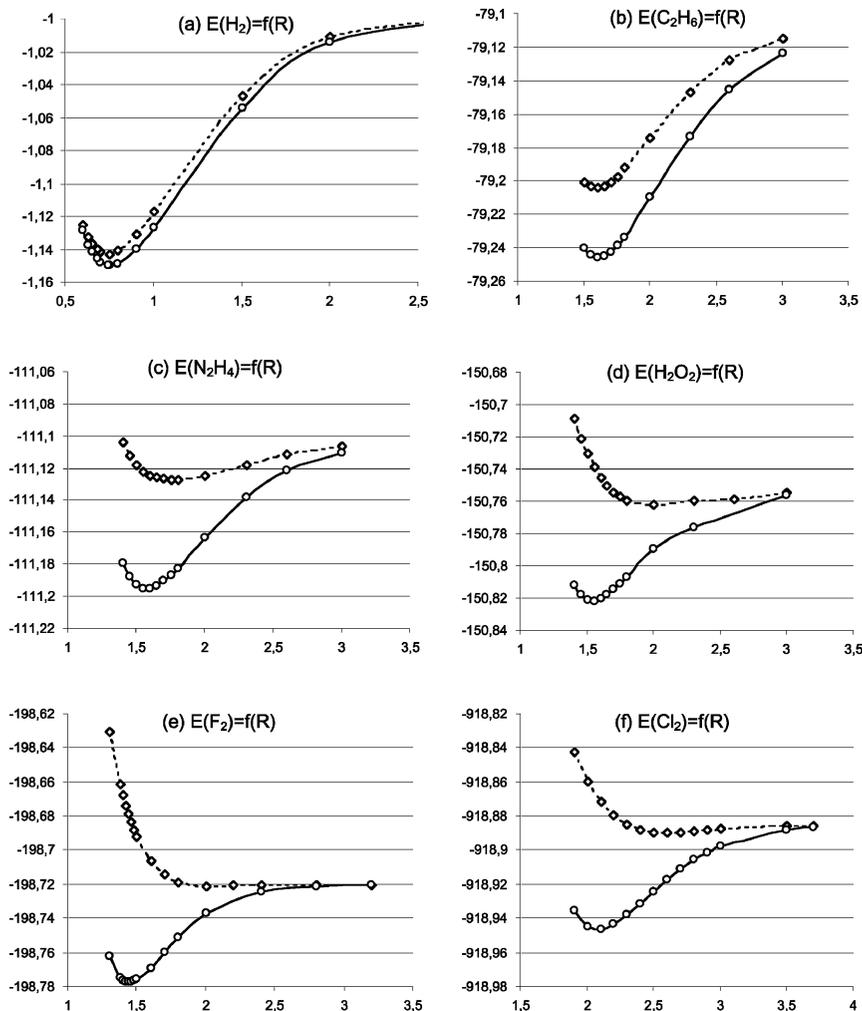
Here both  $E(\Psi_{A \bullet \bullet B})$  and  $E(\Psi_{\text{VB-3}})$  are both determined *variationally* within their respective spaces of VB structures, and as such, the RE<sub>CS</sub> quantity is a quasi-variational quantity.

Another quantity of interest, to be needed later, is the degree of compactness of the  $\chi_a$  and  $\chi_b$  orbitals that are involved in the bond. The index of compactness,  $I_c$ , is defined as follows:

$$I_c = [(c_{\text{so}}^2 + c_{\text{po}}^2)/(c_{\text{si}}^2 + c_{\text{pi}}^2)]^{1/2} \quad (5)$$

Here  $c_{\text{so}}$  and  $c_{\text{si}}$  are the coefficients of the outer and inner basis functions of s type in the atomic orbital  $\chi_a$  ( $\chi_b$ ) while  $c_{\text{po}}$  and  $c_{\text{pi}}$  are analogous coefficients for the p basis functions. Since outer basis functions are more diffuse than inner ones,  $I_c$  will vary like the size of the orbital: the larger the  $I_c$  index, the more diffuse the orbital.

The Gaussian 98 series of programs<sup>13</sup> was employed for Møller–Plesset calculations. The *ab initio* valence bond calculations were performed with the XMVB program.<sup>14</sup>



**Fig. 1** Dissociation energy curves for the  $\text{H}_2$  (a),  $\text{C}_2\text{H}_6$  (b),  $\text{N}_2\text{H}_4$  (c),  $\text{H}_2\text{O}_2$  (d),  $\text{F}_2$  (e) and  $\text{Cl}_2$  (f) molecules. The dotted lines represent the purely covalent wavefunction ( $\Psi_{\text{COV}}$ ). The ground state dissociation curves ( $\Psi_{\text{VB-3}}$ ) are calculated at the L-BOVB level for the  $\text{H}_2$  (a),  $\text{C}_2\text{H}_6$  (b),  $\text{N}_2\text{H}_4$  (c) and  $\text{H}_2\text{O}_2$  (d) molecules, and at the  $\pi$ -SD-BOVB level for the  $\text{F}_2$  (e) and  $\text{Cl}_2$  (f) molecules.

### III Purely covalent vs. real dissociation energy curves

Fig. 1 shows some dissociation energy curves for the six molecules:  $\text{H}_2$ ,  $\text{C}_2\text{H}_6$ ,  $\text{N}_2\text{H}_4$ ,  $\text{H}_2\text{O}_2$ ,  $\text{F}_2$  and  $\text{Cl}_2$ . The curves in dotted lines are the dissociation curves of the purely covalent VB structure ( $\Psi_{\text{A}\cdot\cdot\text{B}}$  in eqn (2)), while the curves in solid lines represent the VB-3 three-structure ground state ( $\Psi_{\text{VB-3}}$  in eqn (2)). The ground state curves are calculated with the BOVB method, and the purely covalent states are calculated separately as a 1-structure VB calculation (in this case the VBSCF and BOVB methods become equivalent).

As can be seen in Fig. 1a, the simplifying assumption of Pauling, that the covalent-ionic resonance energy is small for homonuclear bonds, appears as fully justified as in the  $\text{H}_2$  case. The covalent and VB-3 curves remain very close to each other at all distances, and the equilibrium bond lengths are practically similar. As a

consequence, the  $RE_{CS}$  quantity is quite weak,  $7.1 \text{ kcal mol}^{-1}$ , and accounts for a small part of the total bonding energy. Note that the potential well is deeper, and closer to the experimental value ( $105.4 \text{ kcal mol}^{-1}$  vs.  $109.6$  experimentally) at higher, but less simple, BOVB levels.<sup>8</sup> The latter calculation, however, still yields a small  $RE_{CS}$  energy ( $11.7 \text{ kcal mol}^{-1}$ ).

The covalent and VB-3 dissociation curves for  $C_2H_6$ , shown in Fig. 1b, exhibit their minima at practically the same C–C distance (which, we recall, is slightly larger than the experimental value, owing to our use of the simplest level of the BOVB method). In the ground state curve (BOVB level), the covalent–ionic resonance energy accounts for only 29% of the total bonding energy, thus putting the C–C bond of ethane in the category of classical homopolar bonds in Pauling's sense, *i.e.* a bond that is mainly covalent, and marginally stabilized by further admixture of ionic components.

The characteristics of homonuclear bonding gradually become different as we move from left to right of the periodic table. In  $N_2H_4$  (Fig. 1c), the covalent minimum is right-shifted by some  $0.20 \text{ \AA}$  relative to the true minimum of the ground state. Moreover, the covalent dissociation curve exhibits a potential well of only  $14 \text{ kcal mol}^{-1}$ , much smaller than the VB-3 bonding energy of  $54.6 \text{ kcal mol}^{-1}$ . Clearly then, the N–N bonding energy in  $N_2H_4$  cannot be considered as arising mainly from the covalent interaction, and the  $RE_{CS}$  term becomes the major contributor to the bond energy. The charge-shift character of the homonuclear bond is even more evident in  $H_2O_2$ , whose covalent curve exhibits a tiny minimum of  $6 \text{ kcal mol}^{-1}$ , at an interatomic distance that is  $0.50 \text{ \AA}$  larger than the ground state equilibrium distance. Lastly, the  $F_2$  molecule (Fig. 1e) represents an extreme case, in which the covalent curve does not display any minimum, and is *repulsive at all distances*. Thus, in this molecule, the repulsive covalent interaction is more than compensated by the very large covalent–ionic resonance energy, which becomes the only cause of bonding.

The  $Cl_2$  case is interesting, as it allows a comparison to be made between two isoelectronic compounds,  $F_2$  and  $Cl_2$ , differing by their row in the periodic table. Unlike the  $F_2$  case, the covalent curve of  $Cl_2$  (Fig. 1f) is not entirely repulsive, but exhibits a small potential well of  $2.4 \text{ kcal mol}^{-1}$ , at a distance some  $0.53 \text{ \AA}$  longer than the ground state equilibrium distance. Thus,  $Cl_2$  is clearly a CS-bond, however, less so than  $F_2$ .

Table 1 displays the ground state bonding energies ( $\Psi_{VB-3}$  calculated at the BOVB level) of the six molecules, and the  $RE_{CS}$  energies at the ground state equilibrium geometries  $R_{eq}^{MP2}$ , as optimized at the MP2 level. These values confirm that  $H_2$  and  $C_2H_6$  are classical homonuclear bonds, *i.e.* mainly covalent, while the remaining molecules are all nonclassical and bonded by CS-bonding. Some clear tendencies are apparent: as we move from left to right or from bottom to top of the periodic table, and for molecules taken at their  $R_{eq}^{MP2}$  equilibrium distances, the covalent–ionic resonance energy increases, while at the same time the covalent bonding energy

**Table 1** Bond dissociation energies (BDE), covalent–ionic resonance energies ( $RE_{CS}$ ) and covalent weights of the molecules taken in their MP2-calculated equilibrium geometries. All energies in  $\text{kcal mol}^{-1}$

|                        | $H_2$ | $H_3C-CH_3$ | $H_2N-NH_2$ | HO-OH | F–F <sup>a</sup> | F–F <sup>b</sup> | Cl–Cl <sup>b</sup> |
|------------------------|-------|-------------|-------------|-------|------------------|------------------|--------------------|
| BDE <sup>c</sup>       | 100.8 | 84.1        | 54.6        | 41.7  | 29.1             | 35.2             | 37.5               |
| $RE_{CS}$ <sup>d</sup> | 7.1   | 24.4        | 43.0        | 51.7  | 59.9             | 60.6             | 48.1               |
| $W_{cov}$ <sup>e</sup> | 0.76  | 0.63        | 0.63        | 0.66  | 0.70             | 0.73             | 0.69               |

<sup>a</sup> Calculations at the L-BOVB level. <sup>b</sup> Calculations at the  $\pi$ -SD-BOVB level. <sup>c</sup> Bonding energy of the  $\Psi_{VB-3}$  ground state, as calculated by the BOVB method. <sup>d</sup> According to eqn (4). <sup>e</sup> Weight of the covalent function  $\Psi_{A\bullet\bullet B}$ , according to eqn (3).

decreases or becomes negative. On the other hand, the weight of the covalent component (Table 1, entry 3) remains rather constant for all molecules, in sharp contrast with the variations of  $RE_{CS}$ . These tendencies will be analyzed and explained in the next section.

#### IV Tendencies in the matrix elements in the periodic table

The previous section has put forward some computational results that yield very different values of the covalent–ionic resonance energies, according to the bond that is considered. It is now important to understand the reasons behind the computed facts, and to rationalize the observed tendencies in the periodic table. Accordingly, this section is aimed at answering the three following questions: (i) why does the bonding energy of the covalent component decrease in a series of molecules taken from left to right or from bottom to top of the periodic table? (ii) Why does the covalent–ionic resonance energy  $RE_{CS}$  increase, in the same series, while the covalent bonding energy decreases? (iii) Why are the covalent vs. ionic weights quasi-constant in a series whereas  $RE_{CS}$  widely varies?

The answer to the first question can be related to the known repulsive role of the lone pairs that are adjacent to the considered bond. This repulsive effect, which has been called “lone-pair bond weakening effect” (LPBWE) by Sanderson,<sup>15</sup> is proportional to the number of lone pairs, and increases therefore in the series C–C, N–N, O–O, and F–F. It arises primarily from the repulsion between the bonding electrons and the lone pairs that have the same symmetry as the bond, while the repulsion between the lone pairs themselves makes a lesser contribution. This repulsive effect has been quantified by means of VB calculations, and has been shown to amount to about 53, 70 and 75 kcal mol<sup>-1</sup> for the N–N, O–O and F–F bonds, respectively.<sup>16</sup> It is therefore a significant effect, which increases from left to right of the periodic table, and which explains very well the concomitant decrease of covalent bonding. The LPBWE has also been shown to increase from bottom to top of the periodic table, thus explaining why the covalent curve still has a tiny potential well in Cl<sub>2</sub> but not in F<sub>2</sub>.

The answers to questions (ii) and (iii) will require considerations of the Hamiltonian matrix elements in the VB calculations. Let us consider the ground state wavefunction ( $\Psi_{VB-3}$ ) as the result of a  $2 \times 2$  configuration interaction between the covalent component  $\Psi_{cov}$  ( $\Psi_{A \bullet \bullet B}$  in eqn (2)) and the symmetry-adapted combination of the two ionic structures,  $\Psi_{ion}$ :

$$\Psi_{VB-3} = C_{cov}\Psi_{cov} + C_{ion}\Psi_{ion} \quad (6a)$$

$$\Psi_{ion} = N(\Psi_{A^+ B^-} + \Psi_{A^- B^+}) \quad (6b)$$

A key quantity in our reasoning will be the reduced resonance integral  $\beta$  between  $\Psi_{cov}$  and  $\Psi_{ion}$ , that is related to the Hamiltonian matrix elements through the following transformation:

$$\beta = \langle \Psi_{cov} | H | \Psi_{ion} \rangle - S \langle \Psi_{cov} | H | \Psi_{cov} \rangle \quad (7)$$

where  $S$  is the overlap between  $\Psi_{cov}$  and  $\Psi_{ion}$ . Another useful quantity is  $\Delta E$ , the energy gap between  $\Psi_{cov}$  and  $\Psi_{ion}$  in the Hamiltonian matrix:

$$\Delta E = \langle \Psi_{ion} | H | \Psi_{ion} \rangle - \langle \Psi_{cov} | H | \Psi_{cov} \rangle \quad (8)$$

Table 2 displays the calculated values of  $\beta$ ,  $\Delta E$  and the coefficients  $C_{cov}$  and  $C_{ion}$ , as they appear in BOVB calculations at the MP2 equilibrium geometries, in the series of molecules C<sub>2</sub>H<sub>6</sub>, N<sub>2</sub>H<sub>4</sub>, H<sub>2</sub>O<sub>2</sub> and F<sub>2</sub>, which exhibits homonuclear bonds between atoms taken from left to right of the periodic table. By reasoning in terms of perturbation theory, one would predict that the coefficient  $C_{ion}$  should vary like  $\beta/\Delta E$ , while the covalent–ionic resonance energy,  $RE_{CS}$ , varies like  $\beta^2/\Delta E$ . Perturbation theory, however, is valid only if the  $\beta$  integral is smaller than the energy gap  $\Delta E$ ,

**Table 2** Reduced resonance integral and energy gaps, between the covalent and symmetrized ionic structures, and coefficients of these VB structures. All energies are in hartrees

|                                    | $\beta$  | $\Delta E$ | $C_{\text{cov}}$ | $C_{\text{ion}}$ | $C_{\text{ion}}/C_{\text{cov}}$ |
|------------------------------------|----------|------------|------------------|------------------|---------------------------------|
| $\text{H}_3\text{C}-\text{CH}_3^a$ | -0.15462 | 0.10345    | 0.642            | 0.393            | 0.612                           |
| $\text{H}_2\text{N}-\text{NH}_2^a$ | -0.25257 | 0.16558    | 0.657            | 0.414            | 0.630                           |
| $\text{HO}-\text{OH}^a$            | -0.27920 | 0.22845    | 0.699            | 0.413            | 0.591                           |
| $\text{F}-\text{F}^a$              | -0.28248 | 0.30796    | 0.744            | 0.391            | 0.526                           |
| $\text{F}-\text{F}^b$              | -0.29199 | 0.28977    | 0.732            | 0.400            | 0.546                           |

<sup>a</sup> Calculations at the L-BOVB level. <sup>b</sup> Calculations at the  $\pi$ -SD-BOVB level.

which is clearly not the case as can be seen in Table 2. Therefore, our analysis in terms of perturbation theory will only be qualitative in nature. Thus, it appears from Table 2 that  $\Delta E$ , the covalent–ionic energy gap, regularly increases in the series. In turn, the  $\beta$  integral, which is responsible for the covalent–ionic coupling, also increases, in absolute value, in the series. Thus, the coefficient of the ionic component is proportional to a quantity,  $1/\Delta E$ , that decreases in the series, and proportional to a quantity,  $\beta$ , that increases. As a consequence, one may expect  $C_{\text{ion}}$  to vary only weakly in the series, and indeed this coefficient appears to be remarkably constant in Table 2, even if this result must be tempered by the slow increase of the coefficient  $C_{\text{cov}}$ .

It is now possible to explain why the covalent–ionic resonance energy  $\text{RE}_{\text{CS}}$  increases in the series, while the ionic weights do not. Indeed,  $\text{RE}_{\text{CS}}$  is proportional to a decreasing factor,  $1/\Delta E$ , and proportional to the *square* of an increasing factor,  $\beta^2$ . In other words,  $\text{RE}_{\text{CS}}$  can be considered as a roughly constant factor (the ratio  $C_{\text{ion}}/C_{\text{cov}}$ ) multiplied by an increasing factor  $\beta$ . Of course we recall that the above analysis is only qualitative. Any endeavour to retrieve the quantitative values of  $\text{RE}_{\text{CS}}$  or ionic weights by means of a perturbative theoretical argument whose conditions of validity are not met would be useless.

## V The fundamental mechanism of bond formation: Orbital shrinkage vs. covalent–ionic resonance

While the occurrence of charge-shift bonding is mathematically understood by consideration of Hamiltonian matrix elements and energy gaps, the phenomenon still remains to be understood in a more physical way, and in particular why charge-shift bonding is associated with lone-pair richness. In order to achieve such an understanding we discuss the fundamental changes which occur during bond making,<sup>17</sup> based on the virial theorem.<sup>17a,18</sup> The diatomic virial theorem is expressed in eqn (9) and is satisfied for any wavefunction, whatever the computational method that is used, provided the calculation is performed in a sufficiently flexible basis set:

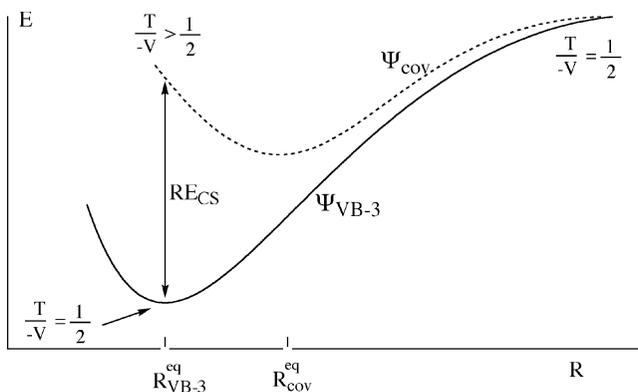
$$-RdE/dR = 2T + V \quad (9)$$

where  $E$  is the total energy,  $V$  and  $T$  are, respectively, the potential and kinetic components, and  $R$  is the interatomic distance. This means that the virial ratio has the value 1/2, as in eqn (10), for any properly optimized wavefunction provided the diatomic is taken at the interatomic distance  $R_{\text{eq}}$  that is optimal for this very wavefunction:

$$T/-V = 1/2; R = R_{\text{eq}} \quad (10)$$

According to eqn (9), the virial ratio is larger (smaller) than 1/2 for interatomic distances smaller (larger) than  $R_{\text{eq}}$  (Fig. 2).

For a molecule that has no lone pair repulsions, like  $\text{H}_2$ , the primary event that takes place when one brings the two fragments together, all other things being equal,



**Fig. 2** Typical balance and off-balance situations for the virial ratio at infinite distance and around the minima of the covalent and ground state dissociation curves.

is a lowering of the kinetic energy, that puts the virial ratio off-balance ( $T/-V < 1/2$ ).<sup>17</sup> At the purely covalent level, the only degree of freedom for the wavefunction to restore the virial is to adjust the orbital size. In  $H_2$ , this is carried out by orbital shrinkage, which has the effect of increasing the kinetic energy and lowering the potential energy, in a measure appropriate for lowering the  $T/-V$  quantity and re-establishing the virial ratio ( $T/-V = 1/2$ ) needed for equilibrium.<sup>17</sup> This condition is reached at the covalent equilibrium distance,  $R_{eq}^{cov}$ . At shorter distances, further orbital shrinking is no more able to satisfy the virial ratio, and the covalent wavefunction has an excess of kinetic energy ( $T/-V > 1/2$ ), according to eqn (9) (see also Fig. 2).

The presence of lone pairs modify the situation somewhat: the Pauli repulsion that is associated with the LPBWE brings an additional rise in the kinetic energy. In such a case, orbital shrinkage, which is an appropriate bonding mechanism in the case of a deficit of kinetic energy, becomes less appropriate, or even not appropriate at all. As a consequence, owing to the lack of efficiency of the mechanism of orbital shrinkage by itself, the equilibrium distance  $R_{eq}^{cov}$  at which the virial relation is established is rather long, and the covalent potential well is small. To establish a stronger bonding in this situation where kinetic energy is in excess, there is the possibility of using another mechanism of  $T/V$  regulation; this mechanism is the covalent–ionic resonance. By contrast to orbital shrinkage, adding ionic structures has the effect of *lowering* the kinetic energy, while having a less important effect on the potential energy. The larger the excess of kinetic energy, the more important will be this mechanism. Thus, at an inter-fragment distance  $R_{eq}^{VB-3}$  which can be much shorter than  $R_{eq}^{cov}$  (Fig. 2), the virial ratio  $T/-V$  is larger than  $1/2$  in the covalent wavefunction, but the covalent–ionic mixing has the main effect of lowering  $T$  so as to re-establish the virial.

However attractive the above qualitative explanation may be, it remains to be verified by quantitative computation. Table 3 displays some quantitative estimations of orbital shrinkage for the six molecules, as calculated at the covalent, VBSCF and BOVB levels. For each computational level, the molecules are taken in the equilibrium geometries that are specific to that level. What is reported in this table is the  $I_c^{eq}/I_c^\infty$  ratio, where  $I_c^{eq}$  is the compactness index, calculated from eqn (5) at the equilibrium distance, and  $I_c^\infty$  is the same index at infinite interatomic distance. A ratio smaller than unity means that the orbitals (that are involved in the bond) shrink in the course of bond formation, whereas a ratio larger than unity means that the orbitals expand.

Let us consider the covalent level first (Table 3, entry 1). It is apparent that the two molecules that have no lone pairs ( $H_2$ ,  $C_2H_6$ ) display a significant orbital shrinkage

**Table 3** Quantitative characterization of orbital shrinkage as the fragments are brought from infinite distance to bonding distance.  $I_c^\infty$  is the compactness index for the separate fragments, according to eqn (5).  $I_c^{\text{eq}}$  is the compactness index at the respective equilibrium distances of the covalent, VBSCF and BOVB distances

| $I_c^{\text{eq}}/I_c^\infty$ | H <sub>2</sub>     | H <sub>3</sub> C–CH <sub>3</sub> | H <sub>2</sub> N–NH <sub>2</sub> | HO–OH              | F–F                | Cl–Cl              |
|------------------------------|--------------------|----------------------------------|----------------------------------|--------------------|--------------------|--------------------|
| $\Psi_{\text{cov}}$          | 0.583              | 0.798                            | 0.940                            | 1.053              | —                  | 1.169              |
| $\Psi_{\text{VB-3}}$ (VBSCF) | 0.521              | 0.602                            | 0.806                            | 0.941              | 0.962              | 0.878              |
| $\Psi_{\text{VB-3}}$ (BOVB)  | 0.519 <sup>a</sup> | 0.497 <sup>a</sup>               | 0.697 <sup>a</sup>               | 0.836 <sup>a</sup> | 0.898 <sup>b</sup> | 0.823 <sup>b</sup> |

<sup>a</sup> Calculations at the L-BOVB level. <sup>b</sup> Calculations at the  $\pi$ -SD-BOVB level.

effect ( $I_c$  gets smaller) from infinite distance to bonding distance. The orbital shrinkage is still present, but smaller, in N<sub>2</sub>H<sub>4</sub>, which is subject to a moderate LPBWE due to the presence of one lone pair on each nitrogen atom. By contrast, for all the molecules that have more than one lone pair on each atom (H<sub>2</sub>O<sub>2</sub>, F<sub>2</sub>, Cl<sub>2</sub>), the orbitals involved in the bond *expand* from infinite distance to bonding distance (although this is not seen in Table 3 since F<sub>2</sub> has no covalent minimum, the calculations show a gradual orbital expansion in the covalent wavefunction as the distance between the F atoms decreases). This is a consequence of a strong LPBWE that brings some excess of kinetic energy: while orbital shrinkage is appropriate when there is a deficit of kinetic energy (as in classical bonds), just the opposite occurs when this energy component is in excess (CS bonds). At the VBSCF and BOVB levels, the ionic component is added to the wave function, and orbital shrinkage takes place, although to a lesser extent than in H<sub>2</sub> and C<sub>2</sub>H<sub>6</sub>. This is not surprising: as the covalent–ionic resonance has the effect of lowering  $T$ , the kinetic energy excess is eliminated, so that orbital shrinkage now becomes possible. This effect is observed at the VBSCF level, and reinforced at the BOVB level which, by better treatment of the ionic structures, further increases charge-shift bonding relative to VBSCF. Remarkably, at both the VBSCF and BOVB levels, orbital shrinkage is less and less important from left to right of the periodic table (C–C → F–F) and from bottom to top (Cl–Cl → F–F), thus varying in the opposite way to RE<sub>CS</sub>.

Let us now consider the effect of charge-shift bonding on the kinetic and potential energies in two typical cases where RE<sub>CS</sub> is important: Cl<sub>2</sub> and F<sub>2</sub> (Table 4). The two molecules are considered at the interatomic distance  $R_{\text{eq}}^{\text{VB-3}}$ , at which the virial relationship is exactly satisfied (that is,  $T/-V = 1/2$  or  $2T + V = 0$ ) in the 3-VB structure ground state wavefunction, as calculated at the BOVB level (these distances differ slightly from the ground state minima, because the basis set is not complete). Let us consider the Cl<sub>2</sub> molecule first. At the covalent level, the kinetic energy is in excess ( $2T + V = +0.161$  au), as predicted by eqn (9) (see also Fig. 2), because the Cl–Cl bond length,  $R_{\text{eq}}^{\text{VB-3}}$ , is shorter than the covalent minimum ( $R_{\text{cov}}$  in Fig. 2).

**Table 4** Kinetic and potential energies of the covalent states ( $\Psi_{\text{cov}}$ ) and ground states ( $\Psi_{\text{VB-3}}$ ) at the  $R_{\text{VB-3}}$  distance, that exactly satisfies the virial relationship (eqn (10)) in the ground state. Calculations at the  $\pi$ -SD-BOVB level, all energies in hartrees

|                         | Cl <sub>2</sub> ( $R_{\text{VB-3}}$ ) | F <sub>2</sub> ( $R_{\text{VB-3}}$ ) |
|-------------------------|---------------------------------------|--------------------------------------|
| $T(\Psi_{\text{cov}})$  | 919.04800                             | 198.93680                            |
| $V(\Psi_{\text{cov}})$  | –1837.93482                           | –397.60755                           |
| $E(\Psi_{\text{cov}})$  | –918.88683                            | –198.67075                           |
| $T(\Psi_{\text{VB-3}})$ | 918.93306                             | 198.77617                            |
| $V(\Psi_{\text{VB-3}})$ | –1837.86621                           | –397.55236                           |
| $E(\Psi_{\text{VB-3}})$ | –918.93315                            | –198.77618                           |

Allowing the covalent–ionic mixing to take place ( $\Psi_{\text{cov}} \rightarrow \Psi_{\text{VB-3}}$ ) will lead to some readjustment of  $T$  and  $V$ . For the virial ratio to be restored by ionic admixture, it is necessary that the following condition be fulfilled:

$$\Delta V < -2\Delta T \quad (11)$$

As can be seen in Table 4, this condition is largely satisfied in the  $\text{Cl}_2$  case, since inclusion of ionic structures causes a large drop of the kinetic energy ( $\Delta T = -0.115$  au) whereas the potential energy is increased by only 0.069 au.

In the  $\text{F}_2$  case, the LPBWE is so large that there is not even a covalent minimum: at any distance, the repulsive effect prevents the covalent interaction to be stabilizing relative to the separate atoms. At the  $R_{\text{eq}}^{\text{VB-3}}$  distance, the covalent wavefunction exhibits, as in the preceding case, a large excess of kinetic energy ( $2T + V = +0.266$  au). Once again, the effect of the covalent–ionic mixing is mainly to lower the kinetic energy ( $\Delta T = -0.161$  au), while raising the potential energy to a lesser extent ( $\Delta V = +0.055$  au). Thus, in both  $\text{Cl}_2$  and  $\text{F}_2$ , the effect of the covalent–ionic mixing is to lower the ratio  $T/-V$ , thus counterbalancing the excess of kinetic energy induced by the LPBWE.

## VI Conclusion

Valence bond (VB) theory and electron-localization function (ELF) calculations of various single bonds have demonstrated, in some previous work,<sup>7,8</sup> that alongside the two classical bond families of covalent and ionic bonds, there exists a class of charge-shift bonds (CS-bonds), which involves homopolar as well as heteropolar bonds, and in which the fluctuation of the electron pair density plays a dominant role. In the present work, the nature of CS-bonding and its fundamental mechanisms are analyzed in detail by means of a VB study of some typical homonuclear bonds, ranging from classically covalent to fully charge-shift bonds.

While classical homonuclear bonds (*e.g.*  $\text{H}_2$ ,  $\text{C}_2\text{H}_6$ ...) are mainly covalent in nature and display a purely covalent dissociation energy curve that is close to the exact dissociation curve of the ground state, CS-bonding is characterized by the following features: (i) a covalent dissociation curve with a shallow minimum situated at long interatomic distance, or even a fully repulsive covalent curve; (ii) a large covalent–ionic resonance energy  $\text{RE}_{\text{CS}}$  that is responsible for the major part, or even for the totality, of the bonding energy.

Atoms (fragments) that are prone to CS-bonding are compact electronegative and/or lone-pair-rich species, albeit with moderate electronegativity; as such, CS bonding increases as the bonded atoms are taken from left to right and from bottom to top of the periodic table, and peaks at fluorine. In this series, the weakening effect of the adjacent lone pairs increases, while at the same time the reduced resonance integral, that couples the covalent and ionic forms, increases. As a consequence, the weakening of the covalent interaction is gradually compensated by a strengthening of CS-bonding.

CS-bonding is shown to be a fundamental mechanism that is necessary to adjust the kinetic and potential energy to the virial ratio at equilibrium. For classical bonds that are not weakened too much by lone pair repulsions, covalent bonding induces a deficit of kinetic energy that is efficiently counterbalanced by shrinkage of the orbitals involved in the bond. On the other hand, for bonds bearing several adjacent lone pairs, some extra Pauli repulsion induces an excess of kinetic energy. In such a case, orbital shrinkage ceases to be an efficient mechanism for restoration of the virial ratio, and it must be relayed by another mechanism which is the addition of ionic structures. This latter mechanism has the effect of lowering the kinetic energy while raising the potential energy to a lesser extent. Thus, the orbital shrinking mechanism gradually loses some importance as one moves from left to right or from bottom to top of the periodic table, while CS-bonding gains some importance at the same time.

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