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SPECIAL ISSUE IN HONOUR OF ANDREAS SAVIN

Two theorems about C_2 and some more

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ABSTRACT

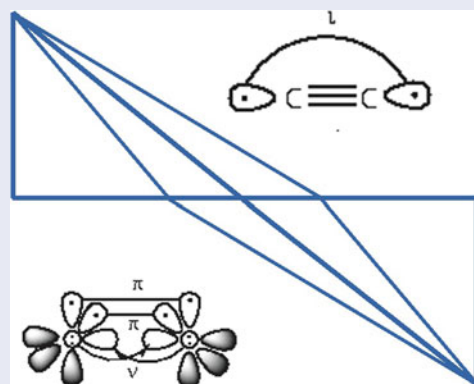
The story of C_2 continues to fascinate chemists spinning around a possibility of quadruple bonds for p -elements and discussing a wealth of options for the nature of an unconventional fourth bond. This led to lively discussions about the ways of counting or measuring bonds, and the interplay between the bond strength (energy), its length, and rigidity/stiffness (elasticity). Even old concerns about the possibility of theorems in chemistry and thus of the place of chemistry among 'true' sciences had been revived. We show that under some mild conditions certain *exact* statements (lemmas and theorems) about the C_2 molecule can be relatively easily proven which, if not resolves the controversy entirely, at least provides some theoretical reference points to the discussion. Some more general consequences from this experience are discussed as well.

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C_2 ; chemistry theorems; bonding measures; analytical models



1. Introduction

The story of C_2 , which, as we learned recently [1], may be dated as long back to Wollaston [2] and Faraday [3], although, the phenomenon itself had been observed by our noble ancestors yet in caverns, ignited a vivid discussion. Attempts to understand bonding in the C_2 molecule had been undertaken by numerous authors using 'electronic computers' [4]. Each of these numerical studies provided valuable information about its possible electronic structure, but no uniform general picture arose so far. The most recent results are largely summarised in [5] to be complemented by [6,7] (depicted in Figure 1). The variety of possible types of the C_2 ground state fits into an alternative between 'tetravalent' and 'divalent' carbons. The 'tetravalent' alternative suggests a series of possible structures for the C_2 molecule involving normal σ - and inverted (ι -) bonds or no forth bond at all

(Structure 5) combined either with two π -bonds (Structures 1 and 5) or with three 'inwards' banana (β -) bonds (originally proposed by Bernstein [8]) complemented by the inverted bond denoted as ($\iota\beta\beta$) or with three 'outwards' (β° -) ones (Scheme 2 in Figure 1) complemented by the usual σ -bond ($\sigma\beta\beta$).¹ Within the class of 'divalent' solutions, a couple of (dative/donor-acceptor) v -bonds proposed in Ref. [9] and eventually established for C_2 in Ref. [10] is here referred to as the ($v\pi\pi$)-structure. In order to contribute to the general picture, we derive in a feasible approximation analytical energy estimates for variously bonded states of C_2 and by this provide a kind of coordinate system allowing to position the numerical results obtained by other researchers.

Another piece of evidence used in the discussion evolving around C_2 is based on some vague 'rules' relating bond length, strength, and rigidity to its more or less

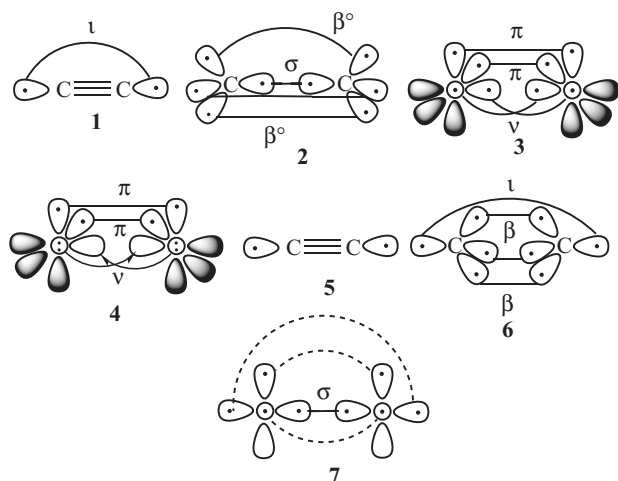


Figure 1. Cartoons, describing bonds between two tetravalent (1–3, 6) and divalent (4) carbon atoms, and the diradical featuring triple bond (5). Structures 1–5 repeat those of Ref. [5]. The circles in 3 and 4 are the 2s orbitals. Structure 6 is a quadruply bound one with the banana-like hybrids featuring more logical orientation of the latter than Structure 2. Structure 7 is one of Ref. [7] featuring a σ -bond accompanied by the antiferromagnetically coupled spin-quartets of triples of electrons on either side of the molecule.

deliberately defined ‘order’ or ‘multiplicity’. These rules are used as a part of argumentation in favour of that or another model of electronic structure of C_2 . Thus, we consider the theoretical basis possibly underlying these rules and check whether the conditions (largely tacitly assumed, but never explicitly formulated) required for their validity are fulfilled. Finally, we address the bonding measures like the Coulson bond orders [11] and Mayer bond order indices [12] and discuss their utility in relation to the problem of establishing the multiplicity of the bond in C_2 .

2. Preliminaries and setting

Our current quantum chemistry largely became an art of numerical computation. Some prominent authors even urge their students to use whatever available program before applying any other means [1]. Thus, the current studies of C_2 are all based on various numerical packages. The fundamental assumption employed by the majority of them (see e.g. [1,5,7]) was that the many electronic wave function of C_2 is adequately represented by the Generalized Valence Bond (GVB) approximation [13]. The approximation of antisymmetrised product of strictly local geminals (APSLG) [14] proposed recently is a close relative of GVB. Within it, the electronic wave function of the molecule is represented as an antisymmetrised

product

$$|\Phi\rangle = \prod_m g_m^+ |0\rangle. \quad (2.1)$$

of *geminals* originally proposed by Fock and then used many times by various authors [15].

$$g_m^+ = u_m r_{m\alpha}^+ r_{m\beta}^+ + v_m l_{m\alpha}^+ l_{m\beta}^+ + w_m (r_{m\alpha}^+ l_{m\beta}^+ + l_{m\alpha}^+ r_{m\beta}^+) \quad (2.2)$$

($r_{m\sigma}^+$, $l_{m\sigma}^+$ are the operators creating an electron with spin projection σ in the respective orbitals; $r_{m\sigma}$, $l_{m\sigma}$ are respective hermitean annihilation operators) built on hybrid orbitals (HOs) r_m and l_m pertaining to the ‘right’ and ‘left’ ends of the m th bond with the amplitudes of two-electron configurations subject to the normalisation condition:

$$u_m^2 + v_m^2 + 2w_m^2 = 1. \quad (2.3)$$

A remarkable feature of the APSLG approach is that the forms and orientations of the involved atomic HOs are determined variationally together with the amplitudes Equation (2.2) by minimising the total energy. Other remarkable features of the APSLG theory are (1) the *transferability* of the main characteristics of the molecular electronic structure expressed by the elements of the reduced density matrices of the k th order (k -RDMs, $k = 1, 2$) [16] and (2) the explicit parameterisation of the manifold of the atomic HOs by that of the $SO(4)$ group of matrices [17] conserves orthonormalisation of the involved orbitals. This allowed us recently to formulate numerically extremely efficient quantum chemically/mechanically substantiated procedures for calculating molecular energies dubbed as deductive molecular mechanics (DMM) in their semiempirical [18,19] and *ab initio* molecular mechanics (AIMM) [20] in its *ab initio* versions. Within these approximations, the energy of a molecule is represented as a sum of resonance energies of its (bond) geminals each supplemented by the energy of electron–electron repulsion classified into one-centre intrageminal, one-centre intergeminal, two-centre intrageminal, and two-centre total Coulomb interaction and one-centre core attraction terms. These contributions can be explicitly written in the APSLG/DMM/AIMM context and are given in Appendix A.2.

Although the expressions for the energy components, Appendix A.2, look rather confusing for the general case, they significantly simplify for a symmetric bond in a diatomic molecule due to the simple explicit form of the involved elements of k -RDMs. For a symmetric geminal,

we have

$$P_m = \frac{4t_m}{\sqrt{16t_m^2 + \Delta_m^2}},$$

$$\Gamma_m^{\lambda\lambda'} = \frac{1}{2} \left(1 - \lambda\lambda' \frac{\Delta_m}{\sqrt{16t_m^2 + \Delta_m^2}} \right), \quad (2.4)$$

where P_m is the off-diagonal matrix element of the one-electron density between the HOs involved in the formation of the m th geminal, with the diagonal one-electronic densities equal to unity due to symmetry; $\Gamma_m^{tt'}$ are the two-electron densities with $\lambda, \lambda' = \pm 1$ referring to the left and right ends of the m th bond, and $\Delta_m = g_m - \gamma_m$ being the difference of the Coulomb interaction of electrons occupying the same HO on either ends of the bond (g_m) and that for electrons residing on its different ends (γ_m).

Now we come to the first important statement. Let us consider a symmetric geminal and collect individual terms contributing to its energy (those referring to a respective value of m in Equations (A.8)–(A.11)). Then, we obtain

$$E_m = g_m(\Gamma_m^{rr} + \Gamma_m^{ll}) - \frac{8t_m^2}{\sqrt{16t_m^2 + \Delta_m^2}} + \gamma_m[2\Gamma_m^{rl} - 1]. \quad (2.5)$$

The expression Equation (2.5) involves two most popular bonding measures: the already mentioned Coulson bond order P_m being the multiplier at the resonance integral β_m and (minus a half of) the Mayer bond index [12]

$$B_m = 1 - \frac{\Delta_m}{\sqrt{16t_m^2 + \Delta_m^2}} \quad (2.6)$$

entering as the multiplier at the two-centre repulsion integral γ_m . Using the relation between the elements of the 2-RDM Equation (A.5), we arrive at

$$E_m = \frac{1}{2} \left[\Delta_m - \sqrt{16t_m^2 + \Delta_m^2} \right] \quad (2.7)$$

corresponding to the optimal values of the amplitudes u_m, v_m, w_m calculated with account of a good portion of correlation (the ‘left-right’ one). It now depends only on the hybridisation (sp -composition and orientation) of the involved HO’s.

This consideration brings us to a bifurcation point where we have to make a choice of a route of subsequent reasoning. Our goal is to provide a general framework for discussion and comparison of the bonding configurations. Therefore, we prefer phenomenological Hamiltonians allowing for analytical description of the electronic structure parameters. It has been established [17] that the dependence of the electron–electron interactions of the

hybridisation is relatively weak, i.e. that the amplitude of its possible variation is much smaller than the quantity itself. Thus, for the ‘sake of simplicity’ [21], we accept an approximate model in which the Coulomb interactions are all independent on the hybridisation. This is possible in the ‘CNDO’-type models where all the intraatomic Slater–Condon parameters of the Coulomb type are set to the same value

$$F_0(ss) = F_0(sp) = F_0(pp) = g$$

and all Slater–Condon parameters of the ‘exchange’ type are vanishing:

$$G_1(sp) = F_2(pp) = 0.$$

Under these assumptions, we arrive to the model with two Coulomb interaction parameters (the one-centre g and the two-centre γ) which will be studied hereinafter. The formulated CNDO-like Hamiltonian is mathematically tractable and as it will be seen, retains the underlying physics. It comprises intra- and interatomic, one- and two-electron contributions. First, one-centre attraction is

$$\sum_{l \in L} U_{ll} \sum_{\sigma} l_{\sigma}^{+} l_{\sigma} + \sum_{r \in R} U_{rr} \sum_{\sigma} r_{\sigma}^{+} r_{\sigma}, \quad (2.8)$$

where L and R are the ‘left’ and ‘right’ C atoms of C_2 . The intraatomic electron repulsion is taken as

$$\frac{g}{2} \left(\sum_{k, l \in L} \sum_{\sigma \tau} k_{\sigma}^{+} l_{\tau}^{+} l_{\tau} k_{\sigma} + \sum_{p, r \in R} \sum_{\sigma \tau} p_{\sigma}^{+} r_{\tau}^{+} r_{\tau} p_{\sigma} \right). \quad (2.9)$$

The resonance contribution describes charge transfer between the atoms:

$$- \sum_{l \in L} \sum_{r \in R} t_{lr} \sum_{\sigma} (l_{\sigma}^{+} r_{\sigma} + r_{\sigma}^{+} l_{\sigma}). \quad (2.10)$$

Finally, the Coulomb repulsion between electrons on different C atoms is

$$\gamma \sum_{l \in L} \left(\sum_{\sigma} l_{\sigma}^{+} l_{\sigma} - 4 \right) \sum_{r \in R} \left(\sum_{\tau} r_{\tau}^{+} r_{\tau} - 4 \right) \quad (2.11)$$

By this, we describe the approximations used hereinafter. Specific procedures used to obtain the values and interatomic dependences of the matrix elements $U_{\lambda\lambda}, g, \gamma, t_{rl}$ are described when actually used.

3. Alternative bond structures

The APSLG/DMM/AIMM methodologies proposed in Refs [16,17,20] allow us to directly write down the energies of the C_2 molecule which in the present context is going to be a very likely cartoon of the numerical results obtained by the GVB. The energies for the patterns under discussion are

$$\begin{aligned} E(\iota\sigma\pi\pi) &= 2E_\pi + E_\sigma + E_\iota + 2E_{\pi\sigma} + 2E_{\pi\iota} \\ &\quad + E_{\sigma\iota} + E_{\pi\pi} + E_{\text{attr}} + E_{CC} \\ E(\iota\beta\beta\beta) &= 3E_\beta + E_\iota + 3E_{\beta\beta} + 3E_{\beta\iota} + E_{\text{attr}} + E_{CC} \\ E(\sigma\beta\beta\beta) &= 3E_{\beta^\circ} + E_\sigma + 3E_{\beta^\circ\beta^\circ} + 3E_{\beta^\circ\sigma} + E_{\text{attr}} + E_{CC} \\ E(\nu\nu\pi\pi) &= 2E_\pi + 2E_\nu + E_{\pi\pi} + E_{\nu\nu} + 4E_{\pi\nu} \\ &\quad + E_{\text{attr}} + E_{CC}, \end{aligned} \quad (3.1)$$

where the terms with one Greek subscript refer to those of the energies of individual geminals given by Equation (2.7), those with two Greek subscripts refer to the interactions between the corresponding geminals, E_{attr} is the core attraction energy, and the last term E_{CC} is the Coulomb interaction energy for the charge distributions centred on two carbon atoms. The lemmas of Appendix 2 lead us to accepting the general ‘CNDO-like paradigm’. Within that latter, all the interaction terms in Equation (3.1) are hybridisation independent. The core attraction term is as well hybridisation independent now for structures formed by symmetric geminals, that is, for all listed in Equation (3.1) except the $(\nu\nu\pi\pi)$ -one. Thus, we arrive to another *Pythagorean*.²

Lemma 3.1: *If the Coulomb interaction matrix elements are hybridisation independent, then for the states of C_2 built of symmetric geminals the only hybridisation-dependent contributions to the energy are the minus halves of $\sqrt{16t_m^2 + \Delta^2}$, that is, minus halves of hypotenuses of the rectangular triangles with catheta $|4t_m|$ and $|\Delta|$.*

3.1. Banana non-existence theorem

We consider first the symmetric structures (first three rows of Equation (3.1)). For the symmetric geminals, describing either the σ -, π -, and ι -components or the β - or β° -components of the multiple bond, the energy contributions of individual geminals have the form Equation (2.7). The structures of the σ - and ι -geminals are tightly related through the orthogonality of the HOs centred on the respective C atoms. Due to symmetry, the HOs in the σ - and ι -geminals have complementary

weights and phases are set according to

$$\begin{aligned} (s_\sigma^L, z_\sigma^L) &= \frac{1}{\sqrt{2}} (\sqrt{1+\varepsilon}, \sqrt{1-\varepsilon}); \\ (s_\sigma^R, z_\sigma^R) &= \frac{1}{\sqrt{2}} (\sqrt{1+\varepsilon}, -\sqrt{1-\varepsilon}) \\ (s_\iota^L, z_\iota^L) &= \frac{1}{\sqrt{2}} (\sqrt{1-\varepsilon}, -\sqrt{1+\varepsilon}); \\ (s_\iota^R, z_\iota^R) &= \frac{1}{\sqrt{2}} (\sqrt{1-\varepsilon}, \sqrt{1+\varepsilon}), \end{aligned} \quad (3.2)$$

where a small parameter ε describes the deviation of the hybridisation from the classical sp -structure. The above phases correspond to an increase of the overlap between the sp -hybrids pointing ‘inwards’ the C-C bond. For the σ -geminal, the resonance integral thus becomes a combination of individual inter-AO components

$$t_\sigma = \frac{1}{2} \left[(t_{\sigma\sigma} - t_{\zeta\zeta}) + 2t_{\zeta\sigma}\sqrt{1-\varepsilon^2} + \varepsilon(t_{\sigma\sigma} + t_{\zeta\zeta}) \right] \quad (3.3)$$

(the individual inter-AO resonance components $t_{\mu\nu}$ are selected so that the first subscript refers to the AO on the left end of the bond and the second to the right one with the molecular z -axis directed from left to right. Thus, $t_{\sigma\sigma}, t_{\zeta\sigma} > 0$ and $t_{\zeta\zeta}, t_{\sigma\zeta} = -t_{\zeta\sigma} < 0$.) For the inverted (ι -)bond, the resonance integral

$$t_\iota = \frac{1}{2} \left[(t_{\sigma\sigma} - t_{\zeta\zeta}) - 2t_{\zeta\sigma}\sqrt{1-\varepsilon^2} - \varepsilon(t_{\sigma\sigma} + t_{\zeta\zeta}) \right] \quad (3.4)$$

is somehow damped as compared to the σ -one, but is not intrinsically small.

The resonance integrals Equations (3.3) and (3.4) enter the estimate for the energy of the $(\iota\sigma\pi\pi)$ -model. It is easiest to compare it with the $(\iota\beta\beta\beta)$ - and $(\sigma\beta\beta\beta)$ models featuring respectively inverted and sigma bonds. Under the assumption of equivalence of three involved banana bonds, the form and orientation of the HOs assigned to them are uniquely determined by the same parameter ε through the HO’s orthonormality. Specifically, one of the pairs of the inward banana hybrids on the two ends can be selected as

$$\begin{aligned} (s_\beta^L, x_\beta^L, y_\beta^L, z_\beta^L) &= \left(\sqrt{\frac{1+\varepsilon}{6}}, \sqrt{\frac{2}{3}}, 0, \sqrt{\frac{1-\varepsilon}{6}} \right); \\ (s_\beta^R, x_\beta^R, y_\beta^R, z_\beta^R) &= \left(\sqrt{\frac{1+\varepsilon}{6}}, \sqrt{\frac{2}{3}}, 0, -\sqrt{\frac{1-\varepsilon}{6}} \right) \end{aligned} \quad (3.5)$$

with other two obtained from these by rotating by 120° around the molecular axis. The resonance integral for

each of the three inward banana bonds reads:

$$t_\beta = \frac{2t_\pi + t_\sigma}{3}. \quad (3.6)$$

The geminal resonance energy E_m Equation (2.7) is a concave function of t_m since its second derivative with respect to t_m is negative:

$$E_m'' = -\frac{8\Delta^2}{\sqrt{(16t_m^2 + \Delta^2)^3}} < 0. \quad (3.7)$$

Thus, the graph of E_m always lies above each chord joining whatever two points of this graph, and the value of this function in any segment of argument values is always larger (negative and smaller by absolute value) than the weighted arithmetic mean of its values on the ends of the segment:

$$3E_\beta \geq 2E_\pi + E_\sigma.$$

The equality is reached in the self-consistent field (SCF) approximation for each geminal (equivalent to the limit $\Delta \rightarrow 0$). In this case, the two bonding structures are identical because one of them is produced from the other by an orthogonal transformation within the set of the occupied MOs. Thus, for each value of the hybridisation parameter ε , the structure with one inverted and three inward banana bonds has a higher energy than that with the inverted and one σ - and two π -bonds. The energy differences between the two bonding patterns appear only from (relatively weak) electronic correlation, characteristic for the strongly bonded π - and σ -geminals.

Acting analogously, we obtain the value for the resonance integral characteristic for the outward banana bonds:

$$t_{\beta^\circ} = \frac{2t_\pi + t_l}{3} \quad (3.8)$$

and for the same reason, we obtain

$$3E_{\beta^\circ} \geq 2E_\pi + E_l$$

and conclude that the structure with the outward banana bonds has a higher energy than that with two π -bonds and a ι -bond. Combining these two results, we arrive at

$$\begin{aligned} 3E_\beta + E_l &\geq 2E_\pi + E_l + E_\sigma \\ 3E_{\beta^\circ} + E_\sigma &\geq 2E_\pi + E_l + E_\sigma, \end{aligned}$$

which allows us to formulate the following sad³

Theorem 3.1: Structures with three banana bonds either inwards or outwards do not represent a ground state of C_2 . Precising the above theorem can be derived (Appendix 3).

Corollary 3.1: The amount of the gain of the $(\sigma\pi\pi)$ -structure relative to that with the triple inward banana bond – the difference of the energies of the $(\sigma\pi\pi)$ - and $(\beta\beta\beta)$ -structures calculated in the APLSLG approximation – is

$$-\frac{\Delta^2 (t_\pi - t_\sigma)^2}{16t_\pi t_\sigma (t_\sigma + 2t_\pi)} < 0.$$

This relation holds irrespective to the composition of the σ -HOs dependent on the above parameter ε . Our calculations, both semiempirical and *ab initio* in different basis sets performed by package [15](n) show that the structure with banana bonds is always several kcal mol⁻¹ higher in energy than the $\sigma\pi$ -structure. Similar expression with an obvious replacement $t_\sigma \rightarrow t_l$ gives the corresponding comparison in case $t_l/\Delta \gg 1$.

3.2. Hybridisation in the $(\iota\sigma\pi\pi)$ -structure

Based on the conclusion of the previous subsection, we do not further consider the structures either with inward or outward banana bonds, but rather study the $(\iota\sigma\pi\pi)$ -model of C_2 having the lowest energy among the structures with symmetric geminals (that is among the ‘tetra-elant’ ones) in more details. The simplest move is to obtain the equation for the optimal value of the hybridisation parameter ε which we do immediately:

$$-\frac{16t_\sigma t'_\sigma}{\sqrt{16t_\sigma^2 + \Delta^2}} - \frac{16t_l t'_l}{\sqrt{16t_l^2 + \Delta^2}} = 0$$

(here the prime stands for the derivative with respect to ε). Comparing Equations (3.3) and (3.4), we notice that

$$t'_\sigma = -t'_l = t'$$

so that the extremal values of the energy are given by either of the conditions:

$$t' = 0 \quad (a)$$

$$\frac{t_\sigma}{\sqrt{16t_\sigma^2 + \Delta^2}} = \frac{t_l}{\sqrt{16t_l^2 + \Delta^2}}. \quad (b)$$

Resolving the condition (b) yields a result:

$$|t_\sigma| = |t_l| = \frac{1}{2} |t_{\sigma\sigma} - t_{\zeta\zeta}| \quad (3.9)$$

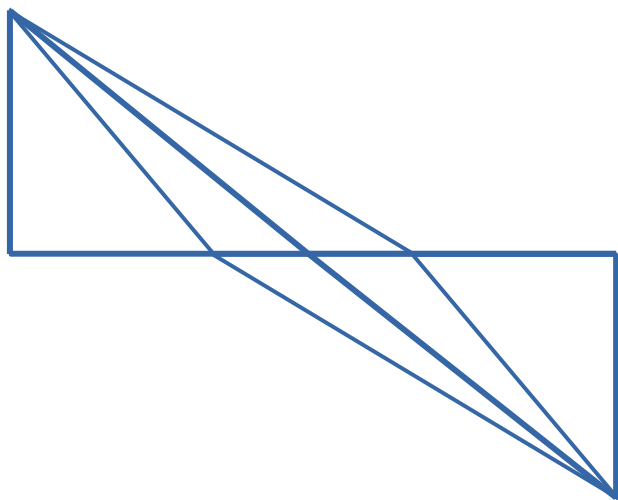


Figure 2. Look!

inconsistent with the idea of σ - and ι -bonds of a different strength. The condition (a) yields another equilibrium value of the hybridisation parameter:

$$\varepsilon_*^2 = \frac{(t_{\sigma\sigma} + t_{\zeta\zeta})^2}{4t_{\zeta\sigma}^2 + (t_{\sigma\sigma} + t_{\zeta\zeta})^2} \quad (3.10)$$

and corresponding equilibrium resonance integrals

$$\begin{aligned} t_\sigma^* &= \frac{1}{2} \left[(t_{\sigma\sigma} - t_{\zeta\zeta}) + \sqrt{4t_{\zeta\sigma}^2 + (t_{\sigma\sigma} + t_{\zeta\zeta})^2} \right] \\ t_\iota^* &= \frac{1}{2} \left[(t_{\sigma\sigma} - t_{\zeta\zeta}) - \sqrt{4t_{\zeta\sigma}^2 + (t_{\sigma\sigma} + t_{\zeta\zeta})^2} \right] \end{aligned} \quad (3.11)$$

relevant for the respective geminals. The resonance integrals Equation (3.9) are thus effectively half sums of those given by Equation (3.11).

Using again the concavity of the geminal resonance energy we arrive to the following.

Lemma 3.2: *The structure with two different σ - and ι -bond/geminals with the resonance integrals given by Equation (3.11) has lower energy than that with two equal ones with the resonance integrals Equation (3.9),*

which can be also proven without referring to the concavity, but purely geometrically, since a segmental line formed by two hypotenuses of the triangles having a common cathetus $|\Delta|$ and other catheti $|4t_\sigma^*|$ and $|4t_\iota^*|$ is longer than twice a hypotenuse of the triangle with the catheti Δ and the halfsum of $4t_\sigma^*$ and $4t_\iota^*$ equivalent to the solution with two equivalent bonds (Figure 2).

Now we can write an important result, namely, the explicit expression for the energy of the C_2 molecule in

the $(\iota\sigma\pi\pi)$ -state. It reads:

$$E_0 + 2\Delta - \frac{1}{2} \left[2\sqrt{16t_\pi^{*2} + \Delta^2} + \sqrt{16t_\sigma^{*2} + \Delta^2} + \sqrt{16t_\iota^{*2} + \Delta^2} \right], \quad (3.12)$$

where $E_0 = 2U_s + 6U_p + 12g$. Obviously, the presence of the ι -bond/geminal always produces an energy gain so that Structure 1 of Figure 1 is always lower in energy than Structure 5. Within the present setting, there is no option for any energy gain for Structure 5 over Structure 1 due to whatever rehybridisation of the HO's involved in the σ -geminal in the absence of the ι -geminal since the value of t_σ^* given by Equation (3.11) is already the maximum with respect to the hybridisation parameter ε .⁴ We notice here, that Structure 5 is a better reference for discussion than the acetylene molecule used previously by other authors, since one can easily obtain its energy by simply dropping the square root with t_ι^* from Equation (3.12). A theory of acetylene similar to the one developed here is also possible, but we postpone its development and application to an analysis of C_2 and other problems for a further occasion.

3.3. Structure of C_2 with asymmetric geminals

The explicit energy of the $(\iota\sigma\pi\pi)$ -structure Equation (3.12) must now be compared to the most popular alternative to the structure with the inverted bond – one with two ν -bonds [10] (Structure 4 of Figure 1). This structure as well contains two π -bonds/geminals supplied by two two-electron groups built upon HO's of the σ -symmetry. In variance with the $(\iota\sigma)$ -structure, where the geminals were formed by the HO's with the same weight of the s -function on the right and the left ends of the bond in the ν -bonds/geminals an HO with a larger s -weight on, say, the left end is involved in the geminal formation with the HO of the smaller s -weight on the right one and *vice versa*. The structure with two ν -geminals is following [5] depicted in Figure 1 twice; Structures 3 and 4 both represent one with two asymmetric geminals. The difference between them is the different contribution of the individual terms of Equation (2.2) in that which is dubbed as a ν - and donor/acceptor geminal. In the former case, it is dominated by the homoeopolar ('Heitler-London') configuration entering with the w -amplitude in the latter by a suitable 'ionic' configuration entering with either u - or ν -amplitude.

We start the analysis of the $(\nu\nu)$ -structure by noticing that the explicit forms of the involved HO's are the same as prescribed by Equation (3.2), but taken in a different

combination:

$$\begin{aligned}(s_v^L, z_v^L) &= \frac{1}{\sqrt{2}} (\sqrt{1+\varepsilon}, \sqrt{1-\varepsilon}); \\ (s_v^R, z_v^R) &= -\frac{1}{\sqrt{2}} (\sqrt{1-\varepsilon}, -\sqrt{1+\varepsilon}) \quad (3.13) \\ (s_{v'}^L, z_{v'}^L) &= \frac{1}{\sqrt{2}} (\sqrt{1-\varepsilon}, -\sqrt{1+\varepsilon}); \\ (s_{v'}^R, z_{v'}^R) &= \frac{1}{\sqrt{2}} (\sqrt{1+\varepsilon}, \sqrt{1-\varepsilon}),\end{aligned}$$

where we additionally changed the overall sign of the ‘acceptor’ (smaller s -weight) HO’s.⁵ This yields the following resonance integral for the ν -bond:

$$t_v = \frac{1}{2} \left[2\varepsilon t_{\zeta\sigma} - (t_{\sigma\sigma} + t_{\zeta\zeta}) \sqrt{1-\varepsilon^2} \right]$$

Like the σ - and ι -HOs, the ν -HOs can be parameterised by a single variable. However, the variable ε suitable in the vicinity of the ‘classical’ sp -hybridisation in the $(\sigma\iota)$ -case is not convenient for the ν -hybrids. Replacing it by

$$\begin{aligned}(s_v^L, x_v^L) &= (\cos \varphi, -\sin \varphi); \quad (s_v^R, x_v^R) = (\sin \varphi, -\cos \varphi) \\ (s_{v'}^L, x_{v'}^L) &= (\sin \varphi, \cos \varphi); \quad (s_{v'}^R, x_{v'}^R) = (\cos \varphi, \sin \varphi)\end{aligned} \quad (3.14)$$

yields the resonance integral for the ν -geminal as

$$t_v = \frac{1}{2} [2t_{\zeta\sigma} \cos 2\varphi - (t_{\sigma\sigma} + t_{\zeta\zeta}) \sin 2\varphi]. \quad (3.15)$$

The vanishing φ parameter exactly corresponds to the HOs depicted in Structures 3 and 4 (Figure 1): pure s - and p -AOs. Structure 4 eventually covers the double bond structure $|C=C|$ between *purely* divalent carbon atoms provided the donor–acceptor/charge-shift ν -bonds are completely turned off.

After defining the carrier subspaces for the ν -geminals and the explicit form of the resonance integral, we need to derive the energy contributions for the $(\nu\nu\pi\pi)$ -structure. Unfortunately, in the case of asymmetric geminals such simple transferable estimates which existed and were helpful for the symmetric ones are not available. A simple description of the ν -bonds is available at the SCF level as that of a doubly occupied MO $(\cos \theta, \sin \theta)$, which yields the amplitudes:

$$(u, v, w) = (\cos^2 \theta, \sin^2 \theta, \sin \theta \cos \theta). \quad (3.16)$$

The strong asymmetry of ν -geminals (ultimately, their donor–acceptor character) means that θ is expected to be small. The correlated treatment of the geminals implies an admixture of the electron configuration formed by doubly occupied antibonding orbital $(-\sin \theta, \cos \theta)$ yielding

the geminal amplitudes as

$$\begin{aligned}(u, v, w) &= \cos \psi (\cos^2 \theta, \sin^2 \theta, \sin \theta \cos \theta) \\ &\quad - \sin \psi (\sin^2 \theta, \cos^2 \theta, -\sin \theta \cos \theta).\end{aligned} \quad (3.17)$$

With these expressions at hand, the total energy of the bonding $(\nu\nu\pi\pi)$ -structure of C_2 can be easily evaluated:

$$\begin{aligned}E &= E_0 + 2E_\pi - 2U \cos 2\varphi \cos 2\theta \cos 2\psi - \\ &\quad - 2t_v \sin 2\theta \cos 2\psi \\ &\quad + \Delta (\sin^2 2\theta - \sin^2 2\theta \sin 2\psi + 2 \cos^2 2\theta \sin^2 2\psi).\end{aligned} \quad (3.18)$$

This expression does not contain γ explicitly; it nicely combines with the one-centre repulsion g and forms the parameter Δ . Next, it can be recognised that Equation (3.18) is the sum of the energy of two sp^3 hybridised atoms E_0 , that of two π -geminals, the hybridisation-dependent attraction energies of two ν -geminals and the corresponding bonding terms: the resonance integral t_v , times Coulson bond order and Δ times the bond order index for two asymmetric geminals. This nice form, actually repeating that available for the symmetric geminal, appears despite the asymmetry of the individual ν -components: the C_2 molecule itself remains symmetric.

For the infinite separation ($R \rightarrow \infty$), all interaction terms disappear and the energy of the $(\nu\nu\pi\pi)$ -structure is by $2U$ lower than that of the $(\iota\sigma\pi\pi)$ -one. The question is thus whether it is possible that the minimum of the energy profile, corresponding to the latter structure nevertheless lies lower than the former one. Apparently, the opposite is true for large values of U . Thus, we need an energy estimate for the limit of small U ’s. The quantity Δ , by definition, is positive and increases, and flows from zero to g with the interatomic separation. Since we are now interested in comparing the energies of the $(\nu\nu\pi\pi)$ - and $(\iota\sigma\pi\pi)$ -structures at short distances, the model needs to be considered in the regime of small Δ . In this case, the ψ -dependent part of the energy is dominated by the terms proportional to $\cos 2\psi$ with a negative factor. Thus, the optimal value of ψ is zero, *i.e.* the ν -geminals are weakly correlated. This result is confirmed by both semiempirical and *ab initio* APSLG calculations. Thus, we drop ψ from the further consideration and consider the SCF model for the ν -geminal.

Optimising Equation (3.18) with $\psi = 0$ with respect to θ gives the equilibrium condition:

$$(U \cos 2\varphi + \Delta \cos 2\theta) \sin 2\theta - 2t_v \cos 2\theta = 0,$$

which we resolve neglecting the higher powers of $\sin 2\theta$ in the expansion for $\cos 2\theta$ in the term proportional to

the small Δ . This yields:

$$\tan 2\theta = \frac{2t_v}{U^* + \Delta},$$

where we introduced a shorthand notation $U^* = U \cos 2\varphi$. Inserting this result in Equation (3.18), we obtain

$$E = E_0 + 2E_\pi - \frac{2U^*(U^* + \Delta)}{\sqrt{4t_v^2 + (U^* + \Delta)^2}} - \frac{8t_v^2}{\sqrt{4t_v^2 + (U^* + \Delta)^2}} + \frac{4\Delta t_v^2}{4t_v^2 + (U^* + \Delta)^2},$$

which in the lowest order with respect to small $\frac{U^* + \Delta}{t_v}$ yields

$$\begin{aligned} E - (E_0 + 2E_\pi) &= -\frac{U^*(U^* + \Delta)}{2t_v} \\ &\quad - 4t_v + \frac{(U^* + \Delta)^2}{2t_v} + \Delta \\ &= -4t_v + \Delta + \frac{\Delta(U^* + \Delta)}{2t_v}. \end{aligned}$$

The difference of the energies of the $(\iota\sigma\pi\pi)$ - and $(\nu\nu\pi\pi)$ -structures thus has the form:

$$E(\iota\sigma\pi\pi) - E(\nu\nu\pi\pi) \approx E_\iota + E_\sigma + 4t_v - \Delta - \frac{\Delta(U^* + \Delta)}{2t_v}, \quad (3.19)$$

where the hybridisation-dependent contributions must be taken at their respective optimal values. The sign of this expression determines the ground-state bonding configuration of C_2 ; if it is negative, the $(\iota\sigma\pi\pi)$ -structure is the ground state. In the above expression, two halves of Δ entering E_σ and E_ι compensate the Δ term stemming from two, thus, expanding the square roots in E_ι and E_σ , we arrive at the following:

$$\begin{aligned} &-2|t_\sigma^*| - 2|t_\iota^*| + 4t_v - \frac{\Delta^2}{8|t_\sigma^*|} - \frac{\Delta^2}{8|t_\iota^*|} \\ &- \frac{\Delta(U^* + \Delta)}{2t_v} < 0 \end{aligned} \quad (3.20)$$

(the $\frac{\Delta}{|t_m^*|}$'s are assumed to be small). The following depends on the signs of the equilibrium resonance integrals t_σ^* and t_ι^* . The first of the two as defined by Equation (3.11) together with the sign agreements given after Equation (3.3) allows us to conclude that $t_\sigma^* > 0$. Then, for a positive t_ι^* , a somewhat stronger inequality conditioning the possibility of the $(\iota\sigma\pi\pi)$ -type of the ground

state reads

$$2t_v - (t_{\sigma\sigma} - t_{\zeta\zeta}) < 0.$$

This condition in fact guarantees that the true energy difference between the $(\iota\sigma\pi\pi)$ - and $(\nu\nu\pi\pi)$ -structures is twice the left side of the above inequality minus the correction of the second order in small parameters Δ and U^* . Optimising the zero-order energy of the $(\nu\nu\pi\pi)$ -structure with respect to the only available variable φ yields the optimal hybridisation parameter:

$$\tan 2\varphi^* = \frac{t_{\sigma\sigma} + t_{\zeta\zeta}}{2t_{\zeta\sigma}}$$

and the respective maximal accessible value of the ν -resonance integral

$$t_v^* = \frac{1}{2} \sqrt{4t_{\zeta\sigma}^2 + (t_{\sigma\sigma} + t_{\zeta\zeta})^2}.$$

Thus, with a good margin, the condition for the possibility of the $(\iota\sigma\pi\pi)$ -structure to be a ground state reads

$$(t_{\sigma\sigma} - t_{\zeta\zeta}) - \sqrt{4t_{\zeta\sigma}^2 + (t_{\sigma\sigma} + t_{\zeta\zeta})^2} > 0. \quad (3.21)$$

For the negative t_ι^* , the above estimates change since $|t_\iota^*| = -t_\iota^*$, so that

$$-2(t_\sigma^* - t_\iota^*) = -2\sqrt{4t_{\zeta\sigma}^2 + (t_{\sigma\sigma} + t_{\zeta\zeta})^2}$$

and the inequality Equation (3.20) in the zero order with respect to the small parameters Δ and U^* reads

$$2t_v - \sqrt{4t_{\zeta\sigma}^2 + (t_{\sigma\sigma} + t_{\zeta\zeta})^2} < 0.$$

However, the half of the square root has been shown just above to be the maximal accessible value of the resonance integral β_ν and thus the inequality written just above is satisfied. Only in this case, one can hope to find a value of U^* , such that the $(\iota\sigma)$ -structure (tetravalent carbon) still has chances to be the ground state of C_2 . Otherwise, the C_2 molecule is a combination of two divalent carbons. This is the second of announced theorems about C_2 .

Theorem 3.2: *If the resonance integrals between AOs at some interatomic separation satisfy the inequality Equation (3.21) the ground state of the $(\iota\sigma\pi\pi)$ -type (tetravalent carbons) is possible. If further, the resonance integral t_ι^* is negative, the energy difference between the mentioned*

structures in favour of the $(\iota\sigma\pi\pi)$ -structure is given by

$$-\frac{\Delta(U^* + \Delta)}{\sqrt{4t_{\zeta\sigma}^2 + (t_{\sigma\sigma} + t_{\zeta\zeta})^2}} - \frac{\Delta^2 \sqrt{4t_{\zeta\sigma}^2 + (t_{\sigma\sigma} + t_{\zeta\zeta})^2}}{8(t_{\zeta\sigma}^2 + t_{\sigma\sigma}t_{\zeta\zeta})}$$

in the limit of small U^* and Δ . Otherwise the ground state always belongs to the $(\nu\nu\pi\pi)$ -type (divalent carbons).

The formulated theorem requires some explanation. It actually states that under the joint condition that the promotion energy U^* and the difference of intraatomic and interatomic electron–electron interaction matrix elements Δ are small and additionally the resonance integral t_i^* for the ι -geminal changes its sign (i.e. as well may become small) the $(\iota\sigma\pi\pi)$ -structure may become the ground state. The theorem does not say at what geometry it happens rather imposes quite strict conditions (smallness of U , Δ , and t_i^*) on the model parameters to make the $(\iota\sigma\pi\pi)$ -structure the ground state. Otherwise the $(\nu\nu\pi\pi)$ -structure dubbed as donor–acceptor or charge-shift (see [9]) bond is the ground state as advocated in [10]. We shall address the geometry issues in the following section.

4. Consequences of the theorems. Bond strength, length, and rigidity in C_2

The experimental CC bond length in C_2 (1.243 Å) is well larger than that in C_2H_2 (1.208 Å). Also the force constant for the CC stretching mode is larger in C_2H_2 than in C_2 ([1,5,10] and references therein). These two facts are frequently presented as arguments against the quadruple bonding in C_2 . This argumentation is based on the so-called Badger rules [24–26] stating an existence of a correlation between length and rigidity/stiffness (elastic constant) of a bond. Also the bond-length/bond-order relations stating that bonds of higher multiplicity are shorter get involved [27]. In the previous section, we considered the two most popular pictures of the C_2 electronic structure and established the condition when a $(\iota\sigma)$ - or a $(\nu\nu)$ -structure is a better candidate for the ground state of the title molecule. Both structures can be represented as containing four (singlet) two-electron groups possibly interpreted as those possessing four ‘bonds’, although one can argue whether ι - or ν -geminals are truly bonding. Thus, in this section, we analyse relations between the energy contributions of the geminals of different types and their effect on the ‘elements’ of the energy profile of the C_2 diatomic: the minimum depth referring to the bond strength, the equilibrium interatomic separation – the bond length, and elastic constant in the vicinity of the energy (profile) minimum

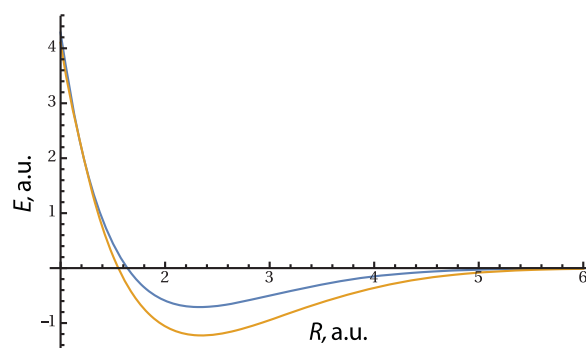


Figure 3. The comparison of the energy profiles for the $(\sigma\pi\pi)$ - (Structure 5 of Figure 1) $D_0 = -0.708814$, $R_{eq} = 2.32826$ all a.u. – blue; and $(\iota\sigma\pi\pi)$ -structure (Structure 1 of Figure 1) $D_0 = -1.22528$, $R_{eq} = 2.34875$ all a.u. – orange.

– the bond stiffness. It will be demonstrated that all the mentioned characteristics of the energy profile do not necessarily conform with either Badger rules or Pauling-like bond-length/bond-order relations based ultimately neither on any physical theory nor even on the ‘common sense’. That latter as condensed, say, in the Morse potential, actually allows independent setting of the elements of the energy profile by assigning three independent parameters defining it. Below we show, how the bonding signatures like dissociation energy (bond strength), bond-length (interatomic separation), and bond stiffness (elastic constant) come out from our consideration of the above models of electronic structures.

4.1. Energy profile of the $(\iota\sigma\pi\pi)$ -structure

In order to analyse the effect of that or another electronic group upon molecular geometry, its dependence on the interatomic separation must be considered. For this end, we need a reference structure. In the present setting, both electronic structures under consideration contain two symmetric π -bonds/geminals. Whatever differences must be attributed to the electronic groups built on the HO's of σ -symmetry (the σ -HO's themselves as well as the ι - and/or ν -HO's). We assume the energy profile of the structure with two symmetric π -geminals as a reference. Details of this construction are given in Appendix 4. Supplying the reference energy profile further by the energy contribution of the σ -geminal, we obtain the energy profile of the Structure 5 of Figure 1 depicted in Figure 3 (blue curve). We see that the σ -geminal gives the leading contribution to the bonding in the $(\sigma\pi\pi)$ -structure (Structure 5) and produces a rather deep minimum. The heuristic rule that the bond of a larger multiplicity is shorter turns out to be valid since the position of the minimum of the structure with a σ -geminal is strongly (by ca. 0.53 a.u.) shifted towards the shorter interatomic separations

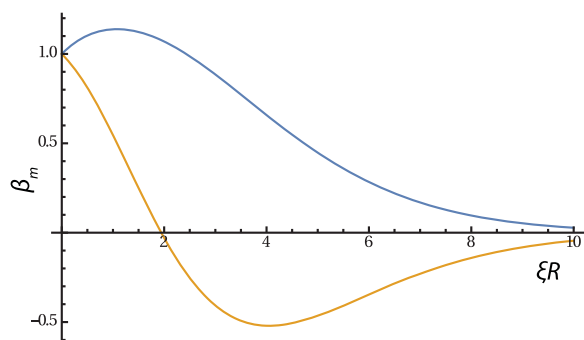


Figure 4. Equilibrium resonance integrals β_σ^* (blue) and β_l^* (orange) in the units of g as functions of the interatomic separation in units of ξR . The node on the β_l^* graph at $\xi R \approx 2$ corresponds to $R = 1.23$ a.u. for the ξ value characteristic for the carbon atom. Respectively, the minimum at $\xi R \approx 4$ corresponds to $R = 2.46$ a.u. or 1.3 Å.

as compared to the shallow minimum of the reference $(\pi\pi)$ -energy profile. Finally, we add the contribution of the ι -geminal and obtain the profiles shown in Figure 3 (orange curve). This picture, first of all, clearly shows that adding a ‘weak’ ι -bond lowers significantly the total energy (by *ca.* 0.52 a.u.) relative to the bottom of the well of the $(\sigma\pi\pi)$ -structure. At the same time, adding one more bond (bonding geminal) clearly shifts the position of the minimum on the energy profiles towards longer interatomic distances by *ca.* 0.02 a.u., that is, by detectable 0.01 Å. The reason of this behaviour is easy to understand. In Figure 3, one sees a tangential point at a distance of *ca.* 1.2 a.u. where the energy profiles of the $(\sigma\pi\pi)$ - and $(\iota\sigma\pi\pi)$ -structures coincide. At this point, the equilibrium resonance integral t_l^* Equation (3.11) vanishes. To the right of it, t_l^* is negative, but increases by absolute value with the distance before it reaches its minimum. The distance dependences of the equilibrium (with respect to hybridisation) resonance integrals underlying the observed behaviour are given in Figure 4 (observe different length scale, namely ξR rather than R in the latter figure). The most important observation is that the conditions of the Theorem 3.2 for the existence of the crossing between the energy profiles of the $(\iota\sigma\pi\pi)$ - and $(\nu\nu\pi\pi)$ -structures – the change of the sign of the resonance integral t_l^* is satisfied and one can expect the intersection of the energy profiles corresponding to the two structures.

We see that the common wisdom ‘the stronger bond is shorter’ does not work and our simple model of C_2 provides a clear counterexample. The shift of the position of the deeper minimum towards larger interatomic separations is predetermined by the fact that the stabilising (negative) energy contribution of the ι -geminal possesses a specific dependence on the interatomic distance of its own. The effective resonance integral t_l^* goes through the maximum of its absolute value right in the range of the

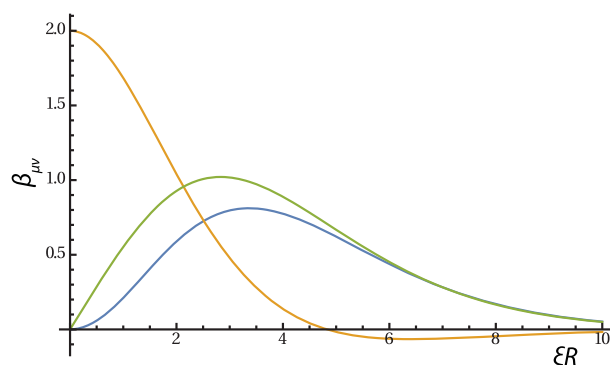


Figure 5. Effective combinations to the elementary resonance integrals $t_{\sigma\sigma} - t_{\zeta\zeta}$ (orange), $t_{\sigma\sigma} + t_{\zeta\zeta}$ (blue), $2t_{\zeta\sigma}$ (green) in the units of g as functions of the interatomic separation in units of ξR .

interatomic separations characteristic for bonding. The repulsive action of the ι -geminal on its parent $(\sigma\pi\pi)$ -structure appears since at the interatomic separation providing the minimum to it the energy contribution of the ι -geminal is on its descending branch, that is, has negative derivative with respect to interatomic separation:

$$\begin{aligned} E'_m &= \frac{1}{2} \left[\Delta'_m - \frac{16t_m^{*'}t_m + \Delta'_m\Delta_m}{\sqrt{16t_m^2 + \Delta_m^2}} \right] \\ &= \frac{1}{2} [\Delta'_m B_m - 4t_m^{*'} P_m] \end{aligned}$$

since the second term, where $t_l^{*'} < 0$ and $0 > P_l \propto t_l^*$ is negative and outweighs the positive first term. This simple form where the distance derivatives marked here by the prime are factorised from the elements of reduced density matrices (RDMs) is a consequence of the Hellmann–Feynman theorem which applies for the APSLG model and reformulated in terms of RDMs in [28].

This behaviour can be further recapitulated to the depth of its origin by considering the distance dependence of the combinations of the elementary resonance integrals $t_{\sigma\sigma} \pm t_{\zeta\zeta}$, $2t_{\zeta\sigma}$, depicted in Figure 5. Specifically, the combination $t_{\sigma\sigma} - t_{\zeta\zeta}$ (orange curves in Figure 5) decrease monotonously for the entire range of interatomic separations, the integral $t_{\zeta\sigma}$ is linear in ξR at the short distances and goes through a maximum at $\xi R \lesssim 3$. Finally, $t_{\sigma\sigma} + t_{\zeta\zeta}$ as well goes through a maximum at $\xi R \lesssim 3$, but is quadratic in ξR for small ξR . All the combinations decay exponentially for $\xi R \rightarrow 0$. This ultimately leads to the monotonous decrease of the effective resonance integral t_σ^* opposed by the sophisticated course of t_l^* involving minimum, maximum, and the nodal point so that the corresponding energy contribution goes through the ranges of interatomic separation where it increases,

decreases and then increases again. Fundamentally, this behaviour is predetermined by the radial nodal structure of the s - and p -AOs which finally assures the existence of the touch point in Figure 3. These features are in a way ‘symmetry imposed’, they do not depend on the details of parameterisation and are thus expected to be universal.⁶

We see that the ‘common knowledge’ that ‘a bond having a larger energy is shorter’ is actually based on a tacit assumption that the resonance integrals stipulating the energy contributions of each additional component of a multiple bond monotonously decrease by absolute value with increasing interatomic separation. It is not like this for the AO’s having complex radial nodal structure of the involved. Moreover, there is no need to seek this type of behaviour in exotic molecules: all radial parts of AOs have nodes except the $1s$ -AO, so that the ‘common knowledge’ itself more likely applies to exceptional cases singled out by the monotonicity condition, rather represents a general rule. Remarkably, the resonance integrals of the π -type respectively controlling the energy contribution of the π -geminals decreases monotonously with the interatomic separation thus justifying the known bond-order/bond-length rule [11] when applied to the conjugated π -systems. Nevertheless, a more sophisticated rule taking into account the nodal structure of the orbitals involved in the bond formation may be eventually formulated in a future.

4.2. Energy profile for the $(\nu\nu\pi\pi)$ -structure

Now we address the energy profile of the $(\nu\nu\pi\pi)$ -structure. In order to construct it on the same energy scale with the $(\iota\sigma\pi\pi)$ -structure, we have to estimate U – the key variable responsible for the energy difference between the divalent and tetravalent carbon. Within the accepted nonchalant approach, the difference between the effective core attraction parameters for electrons residing in the Slater AO’s with the *same* orbital exponent ξ and *different* orbital momentum is the amount of the rotational kinetic energy pertinent to the p -electrons and

vanishing for the s -ones. According to [30,31], the kinetic energy of a p -electron is $\frac{1}{3}\xi^2$. This naïve estimate and the characteristic value of the carbon AO’s orbital exponent [32] yields the numerical value of 23.8 eV. This overshoots significantly whatever available semiempirical estimates of this quantity which all fit in the range of 10–13 eV [33–36]. Furthermore, it is physically evident that the observable quantity controlling the transition between the $(\nu\nu\pi\pi)$ - and the $(\iota\sigma\pi\pi)$ -structures is the energy gap $E(^5S) - E(^3P)$ in the carbon atom, which in our CNDO-like model equals to U exactly. Thus, we introduce an additional energy scale and set U to be $\frac{\alpha}{3}\xi^2$. The experimental value of the triplet–quintet gap in the free carbon atom is 4.18 eV [37] which gives the value of α to be 0.175 whereas semiempirical estimates of U correspond to $\alpha = 0.5$. The energy profiles for the $(\nu\nu\pi\pi)$ - and $(\iota\sigma\pi\pi)$ -structures constructed for $\alpha = 0.5$ and $\alpha = 0.1$ are depicted in Figure 6. The latter value is selected to make the difference between the energy profiles minimally visible. Apparently, the employed two values of the scaling parameter α correspond to the opposite limits with respect to U : the large and the small ones. The procedure used to obtain a solution in the uniform approximation valid for the two limits simultaneously is described in Appendix 5. One can see that in the first case ($\alpha = 0.5$), the $(\nu\nu\pi\pi)$ -structure (blue curve) produces a minimum which is significantly lower than that on the $(\iota\sigma\pi\pi)$ -profile (orange curve). This energy profile flows to the limit of $2U$ (the blue curves flow to zero: the energy of two separated carbon atoms in their ground states which is the natural energy reference point). The minima on either of the orange curves ($\iota\sigma\pi\pi$) lie at a very reasonable 1.242 Å. That on the blue curve ($\nu\nu\pi\pi$) on the left amounts 1.264 and 1.236 Å on the right one. Either represent a significant shrinking as compared to the position of the minimum of the reference $(\pi\pi)$ -structure by 0.14 Å. It is much stronger than the effect of the ι -bond on the $(\sigma\pi\pi)$ -structure despite the fact that the bonds strength is larger in the latter case. The sign of the structure effect of the ν -bonds (shrinking) is predetermined by the fact

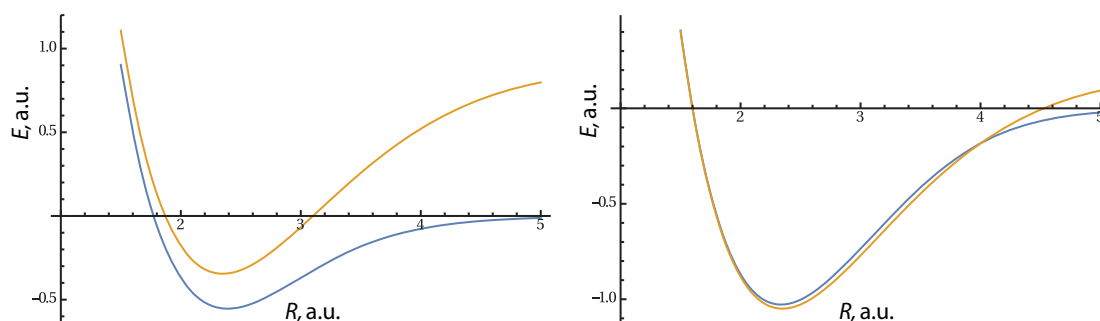


Figure 6. Energy profiles for the $(\nu\nu\pi\pi)$ - (blue) and $(\iota\sigma\pi\pi)$ -structure (orange) structure. Left: $\alpha = 0.5$, right: $\alpha = 0.1$.

that the minimum of the reference energy profile lies in the distance range of the descending branch of the $t_{\zeta\sigma}$ (or t_v^*) integral (Figure 5). This happens since the energy contribution of the ν -geminal has the same form as that of the symmetric geminals:

$$\frac{1}{2} [\Delta B_\nu - 4t_\nu P_\nu]$$

so that its geometry effect is determined by the derivatives of Δ and β_ν (Hellmann–Feynmann theorem applies [28]).

The overall picture for a larger α fairly reproduces the result of the *ab initio* treatment, namely, the $(\nu\nu\pi\pi)$ -type of the ground-state structure of C_2 . We performed a numerical check which showed that the switch from the $(\nu\nu\pi\pi)$ - (for larger α 's) to the $(\iota\sigma\pi\pi)$ -ground state (for smaller α 's) of our model of C_2 takes place in the range of $\alpha=0.17$ – 0.18 with the energy values in the respective minima calculated for $\alpha = 0.175$ coinciding within 0.0005 a.u. and the positions of the minima coinciding within 0.005 a.u. being equal to 1.239 Å. We observe thus a degeneracy most probably predicted by Theorem 3.2 – the energy difference between the $(\nu\nu\pi\pi)$ - and $(\iota\sigma\pi\pi)$ -structures in favour of the latter one is of the second order with respect to the small parameters U and Δ . We conclude that the answer the numerical studies give about the nature of the ground state of C_2 ultimately can be modelled by an ‘effective’ U corresponding to each specific procedure. We performed a series of calculations using the *ab initio* SLG method [15](n) for such a model. First of all, they reasonably reproduce the bond distance (1.234 and 1.248 Å for calculations with minimal STO-6G and larger 6-31G basis sets, respectively) although almost the same result comes from our analytic ‘CNDO-like’ model. The exact positions of the minima depend on the details of either reference profile or that of the resonance integrals. Nevertheless, the approximate degeneracy of the $(\nu\nu\pi\pi)$ - and $(\iota\sigma\pi\pi)$ -structures in the case when the latter one has lower energy is a coarse feature.

4.3. Components of the multiple CC bond and its rigidity

Now we consider attempts to put the bond energy/strength in a kind of correlation with the bond rigidity. Above we could show that not only there is no simple general relation between the length and the strength of the bond, but we managed to show that much more complicated relations can exist as predetermined by the details of the radial nodal structure of the involved orbitals controlling the distance dependence of the resonance integrals contributing to the bonding. One can

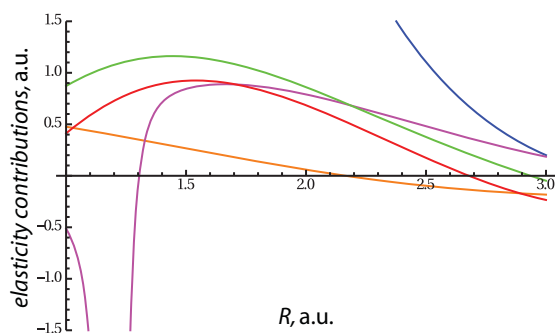


Figure 7. The contributions to the C–C bond elastic constant. The second derivatives of the respective contributions to the energy are depicted (a.u.). Colour code: blue: the reference stiffness, orange: the σ -geminal contribution, magenta: the ι -geminal contribution, green and red: twice the ν -geminal contribution for $\alpha = 0.1$ and $\alpha = 0.5$, respectively.

expect that the situation with the bond rigidity/stiffness is even more sophisticated. Indeed, any ‘rule’ relating the bond multiplicity with its stiffness can only be based on a tacit ‘harmonicity’ hypothesis, that is, that a contribution of each individual component of a multiple bond to the total energy has a quadratic form as a function of interatomic separation and the corresponding positive partial elasticity constant adds to the total. The C_2 example is very illuminative since for it the complex character of all distance dependences can be and has been explicitly established right above. In fact, either the $(\iota\sigma)$ - or $(\nu\nu)$ -energy contributions are either convex (stiffening) or concave (softening) functions of the interatomic separation for its different ranges. The effect of that or another component of a multiple bond upon its rigidity depends on the sign of the corresponding second derivative of the energy contribution at the position of the total energy minimum – pretty sophisticated construction. This situation as it comes from the proposed simple model is depicted in Figure 7. We see that the employed reference energy profile always supplies positive contribution to the stiffness monotonously decreasing with the interatomic separation (blue curve). It is, nevertheless, the largest contribution to the total elasticity constant in the entire considered range of the interatomic separations. In the contradiction to the above mentioned, but never proven ‘rule’, the strongest contribution to the bonding energy, that of the σ -bond/geminal, produces rather moderate stiffness contribution (orange curve). It vanishes almost in the energy minima of the $(\sigma\pi\pi)$ - and $(\iota\sigma\pi\pi)$ -structures and is softening rather than stiffening at the equilibrium distance (ca. 2.4 a.u.), although continues to provide considerable stabilising and shrinking contribution to the total energy. The behaviour of the stiffness contribution supplied by the ι -geminal is the most sophisticated. At shorter interatomic distances, it

produces a softening contribution which diverges at the tangential point ($t_l^* = 0$) due to singularity characteristic to the square root. In the entire ‘physical’ range (say, $R > 1.5$ a.u.), the ι -geminal gives the second leading contribution to the overall stiffness of the $(\iota\sigma\pi\pi)$ -model despite (1) its bonding energy contribution is always smaller (by absolute value) than that of the σ -geminal and (2) this contribution is in fact (weakly) repulsive (!) in the minimum point of the $(\iota\sigma\pi\pi)$ -energy profile. So, we face here seemingly paradoxical, but most probably very common situation – at the equilibrium geometry of C_2 , the ι -geminal produces a contribution to the energy which is at once stabilising and stiffening, but repulsive. By contrast, the σ -geminal produces a stabilising, shrinking, but softening contribution. Obviously, this (counter)example on one hand prevents any possibility of the high-sounding “rules” which are widely spread in the literature, but on the other hand shows that the situation is not desperate: it is clear what components of the theory determine the true relations between different elements of the energy profiles (or more generally – potential energy surfaces), e.g. the depth of the potential well, its geometrical position (interatomic separation), and the form of the well (the stiffness). The required relations can be established by a sequential analysis similar to that presented above.

Finally, we address the rigidity of the $(\nu\nu\pi\pi)$ -structure. As one can see from Figure 7 the ν -geminals produce much more stiffness than the σ - and approximately the same amount as the ι -geminal despite the fact that the energy contribution (strength of the bond) is much smaller for $(\nu\nu)$ - than for the $(\iota\sigma)$ -components. The ν -contribution to the stiffness decreases as one could expect with the interatomic separation. Nevertheless, at the equilibrium distance of the $(\nu\nu\pi\pi)$ -structure, it is still stiffening. A counterintuitive aspect is that the ν -contribution to the elastic constant is always smaller (red curve) in the situation when the total energy of the $(\nu\nu\pi\pi)$ -structure is lower (larger α). We also notice that the elastic constant of C_2 with four electronic groups is always larger than that of the $(\sigma\pi\pi)$ -model (Structure 5). That means indirectly that the CC elastic constant of acetylene does not reduce to that of the $(\sigma\pi\pi)$ -model and some other contributions not existent either in C_2 or in our model may be involved. One also cannot exclude that the exact boundaries of the distance ranges where different energy contributions are convex or concave differ from those depicted in Figure 7. We shall address this issue at a further convenience. In general, no relation between the contributions of each individual geminal to the energy and the elastic constant except that between a function and its second derivative (taken in some additionally defined point) is possible. Provided the geometry

dependence of the energy contribution of a geminal may be rather sophisticated if AOs with a complex nodal structure are involved (and having principal quantum number two and azimuthal quantum number unity is enough to produce significant complications), the relations between the energy effect and the elasticity effect of each specific geminal (electronic group) must be analysed separately.

5. Discussion

5.1. Counting versus measuring bonds

The controversy [1,10] touches as well a relation between the bond multiplicity and bond measures used to quantify bonding on the basis of analysis of the electronic wave function or RDMs – like the Coulson bond order or Mayer bond order index. The problem is that there is no proven way to establish correspondence between the bond measures obtained by processing results of numerical experiments and the more qualitative description in terms of bonds of some integer multiplicity. In English (to the best of our knowledge), there is a subtle distinction between ‘how much?’ and ‘how many?’ unknown to the native languages of the present authors. Although both the questions formulate in English *quantitatively*, the answers ‘three’ or ‘four’ to the question ‘how many bonds are there in C_2 ’ is of more qualitative rather than quantitative nature. Remarkably, this grammatical distinction absolutely had not manifested itself in the discussion [1,10]. Moreover, the entire controversy spinned around an unsolvable question: how *much* of how *much* makes that *many*: or what values of various bond indices measured in some decimal fractions (how much) makes that many bonds in this at a first glance simple molecule.

Despite the fact that no universal relation between these ‘elements’ of the energy profiles exist, these elements are used in the literature to support hypotheses about the bond multiplicity. Within such a discussion, it is also taken for granted that either a bond of higher multiplicity or that with a higher bonding measure is to be shorter, stronger, and stiffer. A tentative relation between the bond measures and the above-mentioned elements of the energy profiles could be a background for the correlation between these latter.

In this section, we analyse the bond measures for the models of C_2 electronic structure. The definitions of the bonding measures are given by Equations (A1) and (A3). They are valid for all involved geminals including the highly asymmetric ν -geminals unlike Equations (2.4) and (2.6) valid for the σ -, π -, and ι -types. The graphs of these individual contributions are given in Figure 8. The Coulson bond order demonstrates most sophisticated

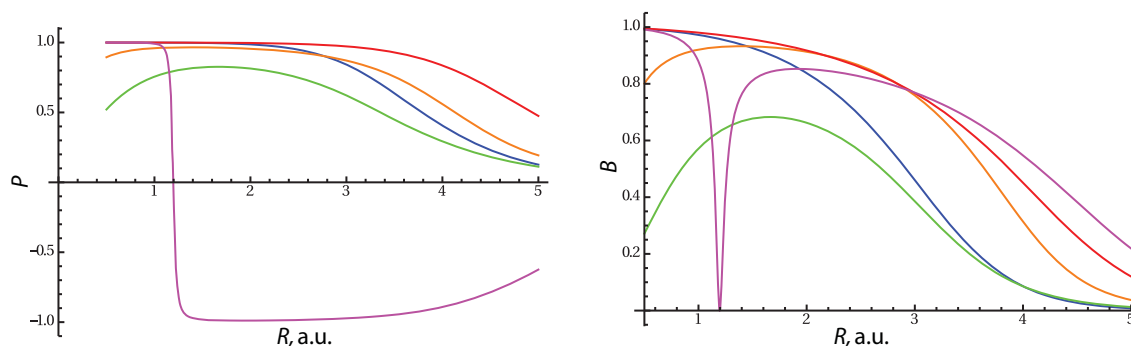


Figure 8. Bond order indicators for different electronic groups of C_2 . Colour code: blue: π , red: σ , magenta: ι , orange, green: ν . Left: Coulson bond orders; right Mayer bond order indexes.

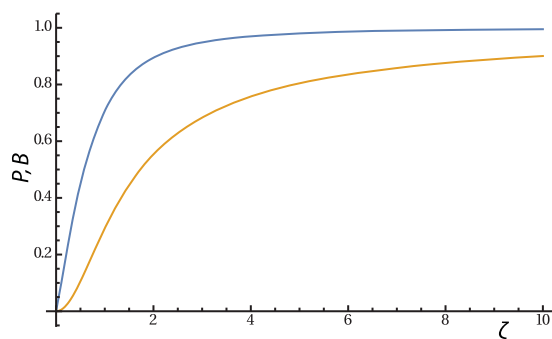


Figure 9. Coulson bond order (blue) and Mayer bond order index (orange) for a symmetric geminal depicted as functions of the dimensionless Anderson parameter $\zeta = \frac{4t}{\Delta}$.

behaviour of the ι -bond/geminal, which is, however, not confusing rather instructive. Indeed, according to the definition Equation (A.11) and the estimates Equation (A.2) valid for the symmetric geminal, the Coulson bond order must be proportional to the effective resonance integral of the corresponding geminal. As we already know, the resonance integral for the ι -geminal changes its sign at 1.2 a.u. thus the change of the sign of P_ι is by itself not surprising. What may seem to be somewhat unexpected is the extreme narrowness of the distance range where the corresponding switch occurs as compared to the range required by the resonance integral t_ι^* to switch to its minimum (maximum negative absolute value) from the opposite positive value (see Figure 4). This can be understood if one recollects that the Coulson bond orders had been proven to be transferable in symmetric geminals upto the inverse second power of the *large* Anderson parameter $\zeta = \frac{4t}{\Delta}$ [16]. In the correlated model, the deviation of the Coulson bond order from the unity is proportional to ζ^{-2} which is the basis for constructing the DMM model [17]. In the SCF approximation (or equivalently $\Delta \rightarrow 0$), the Coulson bond order is always equal to unity by absolute value irrespective to the actual magnitude of the resonance integral. This may be also traced in Figure 9, where one can see that the Coulson bond order reaches 80%

of its limiting value at the argument $\zeta = \frac{4}{3}$ and 90% at $\zeta = 2.065$, that is, the width of the switch range between -0.9 and $+0.9$ in the vicinity of the touch point reduces to 0.14 a.u., which looks out as almost vertical transition in the left panel of Figure 8. That is to say, the Coulson bond order has high sensitivity, but low resolution. From a different viewpoint, the Coulson bond orders somehow exaggerate the bonding since the value of this indicator turns out to be too large for the relatively small values of the resonance integral. What needs to be stressed is that the standard procedures implemented in the numerical packages prescribing summation of the Coulson bond orders apparently fail here since in the distance range where the bonding in the $(\iota\sigma\pi\pi)$ -model fully develops its Coulson bond order turns out to be pathologically small since the contributions of the σ - and ι -geminals compensate each other. In a way, redefining the Coulson bond orders in terms of always positive *catheti* $|4t|$ and alike *hypotenuse* $\sqrt{16t^2 + \Delta^2}$ may locally lift this contradiction.

Although the Mayer bond order index has somewhat worse sensitivity, but better resolution, than the Coulson bond order (it reaches the value 0.8 for the value of Anderson parameter *ca.* 4.9 and 0.9 at *ca.* 10), which eventually explains the larger width of the spike on the graph of the Mayer bond order index for the ι -geminal contribution. Somewhat surprising is that for the equilibrium distance of the $(\iota\sigma\pi\pi)$ -model, the Mayer bond order index deviates from unity most of all for the π -geminals. This deviation is even stronger for the equilibrium interatomic separation of the $(\nu\nu\pi\pi)$ -models. Due to higher resolution of the individual specific of each bond/geminal, summing the Mayer bond order indices referring to different bonds leads to even more confusing results and for a peculiar reason. For the $(\iota\sigma\pi\pi)$ -model, the bond order index of the π -geminals is only 0.75 for each so that their overall contribution amounts to only 1.5 instead of *ca.* 2 which one would expect for two rather short π -bonds. The former amount is difficult to interpret. The situation

complicates further if one adds the bond order indices for the σ - (0.87) and ι - (0.85) geminals which produces altogether 3.22 – an amount which cannot be unequivocally understood: it is much less than 4, but the reason is by no means any particular weakness of the ι -bond as one could expect; by contrast, the most of the discrepancy comes from the seemingly innocent π -bonds. In a way, it shows that redefining the Coulson bond orders in *Pythagorean* terms together with the transferability/sensitivity makes them a better tool for approximate *counting* the number of bonds.

Considering the bond measures of the ν -geminals also leads to a somewhat counterintuitive result. Both the measures are relatively small for the ν -geminals which could be expected. Nevertheless, they are not fatally small, so that any fundamental conclusion about existence or nonexistence of a bond in the ν -geminals could be drawn. For the $(\nu\nu\pi\pi)$ -structure, the total bond order amounts $1.5+1.9=3.4$ whereas the bond order index $1.5+1.1=2.6$; neither again seems to be easily interpretable nor mutually consistent. This observation probably suffice to explain the observed ‘elusivity’ [6] of the bond multiplicity in C_2 since the bonding measure used there is a close descendant of the Mayer bond order index. Both considered bonding measures turn out to be considerably smaller for the value of α which makes the $(\nu\nu\pi\pi)$ -structure the ground state, i.e. for larger values of U . By contrast, for the U values making the ground state to belong to the $(\iota\sigma\pi\pi)$ -one, the bond indicators of the ν -geminals are comparable with those of the symmetric geminals. The bond order index in this case is even larger for the ν -geminals than either for π - or ι -geminals.

The obtained results provide a good opportunity for a more conceptual discussion since they highlight some weakness of our concepts which have to be precised and refined. Statements relating bonds’ multiplicity with the elements of the energy profiles are not basically valid either in their simplistic, that is, too universal form (e.g. when applied to all elements of the energy profiles). However, even an attempt to formulate some ‘minimalistic’ rules like a relation between the bond energy (strength) and some of the bond measures also faces serious complications. At a first glance, the situation looks out to be consistent: weaker bonds like ι - or ν -ones are characterised by somewhat smaller (absolute) values of the bonding measures. However, here we confront the problem of the reference state/dissociation limit to be used to define the bond strength. A significant part of the controversy between [1,5] and [10] is that while suggesting the quadruple bond of $(\iota\sigma\pi\pi)$ -type in C_2 the authors of [1,5] also suggest to count the bond energy from the limit of separated ‘promoted’ atoms. By contrast, in [10], it is suggested to count the bond energy (its strength) from

the physical dissociation limit which in the case of C_2 is that of two ground state (^3P) carbon atoms. For the $(\nu\nu\pi\pi)$ -ground state, this represents no problem: a relatively weaker bond has smaller bonding measures. However, in the case when the deepest minimum corresponds to the $(\iota\sigma\pi\pi)$ -structure it is not that obvious. Both structures represent a singlet many-electron function, thus an avoided crossing of the two curves cannot be excluded (see below) so that an energy profile to which the $(\iota\sigma\pi\pi)$ -minimum pertains flows to the dissociation limit of two s^2p^2 ground states. This produces a shallow minimum (weak bond), but the bond measures characteristic for the $(\iota\sigma\pi\pi)$ -structure, i.e. large ones. This breaks any tentative relation between the bond measures and elements of the energy profile. It looks like that for the purpose of formulating provable *statements* about relations between bond measures and bond strength the dissociation limit must be selected accordingly, although taking the experimental one may seem to be more practical. Apparently ignoring possible switches between the electronic structures of different types well possible along the dissociation path completely confuses already quite confusing picture and should be avoided. On the other hand, it is well possible to use these indicators for diagnostic of the suspected transition between different types of electronic structure. It is also obvious from the performed analysis that say a bond can produce almost arbitrarily large energy contribution (if only its Anderson parameter exceeds *ca.* two) on account of increasing the absolute value of the resonance integral. The feasible solution is, probably, to transit to the energy-based measures, as argued in [38] and implemented in the solid state context by the COHP analysis [39].

5.2. Physical consequences

The performed study allows us to address more physical aspects of the C_2 problem in relation to our results. First of all, one notices that the low-energy electronic spectrum of C_2 in the vicinity of the minimum of its ground-state energy profile is rather complex [40–43]. The lowest four states are $X\ ^1\Sigma_g^+$ – the ground state, two states with non-vanishing projection of the angular momentum on the molecular axis, $A\ ^1\Pi_u$ and $B\ ^1\Delta_g$ are not covered by our study, and the excited state $B'\ ^1\Sigma_g^+$. The numerical energy profiles [41–43], calculated pointwisely, consistently show the avoided crossing yielding the physical X and B' states. Clearly, the avoided crossing/quasidegeneracy itself indicates that a unique interpretation of the electronic structure of C_2 in terms of the $(\iota\sigma\pi\pi)/(\nu\nu\pi\pi)$ -archetypes is hardly possible for the ‘exact’ solution. It would be thus of interest to establish what

particular type of the Hamiltonian matrix element mentioned in [42] is responsible for the observed avoided crossing. Nevertheless, the above result shows that a close position of the two structures in the small U range could be predicted by very simple means and is most probably a crude feature of C_2 and its relatives.

Turning to more physical evidences of the existence of the quadruple bonding of tetravalent carbons involving the weak ι -bond in the physical C_2 , we notice that the true ‘smoking gun’ rather than a ‘canon drum’ for the existence of the *weak* fourth ι -bond would be the presence of the low-lying triplet state corresponding to unpairing electrons in this geminal, which is equivalent to a cleavage of this bond (Structure 5). It is not there, moreover, the relevant triplet excited state of C_2 is the ${}^3\Sigma_u^+$ [44] with the energy somewhat lower than the experimental energy of the intraatomic ${}^3P \rightarrow {}^5S$ excitation. It looks like an intraatomic excitation delocalised to the neighbour carbon atom by some exchange mechanism like in Davydov excitons [45] – the feature more consistent with the $(\nu\nu\pi\pi)$ -structure of the ground state formed by the ${}^3P$ carbon atoms. Our estimates indicate that the ι -geminal at the equilibrium separation adds quite an amount of the bonding energy and cleaving of this bond eventually produces a high-energy excited state.

6. Conclusion

In this study, we concentrated on providing a theoretical framework to the vivid discussion around the tentative quadruple bonding in C_2 . Although, in general, a quadruple bonding of carbon had been established [46], the quadruple bond in C_2 had been considered as an artefact of the RHF treatment [47], until recent activity [1,5] reignited the interest to this problem. At variance, with a predominant number of studies on C_2 performed purely computationally, in this paper, we considered a simplified Hamiltonian and a wave function capable to capture the most important electronic correlations although remaining analytically tractable in order to put the specific problem of C_2 into a more general parametric context. By doing so, we reproduced the most important features of C_2 previously found only numerically. The performed study was more mathematical in style since we were more concerned with the properties of the *models* of C_2 , being exemplary/archetypic, rather than with the properties of C_2 itself. This follows a general mathematical strategy of *imbedding* that is considering any given (numerical) problem as a specific case of a class of similar problems [48]. To understand the properties of these models and to make sense of the results of the numerous computational studies, we answered the following questions:

- What are the parameters governing the choice among bonding patterns (inverted ι -bond versus σ/π -separation versus banana bonds versus asymmetric ν -bonds)?
- What are the effects of various bonding patterns on the CC distance and the elasticity constant?
- How to count or measure bonds, and are numbers or measures of bonds anyhow related with bond strength, length, and rigidity?

We established that a good part of the solution types mentioned in [1,5] cannot pretend to be ground state (those with the banana bonds and a missing ‘fourth’ bond). This conclusion does not depend on the details of the parameterisation, rather is predetermined by the general structure of the class of the problems. It also turned out that the key parameter controlling the type of the ground state is the promotion energy U of the ‘divalent’ s^2p^2 configuration to a ‘tetravalent’ state in different disguises. The fact that the tetravalent $(\iota\sigma\pi\pi)$ -solution appears as a ground state only in the range of very low values of U translates into the difficulty of its reproducing in the numerical experiments. The entire story considered from a general perspective is nothing but one of the interrelation between promotion of a ‘divalent’ four-electron atom to its ‘tetravalent’ state previously extensively numerically studied [49]. Clearly, the promotion must be compensated by the additional bonding allowing to spend extra valencies. The results of the papers reporting a ‘weak’ ι -bond apparently refer to the distance range near the node of the t_i^* integral wherever it is.

We also could establish that the range of the geometry/parameter space corresponding to the ‘strong’ bonding cannot be identified with use of the Coulson bond orders due to its very high sensitivity – the other side of its transferability: too small values of the resonance integral produce already too large (close to the limiting ones) values of this bond measure. The range of the Mayer bond order indices corresponding to the ‘weak’ bond is somewhat wider, but (1) the bond order index has no direct relation to the bond strength itself and (2) the range of the interatomic separations where the bond order index is relatively small is, nevertheless, narrow as compared to that where the switch of the resonance integral t_i^* (and that of its respective smallness) takes place. It is any way pretty much different from the range where the contribution of the ι -geminal to the energy is small – that is, the only range which is of interest for whatever interpretation purposes. By contrast, after some modification (redefining it in geometrical terms, see above), the Coulson bond order may be a tool for an approximate counting of bonds. Nevertheless, even in this case, the counting is related to sensitivity, which is determined by the quantity Δ which in principle is

different for different bonds (in the present ‘CNDO-like’ model it is not like this – all Δ_m ’s are the same) and for different interatomic separations.

An interesting option for the C_2 ground-state electronic structure not covered directly by the wave function adopted in the present work is that proposed in [7], where it had been suggested that a σ -bond formed by the HOs very similar to those used here is complemented by the antiferromagnetically coupled three-electronic quartets eventually using the HOs remaining decoupled after the formation of the σ -bond. However, the bonding contribution Equation (2.7) covers both the strong bond limit, that is, $\zeta = \frac{4t}{\Delta} \rightarrow \infty$, and the weak bond limit $\zeta \rightarrow 0$, the latter being nothing, but the (weak) antiferromagnetic coupling of electrons residing on the two ends of a geminal. Thus, it is not clear whether [7] indeed proposes a separate kind of bonding structure in C_2 or it is only a version of already proposed Structure 1 featuring for some reasons small values of the resonance integrals t_m^* . We incline to the latter conclusion. The preference of the state obtained in [7] is easily explained by the stabilising effect of the intraatomic exchange – the same which assures the Hund’s rule validity for the isolated atoms to assuring as well the triplet ground states of the O_2 and B_2 molecules. These terms are omitted in our study, but their effect indirectly manifests in the small critical value of U equal to that of the triplet–quintet gap being the true threshold between the divalent and tetravalent structures. It is worth noticing that the method adopted in [7] excludes any possibility of reproducing the ground state of the $(\nu\nu\pi\pi)$ -type, since it takes into account only the configurations with singly occupied HOs – suitable for the weak bonding ($\zeta \rightarrow 0$) limit. Thus, although, the weight of the configurations with locally unpaired electrons on each of the two carbon atoms is most probably higher in the reality than it is in our naïve APSLG model, the model [7] is nonetheless unbalanced in another sense, so that conclusions derived from its numerical analysis cannot be final. More insight concerning the interrelations of electrons residing in different geminals of the C_2 molecule can be obtained by extending the approach of [50] that is enhancing (variationally) the weight of the structure with high-spin multipliers in the expansion. It also seems to be possible to extend our approach to the ‘INDO-like’ one so that the intraatomic exchange is explicitly included. We shall undertake the corresponding study under further occasion.

Notes

1. The presence of either σ or ι in the notation allows one to uniquely determine which type of banana geminal is meant.

2. The importance of the Pythagorean theorem had been recently recognised on the highest international economical level [22].
3. In a book [23], a boy has to get three banana from an enigmatic planet. We also undertook an expedition to a mostly unstudied planet of DMM/AIMM trying to find them there, but, as we see, they do not exist.
4. Of course, there is an option to receive some gain through the exchange between single electrons in the HO’s pointing outwards looking of the Structure 5 (see below).
5. In qualifying a smaller s -weight as an acceptor one, we follow the Bent rule recently *proven* [17] in the DMM context.
6. It is worth to notice that the nodal structure of the AOs recently regained a considerable interest under the new nickname of ‘nonuclear density maxima’. In the older times, every second year chemistry student in order to become a third year one had to know that the maximum of the electronic density of a $2p$ -AO lays outside the nucleus. In our days, this ancient wisdom seems to be forgotten as manifested in recent publications [29].
7. Mr Kaushik Basu is a senior vice-president and chief economist of the World Bank and professor of economics at Cornell. According to Wiki, he ‘believes strongly that good moral qualities are essential for growth and development within the economy’.

Acknowledgments

Knowing the addressee of this *Festschrift* as someone who is not much interested in ‘how much’ we hope that present piece will interest him. We are thankful to the Referee for the benevolent comments. Prof. I. Mayer and Prof. Dr W.H.E. Schwarz are acknowledged for valuable discussions. Dr A.M. Tokmachev contributed to this study at an earlier stage and took part in the discussion which is gratefully acknowledged. We are thankful to Prof. R. Ponc and Dr. B. Braida for sending us reprints of their works.

Note added in proof

Upon acceptance, S. Shaik et al. published ‘The Quadruple Bonding in C_2 Reproduces the Properties of the Molecule’ [Chem. Eur. J., 22, n/a (2016)], as reached us through Dr B. Braida. Although their numerical results conform to our analytical study, the interpretation diverges. (1) Lewis was apparently not right. Either Boutleroff (1865) or Alexejeff (1901) would unanimously say that C_2 possesses a quadruple bond, as published in French, German, and Russian languages [38]. Rumer (1938), by contrast, disliked tetravalence and thus C–C quadruple bonding since the C ground state has only two unpaired electrons and thus must be divalent. (2) Bonding measures are useless for *counting* bonds. The problem becomes trivial if one uses the ‘tendency to “break” the characteristic of multiple bonds, as stressed by Lewis. *Four* H_2 molecules are to be added to C_2 , that is, *four* bonds to be broken, in order to completely separate two carbon atoms. (3) The presence of the low-lying $^3\Sigma_g^+$ state by itself does not imply whatever reactivity since no concrete reaction is specified, as seen from the triplet O_2 ground state. This problem is discussed in our recent publication [52].

Disclosure statement

No potential conflict of interest was reported by the authors.

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Appendices

Appendix 1. Relations based on the APSLG form of the wave function

A.1 Elements of reduced density matrices

The APSLG form of the wave function Equation (2.1) ensures that the total energy can be written in terms of intrageminal elements of RDMs. The summed over spin 1-RDM is defined as

$$P_m^{pq} = \sum_{\sigma} \langle 0 | g_m p_{m\sigma}^+ q_{m\sigma} g_m^+ | 0 \rangle. \quad (\text{A1})$$

The actual values are thus

$$\begin{aligned} P_m^{rr} &= 2(u_m^2 + w_m^2), \quad P_m^{ll} = 2(v_m^2 + w_m^2), \\ P_m^{rl} &= 2(u_m + v_m)w_m. \end{aligned} \quad (\text{A2})$$

Similarly, the 2-RDM summed over spin is defined as

$$\Gamma_m^{pq} = \sum_{\sigma} \langle 0 | g_m p_{m\sigma}^+ q_{m-\sigma}^+ q_{m\sigma} p_{m\sigma} g_m^+ | 0 \rangle, \quad (\text{A3})$$

leading to expressions

$$\Gamma_m^{rr} = 2u_m^2, \quad \Gamma_m^{ll} = 2v_m^2, \quad \Gamma_m^{rl} = 2w_m^2. \quad (\text{A4})$$

Due to normalisation of the amplitudes, a remarkable relation holds:

$$2\Gamma_m^{rl} + \Gamma_m^{rr} + \Gamma_m^{ll} = 2. \quad (\text{A5})$$

In the SCF approximation for the individual symmetric bonds (geminals), the following holds:

$$u = v = \frac{1}{2}; \quad w = \pm \frac{1}{2}; \quad P^{rl} = \pm 1. \quad (\text{A6})$$

A.2 Energy contributions in APSLG

The intrageminal matrix elements U_m can be expressed as

$$U_m^L = U_{pp} - U(s_m^L)^2, \quad U_m^R = U_{pp} - U(s_m^R)^2, \quad (\text{A7})$$

where s_m is the coefficient of the s -AO in the corresponding HO expressed in the $\{sp\}$ -basis and $U = U_{pp} - U_{ss} > 0$ is the difference of the core attraction energies for p - and s -orbitals. Different Hamiltonian terms give rise to respective contributions to the energy. First, one-centre attraction is

$$E_{1c, \text{attr}} = \sum_m (U_m^L P_m^{ll} + U_m^R P_m^{ll}). \quad (\text{A8})$$

The intergeminal repulsion is simply

$$E_{1c, \text{inter}} = g \sum_{m < m'} (P_m^{ll} P_{m'}^{ll} + P_m^{rr} P_{m'}^{rr}). \quad (\text{A9})$$

The intrageminal part of the one-centre electron repulsion is

$$E_{1c, \text{intra}} = \frac{g}{2} \sum_m (\Gamma_m^{ll} + \Gamma_m^{rr}). \quad (\text{A10})$$

The resonance energy is

$$E_{\text{res}} = -2 \sum_m t_m P_m^{rl}, \quad (\text{A11})$$

where the intrageminal resonance integral is given by

$$\begin{aligned} t_m &= t_{\sigma\sigma} s_m^L s_m^R + t_{\zeta\zeta} x_m^L x_m^R + t_{\zeta\sigma} (z_m^L s_m^R - s_m^L z_m^R) \\ &\quad + t_{\pi\pi} (y_m^L y_m^R + x_m^L x_m^R) \end{aligned} \quad (\text{A12})$$

assuming that the C-C bond is along the z -axis and (s_m, x_m, y_m, z_m) represent coefficients of HOs in the $\{sp\}$ -basis.

The last energy contribution comes from intrageminal two-centre repulsion:

$$E_{2c, intra} = \sum_m \gamma_m (\Gamma_m^{rl} - P_m^{rr} P_m^{ll}). \quad (A13)$$

Equations (A.10) and (A.13) can be combined resulting in

$$E_{intra} = \sum_m \left[\frac{\Delta_m}{2} (\Gamma_m^{ll} + \Gamma_m^{rr}) + \gamma_m (1 - P_m^{rr} P_m^{ll}) \right], \quad (A14)$$

where $\Delta_m = g_m - \gamma_m$. This is used in the considerations of the main text.

Appendix 2. Lemmas concerning the hybridisation dependence of energy contributions

B.1 Core attraction dependence

Lemma B.1: *In symmetric case, the one-centre attraction energy does not depend on hybridisation.*

Indeed the one-centre core attraction matrix elements U_m entering Equation (A.8) are given by [17]

$$U_m = U_p - U s_m^2; \quad U = U_p - U_s > 0.$$

The matrix elements U_m enter the total energy as a sum with the weights equal to diagonal elements of 1-RDM. In the symmetric diatomic, they all are equal to unity; thus, the attraction energy reads

$$\sum_{m=1}^4 [U_p - U s_m^2]$$

and due to the normalisation condition for the HOs

$$\sum_{m=1}^4 s_m^2 = 1 \quad (B1)$$

the one centre attraction is

$$U_s + 3U_p$$

QED.

B.2 Intergeminal one-centre interactions

The one-centre intergeminal Coulomb interactions are contributed by the terms of the form:

$$\frac{1}{4} \sum_m \sum_{k \neq m} g_{km},$$

where the factor one quarter is the product of two diagonal elements of the 1-RDM. The explicit form of the matrix elements $g_{km} (k \neq m)$ are known [17]:

$$\begin{aligned} g_m &= C_1 + C_2 s_m^2 + C_3 s_m^4, \\ g_{km} &= C_4 + C_5 [s_m^2 + s_k^2] + C_3 s_m^2 s_k^2, \end{aligned} \quad (B2)$$

where C_i 's are the known combinations of atomic Slater-Condon parameters [17], but are not required so far. Performing the summation and using again the normalisation condition Equation (B.1), we arrive to the result:

$$\frac{1}{4} \sum_m \sum_{k \neq m} g_{km} = 3C_4 + \frac{3}{2}C_5 + C_3 - \frac{C_3}{4} \sum_m s_m^4, \quad (B3)$$

which as well deserves the name:

Lemma B.2: (Hellmann) *The Coulomb interaction energy between and only between HOs with the unity occupancy is maximal for the sp^3 hybridised carbon atom (all $s_m = \frac{1}{2}$) and minimal for the unhybridised carbon atom (one of $s_m = 1$; all others are vanishing).*

Appendix 3. Banana bond energies (A.M. Tokmachev)

Since all the bonds under consideration are only weakly correlated, it is reasonable to use Anderson parameters ζ_m defined in the main text. In its terms, the energy Equation (2.5) of a symmetric geminal can be rewritten as

$$\begin{aligned} E_m &= \frac{\Delta_m}{2} [1 - \Gamma(\zeta_m)], \\ \Gamma(\zeta_m) &= \sqrt{1 + \zeta_m^2}. \end{aligned} \quad (C1)$$

For a strong bond $\zeta_m \gg 1$ holds and thus

$$\sqrt{1 + \zeta^2} = \zeta \sqrt{1 + \frac{1}{\zeta^2}} \approx \zeta \left(1 + \frac{1}{2\zeta^2} \right) = \zeta + \frac{1}{2\zeta}. \quad (C2)$$

It means that E_m can be approximated as a sum of three contributions:

$$E_m \approx \frac{\Delta_m}{2} \left[1 - \zeta_m - \frac{1}{2\zeta_m} \right]. \quad (C3)$$

The relation between the resonance integrals between σ -, π -, and β -HOs Equation (3.6) implies that

$$\zeta_\beta = \frac{2\zeta_\pi + \zeta_\sigma}{3} \quad (C4)$$

and thus the terms linear in ζ_m compensate each other. The last contribution to E_m approximation determines

the energy difference:

$$\Delta E = -\frac{\Delta^2 (t_\sigma - t_\pi)^2}{8t_\sigma t_\pi (2t_\pi + t_\sigma)} < 0. \quad (\text{C5})$$

It basically means that the bonding structure with the σ/π -separation is lower in energy than that with the banana bonds.

Appendix 4. Interpolation of distance-dependent quantities

After we neglected the hybridisation dependence of the one-centre electron–electron interactions and replaced them by one single parameter g as in the CNDO approximation, it is logical to take the interatomic electron–electron interaction in this approximation as well. An explicit expression for the Coulomb interaction matrix element γ between electron distributions stemming from two 2sSlater AO's is known [30], but is too tedious to be given here. Fundamentally it goes about an exponential/polynomial interpolation between the Coulomb decay $\frac{1}{R}$ at a long range and the finite limiting value g at $R \rightarrow 0$. Thus, we follow the Sichel–Whitehead interpolation [34] for the two-centre Coulomb integrals by setting $V = \gamma$ and by this arrive to the monotonously decreasing Coulomb term

$$Z^2 \left(\frac{1}{R} - \gamma \right). \quad (\text{D1})$$

It eventually absorbs the opposite effects of the Coulomb interaction of the atomic charge distributions and Pauli repulsions between the latter [51]. More detailed treatment of these contributions will be performed elsewhere.

The limit of the two-centre Coulomb integral γ between the Slater 2s-AOs with an *orbital exponent* ξ produces the one-centre Coulomb integral

$$g = \frac{93}{256} \xi.$$

The quantity Δ defined in Section 2.4 flows to zero and is quadratic in R when $R \rightarrow 0$; thus, it can be considered to be small at short interatomic separations as it was necessary for obtaining the estimates for the $(\nu\nu\pi\pi)$ -energy in Section 3.3.

For the value of $\xi = 1.625$ characteristic for the carbon atom [32], the value of g is 15.93 eV. This is somewhat larger than the values recommended in different semiempirical parameterisations of the CNDO type being closer to 10–11 eV, but these latter load on this value smaller

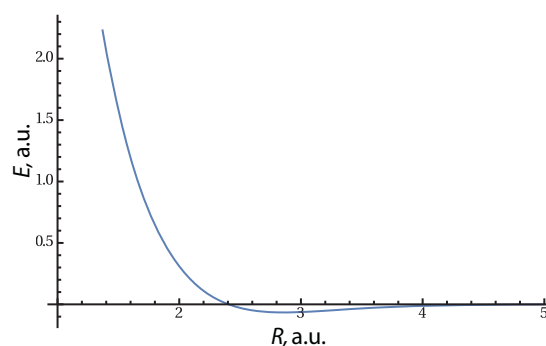


Figure 10. Energy profile for the reference $(\pi\pi)$ electronic structure with two π -bonds.

repulsions characteristic for p -AOs and the smaller inter-AO interactions. Comparing this value with the recommended ones for the energy scale of the resonance integrals (21 eV – CNDO/1, CNDO/2 [33]; 17.5 eV – CNDO/S [35]; 15 eV [36]) we conclude that taking g as an energy scale for the resonance integrals is an acceptable estimate. The distance dependence in all cases is taken as that of the overlap integral between the involved AOs: $t_{\mu\nu} = gS_{\mu\nu}$.

Now we are equipped to build the reference structure as described above. We supply the Coulomb interaction term Equation (D.1) by the energy of two π -geminals. The distance dependence of the electronic energy of the $(\pi\pi)$ reference model is depicted in Figure 10.

The presence of two π -bonds provides a shallow minimum of a depth of *ca.* 0.07 a.u. at the interatomic separation of 2.86 a.u. (1.52 Å). Remarkably, the reference energy profile is *not* one for the bond structure $|\text{C} = \text{C}|$ between *purely* divalent carbon atoms: the latter differ from that in Figure 10 by interatomic repulsion. In the $|\text{C} = \text{C}|$ structure, the effective atomic charges are vanishing whereas in the reference structure they are equal to two. By this, we finalise our preparations for the analysis of the energy profiles of various models of electronic structure of C_2 .

Appendix 5. Solution for the ν -geminals (A.M. Tokmachev)

Here we provide the information about the method used to calculate the energies of the ν -geminals used to construct the respective energy profiles in Section 4.2. Minimisation of the energy of the $(\nu\nu\pi\pi)$ -structure Equation (3.18) with respect to φ ($E'_\varphi = 0$) leads to a simple formula

$$\tan 2\varphi = \frac{(t_{\sigma\sigma} + t_{\xi\xi}) \tan 2\theta}{2t_{\xi\sigma} \tan 2\theta + U}. \quad (\text{E1})$$

Minimisation of the energy Equation (3.18) with respect to θ ($E'_\theta = 0$) is less trivial:

$$4U \cos 2\varphi \sin 2\theta - 4(t_{\sigma\sigma} + t_{\zeta\zeta}) \sin 2\varphi \cos 2\theta - 8t_{\zeta\sigma} \cos 2\varphi \cos 2\theta + 4\Delta \sin 2\theta \cos 2\theta = 0. \quad (\text{E2})$$

Like in Section 3.3, we formally express $\cos 2\theta$ through $\sin 2\theta$ and neglect the powers of $\sin 2\theta$ in the expansion of the square root. This yields a quadratic equation for

$\tan 2\theta$ whose solution is

$$\tan 2\theta = \frac{\mu + \sqrt{\mu^2 + 16t_{\zeta\sigma}^2 U (U + \Delta)}}{4t_{\zeta\sigma} (U + \Delta)}, \quad (\text{E3})$$

where

$$\mu = 4t_{\zeta\sigma}^2 + (t_{\sigma\sigma} + t_{\zeta\zeta})^2 - U (U + \Delta). \quad (\text{E4})$$

Substitution of φ, θ given by Equations (E.1) and (E.3) into Equation (3.18) yields the required result.