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Chemical Bonding in "Simple" Compounds

Valence Bond Analysis of Carbon Monoxide, Dioxide and Suboxide

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Contents

1	Summary	2
2	Introduction	3
2.1	Analytical methods	5
2.2	Carbon monoxide, CO	6
2.3	Carbon dioxide, CO ₂	7
2.4	Carbon suboxide, C ₂ O ₃	7
3	Theory	10
3.1	Valence Bond Theory	11
4	Computational details	14
4.1	Geometry optimization	14
4.2	Valence Bond calculations	14
5	Results	16
5.1	Geometry optimization	16
5.2	Carbon monoxide, CO	16
5.3	Carbon dioxide, CO ₂	19
5.4	Carbon suboxide, C ₃ O ₂	22
6	Conclusions	27

1 Summary

Quantum mechanical studies show that there is a new class of compounds called carbone, with the general structure of CL_2 , where the carbon retains two lone pairs and L, the ligands, donate their electrons, forming dative bonds with the divalent (0) carbon.

A Valence Bond analysis of carbon monoxide, dioxide and suboxide allowed to investigate the nature of the bonding scheme and definition of these molecules, as an attempt to clarify whether they can be classified as carbones. For carbon dioxide the already known linear structure with two double bonds has been confirmed, while for carbon monoxide and suboxide it was found that the use of bond arrows is more appropriate, indicating the presence of dative rather than covalent bonds. While carbon monoxide is characterized by both covalent and dative bonds that generate a triple-bond structure, carbon suboxide's main contribution is from the dative bond perspective, thus making it a carbone.

2 Introduction

Carbon is one of the most important elements of the periodic table, being one of the corner stones of organic life on Earth. Its versatility allows it to form a wide variety of bonds, ranging from covalent single, double and triple bonds, which can be formed with virtually every other atom of the periodic table. In most of these situations, carbon is found in its tetravalent state, in which it generates rather stable compounds; however, in the 1950s, the first molecules with a divalent (II) carbon, carbenes, were found and introduced into organic chemistry by Doering [1]. Carbenes are neutral unstable compounds where carbon remains with two unshared valence electrons; an example of a carbene is dichlorocarbene, CCl_2 .

Recently, theoretical and experimental results have identified a new class of compounds where carbon is found in its divalent (0) state, meaning that its oxidation state is zero: carbones. The peculiarity of these molecules is that the carbon's electrons appear not to participate in the bonding and the atom remains with a lone pair in one of the $2p$ orbitals; thus, the bonding of these molecules, generally with the structure of CL_2 , where L is a ligand, is comprised of two donor-acceptor bonds: $\text{L} \rightarrow \text{C} \leftarrow \text{L}$. Figure 1 displays a schematic representation of the bonding scheme in CL_2 , with the ligands behaving as π donors into the empty $2p$ orbitals of the carbon.

Firstly, it is perhaps important to define what the difference between a covalent and a dative bond is, concepts introduced into Chemistry by Lewis, in his book "Valence and the structure of atoms and molecules" [2]. When the two electrons forming the bond come each from one atom, there is a covalent bond; when the two electrons come only from one of the two atoms forming the bond, it is said to be a dative bond. When the bond is formed it is impossible to state where the electrons came from, due to the fact that they are indistinguishable. One way to classify the type of bond is by looking at the fragments obtained once it is broken: depending on if it breaks homolytically or heterolytically it can be interpreted as a covalent or a dative bond, respectively [3]. Moreover, dative bonds have been classified as rather weak, longer than single covalent bonds and with a small degree of charge transfer [4].

The first isolated synthesized carbene was hexaphenylcarbodiphosphorane, $\text{C}(\text{PPh}_3)_2$ by Ramirez in 1961 [5]. Figure 2 represents the bent structure of $\text{C}(\text{PPh}_3)_2$, and reports values both from theoretical and experimental results (in italics). There are two peculiar properties of this molecule which arose doubts about what types of bonds are present between the phosphorus and carbon: the molecule was found to be bent in the solid state through X-Ray diffraction analysis, with angles ranging from 130.1 to 143° [8, 9], rather than being linear as expected, with C-P double bonds. In fact, carbon-phosphorus bonds in carbodiphosphoranes had usually been classified as diylides, with structures resonating between double bonds and two negative

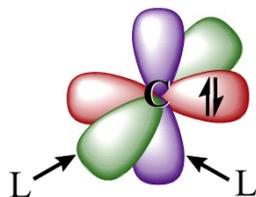


Figure 1: *Schematic representation of the bonding situation in carbene.*

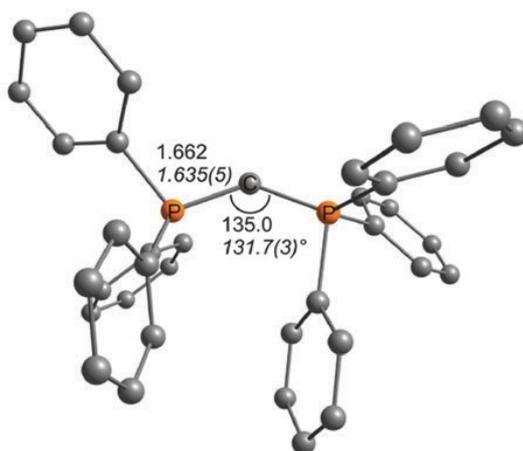


Figure 2: *Representation of the first synthesized carbene, carbodiphosphorane; picture taken from Frenking et al. (2014) [6]. The values reported are from DFT calculations [7], while in italics are reported the experimental ones [8].*

charges on the carbon and one on each phosphorus. Secondly, its peculiar reactivity provides support to the presence of dative bonds rather than covalent ones; in fact, the molecule was found to be an effective ligand, able to bind to several metals and non-metals. Implementing experimental results with theoretical ones, the best description for the bonding characteristics of $\text{C}(\text{PPh}_3)_2$ was given in 2006 by Frenking, stating that they can be described in terms of donor-acceptor bonding rather than electron-sharing ones, with carbon in its ^1D state [10]. When carbon is in the ^1D state, its electronic configuration is $[\text{He}]2s^22p_x^02p_y^02p_z^2$: the two vacant p orbitals will serve as π and σ acceptors from the ligand orbitals; thus the carbon would retain two lone pairs, and for this reason is considered a ‘naked atom’. Furthermore, by looking at the molecular orbitals, it is possible to identify the HOMO as a π type lone-pair orbital, while the HOMO-1 presents a σ lone-pair character, as one would expect by the ^1D electronic configuration. From these

findings, the search for other complexes presenting the same properties as carbodiphosphorane started: molecules such as $C(NR_2)_2$ and $C(CR_2)_2$ were theoretically investigated [7].

The introduction of this class of compounds has, however, caused some controversies in the scientific environment. According to Himmel *et al.* [4], in fact, the use of bond arrows in order to describe the structure of main-class compounds has been used with exaggerating frequency and as a marketing device, as the concept of donor-acceptor carbon complexes is a valid yet not entirely new concept [11]. Moreover, the authors point out the importance to use notations that are in agreement with the results of experiments and the general properties of the molecules. In the following investigation, a comparison between experimental and theoretical results will be presented. Moreover, the calculations have been performed using Valence Bond Theory, as all other data found in literature has approached the problem by using Molecular Orbital Theory instead; it is hoped that this alternative method will allow to determine whether the use of bond arrows is an appropriate description for the structure of a few specific molecules.

2.1 Analytical methods

Since the publication of the 2006 paper from Frenking, introducing for the first time dative bonds in order to describe bonds in carbones, several experimental and theoretical analyses of a few different molecules have been described using the same model. The main analysis tool used in order to investigate the properties of carbones has been calculations of proton affinities (PA), where the molecules displayed a high second PA, due to the high electron density at the central carbon even after the removal of the first electron; analysis of the donor strength showed that carbones are strong electron donors, able to bind two ligands [12]. In these cases, experimental and theoretical values come to good agreement. Calculations of the energy decomposition analysis (EDA) have often been performed as well, allowing a calculation of the instantaneous interaction energy; EDA specifies the importance of the contribution from the electrostatic interaction, the exchange energy (Pauli interaction) and the orbital interaction, due to orbital mixing and relaxation. The interaction energy can provide detailed information about donor-acceptor interactions, reveal the strength of the π and σ contribution to the bonding, thus giving insight into the type of bonding between the atoms or fragments of molecules [13]. In conclusion, numerous molecules that can be classified as carbones have been identified and studied in various different ways, with experimental and theoretical results supporting one another.

In the study here presented, the concepts from the above behavior of carbon were analyzed in three molecules, CO, CO₂ and C₃O₂, in order to attempt to define a precise bonding description. The analysis was performed

using Valence Bond Theory (VB), which allows the contribution of each atom to the bonding of the molecule to be specifically determined and, in particular, to determine which atomic state of the atoms has greater weight, thus giving insight to the electronic configuration of the atom as it is bonded. In order to do so, the term symbols for each atom are determined, allowing the description of its electronic configuration by expressing the angular momentum (a.m.) quantum numbers in the contracted expression ^{2S+1}L : S is the total spin a.m., while L is the total orbital a.m.. As L and S are vector operators, which commute with the atomic Hamiltonian, it is possible to determine the eigenfunctions of the Hamiltonian in terms of L and S, which then represent the length of the vectors of the operators. By attributing the term symbol, the term for the eigenfunction of the Hamiltonian is defined, giving the energy level of that specific configuration as well. Carbon, in its ground state, can be found either in a singlet (1S or 1D) or a triplet (3P) state; if the hybridized configuration is taken into account as well, it can be found in a quintet (5S) state. Oxygen can, as well, be found in either a singlet (1S or 1D) or triplet (3P) state. All possible configurations and combinations thereof are taken into account in the Valence Bond analysis. Moreover, as ionic structures are taken into account as well, Table 1 displays all the possible term symbols in which the atoms under investigation can be found.

Table 1: *All possible term symbols for the different configurations of carbon and oxygen both in the neutral and ionic states.*

Species	Term symbols
C, O	$^1S, ^1D, ^3P$
C^+, O^-	2P
C^-, O^+	$^2P, ^2D, ^4S$

2.2 Carbon monoxide, CO

The most common picture of carbon monoxide, given by MO, is that of a triple bond (the bond order is indeed 3), comprised by two covalent and one dative bonds [14]; this is further supported by an experimental bond length of 112.8 pm [15]. Moreover, the molecule retains an intrinsic dipole moment, which was found experimentally to be of 0.112 D, which can be represented by having a negative charge on the carbon and a positive one on the oxygen. This is however counterintuitive, as the oxygen is more electronegative than carbon and thus a negative charge on the oxygen atom would further stabilize the molecule. By investigating the bonding of carbon monoxide, different Lewis structures can be drawn, as displayed in Figure

3, comprising of one covalent and two ionic configurations, where the bond shifts from single to double to triple. By including all three structures, a complete VB wavefunction for this molecule can be obtained.

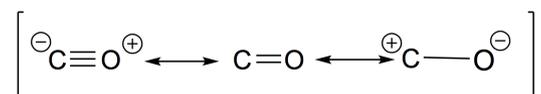


Figure 3: *Schematic representation of the covalent and ionic structures of carbon monoxide.*

2.3 Carbon dioxide, CO₂

Carbon dioxide, according to MO theory, is also commonly depicted with two C-O double bonds; this is indeed supported by experimental bond lengths of 116.1 pm and a linear bond of 180° [16]. Now, the molecule can be represented either with two covalent double bonds (with carbon being *sp* hybridized), or with dative bonds. The former case implies that carbon is in its excited ⁵S state and the two oxygen atoms are in their ³P ground state. Thus, promotion energy (energy needed to excite the atom from its ground state to its excited one) is needed in order to excite the carbon: ³P→⁵S, excitation of 94.4 kcal/mol. On the other hand, however, if the molecule was depicted with dative bonds, promotion energy would be needed both for carbon (³P→¹D, transition of 29.1 kcal/mol) and for the two oxygen atoms (³P→¹D, transition of 45.3 kcal/mol); thus, the overall cost of these transitions would be of 119.9 kcal/mol, which is more than the previous case [17]. It would therefore be expected that the best way to represent the bonds in carbon dioxide is by double bonds rather than dative ones, as they are more energetically favored (Figure 4).

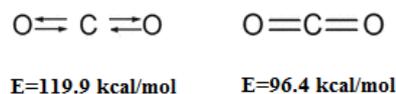


Figure 4: *Schematic representation of the covalent and dative structures of carbon dioxide, with the respective promotion energies.*

2.4 Carbon suboxide, C₂O₃

Carbon suboxide played a particularly important role in the development of carbonates. Its structure has been investigated since the 1950s, trying to find satisfactory answers to observations of the infrared spectrum of the fine structure; despite the fact that contrasting results have been obtained, the

molecule is now commonly defined as quasi-linear. The vibrational amplitudes display deviations from linearity, due to a very low barrier for bending around the central carbon atom, which only differs slightly from the vibrational ground state. Koput *et al.* [18] investigated the molecule by an *ab initio* theoretical study on the structure and the bending energy levels; the calculations were performed with the coupled-cluster method (CCSD(T)), while the bending analysis was done by using a semi-rigid bender Hamiltonian. The barrier between the bent and linear structures of the molecule was found to be 0.0513 kcal/mol (18 cm^{-1}), thus making it quite difficult to determine its favored state. In particular, the C-C-C bond angle was found to have a minimum at 157° , found by treating carbon suboxide as a semi-rigid bender [19]. Considering that there is quite some controversy in literature concerning this molecule, another way to analyze its type of bonding is by looking at the bond lengths. Table 2 compares some values found in literature: computationally calculated bond lengths and the experimental values; the first ones calculated using the coupled-cluster method, CCSD(T), while experiment of the solid state of carbon suboxide led to the latter results.

Table 2: *Theoretical and experimental values for the bond lengths (pm) of carbon suboxide.*

	Theoretical ¹	Experimental ²
C-C	128.4	125.1
C-O	116.4	114.6

The results appear to be in agreement, deviating from each other only by 2-3 pm; furthermore, the values for both the C-C and C-O bonds indicate that they can be represented as double bonds. However, when taking into account that the bent structure presents a C-C-C angle of 157° , it seems rather counterintuitive to draw double bonds when there is no linearity. Thus, an alternative depiction of the bonding situation for this molecule can be given as $\text{OC}\rightarrow\text{C}\leftarrow\text{CO}$, as proposed by Frenking [7]. If the molecule is linear, and the central carbon forms double bonds with the two neighboring carbons, it would be found primarily in its hybridized ^5S state; in the structure proposed by Frenking, the bonds between the $-\text{CO}$ moieties and the central atom could be described as dative bonds, implying that the central carbon retains two lone pairs and thus would be found in its ^1D state. By applying the same method as for carbon dioxide, a comparison between the two representations can be given by looking at the cost of the promotion energies. If the molecule is represented by dative bonds, the only

¹[20]

²[18]

cost from the ground state is the ${}^3\text{P}\rightarrow{}^1\text{D}$ transition of the carbon, while the -CO moieties remain in their ground state; thus the overall cost is of only 29.1 kcal/mol. In the other case, that of covalent double bonds, two transitions need to be taken into account: ${}^3\text{P}\rightarrow{}^5\text{S}$ for carbon, and ${}^1\Sigma\rightarrow{}^3\Pi$ (from the singlet to the triplet state) for -CO, with a cost of $139.3\times 2=278.6$ kcal/mol. The total promotion energy would be 375.0 kcal/mol, thus much more energetically unfavorable with respect to the dative-bond picture [17].

3 Theory

The early XXth century was a revolutionary period for the progress made in physics, which led to the foundation of Quantum Mechanics. It originated from the need to look for explanations to several experiments to which classical Physics could not give answers to; observations such as the black-body radiation, the photoelectric effect, atomic spectra and, in general, issues concerning microscopic bodies required the development of new interpretations and justifications. Thus, with the contributions of several physicists, starting from Planck and his concept of quantized energy, to Bohr's vision of the atom, to Schrödinger's equation, Quantum Mechanics established itself as the subject trying to provide answers for the phenomena occurring in nature at the atomic scale. The basis of QM relies on the introduction in Physics of the wavefunction, which fully describes the state of a system: $\psi(r_1, r_2, \dots, r_n, t)$, where r_1, r_2, r_n represent the spatial coordinates of particles 1, 2, ..., n that form the system under consideration, while t is the time. The wavefunction contains all information about any experimental property of the system. It is a solution to the non-relativistic Schrödinger equation (Equation 1), where H is the Hamiltonian, the energy operator, which is the sum of the kinetic and potential energy for the system.

$$i \frac{\hbar}{2\pi} \frac{\partial}{\partial t} \Psi(x, t) = \hat{H} \Psi(x, t) \quad (1)$$

Furthermore, often the interest is not in how the system changes over time, but rather only in the change over space, thus the problem is restricted to the time-independent Schrödinger equation, and, the wavefunction, now $\psi(r_1, r_2, \dots, r_n)$, is a solution to the stationary equation (Equation 2), where ε is the eigenvalue of the Hamiltonian, that is the energy of the system.

$$\hat{H} \Psi(x) = \varepsilon \Psi(x) \quad (2)$$

Although it may seem that Equation 2 is easy to solve, the number of variables when considering many-particles bodies rapidly increases and the differential equations become rather complex to solve. In fact, analytical solutions can only be given for very few systems, such as the hydrogen atom. This means that approximations need to be made in order to approach results close to the reality of the system. The main one is the Born-Oppenheimer approximation, which considers the nuclei as fixed particles compared to the electrons, as nuclei have a much greater mass; the Schrödinger equation is then solved only for the electrons, which instantaneously respond to the electric potential caused by the nuclei. Now, the electronic wavefunctions depend on the nuclear coordinates, meaning that to each different arrangement of the molecule or atom, corresponds a different wavefunction.

3.1 Valence Bond Theory

In this framework, QM has developed two methods in order to describe the electronic structures in molecules from a chemical point of view, Molecular Orbital Theory (MO) and Valence Bond Theory (VB). Although the starting point for writing the wavefunction differs significantly, these two approaches can simply be considered two different interpretations of the same reality, rather than two contrasting theories. In MO theory, which was developed by Mulliken and Hund, the electrons of the atoms, once they have formed a bond, are found in molecular orbitals, distributed over the entire molecule, given by a linear combination of atomic orbitals. Thus, the atomic orbitals are allowed to fully mix and combine; their wavefunctions can combine either in phase (constructive interference), leading to a bonding MO, or out of phase (destructive interference), leading to an anti-bonding MO. These newly generated molecular orbitals can then be filled according to the same rules as AOs. On the other hand, VB is based on atomic orbitals that, when atoms form molecules, overlap between each other, but still retain their initial character. VB theory finds its origin after the introduction of the octet rule and the concept of electron-pair bonding, developed by Lewis in his ground-breaking paper “The Atom and The Molecule” [21], which later led him to describe bonding in molecules as either covalent or ionic, depending on the shift of the electron-pair that forms the bond. His innovative concepts were the basis for the subsequent understanding of the chemical bond and greatly contributed to the development of quantum mechanics, as well as that of Valence Bond Theory. In fact, based on Lewis’ ideas, Heitler and London (H-L), two German physicists, with the help of Schrödinger, developed a bonding scheme for H_2 . The bond in the H_2 molecule was described by a wavefunction written as a superposition of two covalent structures, one in which electron 1 has spin α and one in which it has spin β , as shown in Equation 3.

$$\Psi_{HL} = (1s_1(1)1s_2(2) + 1s_1(2)1s_2(1))(\alpha(1)\beta(2) - \beta(1)\alpha(2)) \quad (3)$$

The bond could then be seen as a resonating structure between these two different spin-configurations; however, to obtain a complete picture of the bonding situation of H_2 , later on, Pauling included two possible ionic structures as well; all possible spin configurations for the molecule are shown in Table 3. Ionic structures often represent the greatest contribution to the bonding of molecules, and therefore, including those structures as well, allowed to write the full VB wavefunction for H_2 .

Considering the H_2 bonding description as the starting point of VB, a general wavefunction is shown in Equation 4: Ψ is a multi-determinant linear combination of VB structures.

$$\Psi_{VB} = \sum_i c_i \phi_i \quad (4)$$

Table 3: *All possible spin configurations for H₂.*

H ₁	H ₂
↑	↓
↓	↑
	↑↓
↑↓	

ϕ_i represents each VB structure, an anti-symmetrized product of one-electron atomic orbitals, ϕ and N-electron spin functions, $\Theta(N, S, M_S, i)$ (Equation 5) [22]:

$$\phi_i = \hat{A}\varphi_1\varphi_2\dots\varphi_N\Theta(N, S, M_S, i) \quad (5)$$

The number of determinants in the wavefunction varies exponentially with the number of bonds present in the molecule under consideration, namely 2^n (n being the number of bonds) [23]. The main characteristic of VB AOs is that they do not need to be orthogonal, making it difficult to use VB when describing large molecules. The difficulty arises because, in order to get closer to the true ground energy of the system, approximations are made to optimize the wavefunction describing, in this case, the atomic orbitals. One way to do so is by using the variational principle, based on defining a trial wavefunction (Ψ_{trial}) and calculating its expectation value, as shown in Equation 6; Ψ_{trial} is written as a linear combination of eigenfunctions of the Hamiltonian, which depend on variational parameters found so that the energy with the lowest value can be determined.

$$E = \frac{\langle \Psi_{trial} | \hat{H} | \Psi_{trial} \rangle}{\langle \Psi_{trial} | \Psi_{trial} \rangle} \quad (6)$$

Thus, the expectation value needs to be minimized: its first derivative is set to be equal to zero and Equation 7 is obtained, a set of simultaneous equations for the coefficient c_j , where H_{ij} is the exchange integral and S_{ij} is the overlap integral; the condition for the equation to be true is that the secular determinant is equal to zero, Equation 8.

$$\sum c_j (H_{ij} - ES_{ij}) = 0 \quad (7)$$

$$\det | (H_{ij} - ES_{ij}) | = 0 \quad (8)$$

Now, the determinant needs to be solved: if the wavefunctions are assumed to be orthogonal, the overlap integral, S_{ij} , is zero when i and j are different. This greatly simplifies the problem, as only the H_{ij} non-diagonal elements of the determinant need to be determined, and not the overlap

integrals [24]. On the other hand, as occurs in VB, if the wavefunctions are not assumed to be orthogonal to each other, each S_{ij} integral present in the secular determinant needs to be specifically calculated, thus making the overall calculation rather complex [25]. One drawback of this property of the VB orbitals is that, now, the square of the coefficients no longer sums up to one, and it cannot be stated directly which structure is the most relevant one. Thus, different ways of assigning a weight to each structure have been developed; the one used in this study was suggested by Gallup and Norbeck, as displayed in Equation 9:

$$w_k^{\text{GN}} = \frac{N_{\text{GN}}c_k^2}{(S^{-1})_{kk}} \quad (9)$$

Where w_k^{GN} is the Gallup-Norbeck weight of the k th structure with its respective coefficient c_k , $(S^{-1})_{kk}$ is the kk th element of the inversed overlap matrix and, finally, N_{GN} is the normalization constant [26].

Moreover, Valence Bond theory can be applied with different methods, each one describing AOs in molecules differently. *Localized VB* constrains the orbitals to remain fully localized on their original atom, an example is the H-L wavefunction for H_2 (Equation 3), where the covalent and ionic structures need to be explicitly generated; *Delocalized VB* allows the orbitals to freely delocalize over two or more centers. In the latter case, an example is given by the Coulson-Fischer wavefunction for H_2 , which can be considered a correction to the previous one: the delocalized orbital is obtained by adding a contribution from other AOs, as shown in Equation 10; this approach allows for greater degree of freedom of the wavefunction and for the orbitals to obtain an optimal shape.

$$\begin{aligned} \phi_a &= a + kb \\ \phi_b &= b + ka \\ \Psi_{\text{CF}} &= |\phi_a\bar{\phi}_b| - |\bar{\phi}_a\phi_b| \end{aligned} \quad (10)$$

Finally, the last VB method is one that involves *Fragment Orbitals*, it is used if the analysis of the molecule is wanted only for a specific part. The wavefunction of the fragment of the molecule is still a linear combination of determinants based on AOs, which only overlap weakly with the remaining part of the molecule [27].

4 Computational details

4.1 Geometry optimization

The program MOLDEN was used in order to initially draw and visualize the molecules of interest. The calculations to optimize their geometries were performed using the cc-pVTZ basis set, a correlation consistent basis set that includes larger shells of polarization functions and comprises only of valence sets (includes functions that only describe the valence orbitals) [28]. The level of theory used was second-order Moller-Plesset perturbation theory (MP2), a post Hartree-Fock method which also includes electron correlation effects. It is a simple method that allows an *ab initio* description of the physical interactions (electrostatic, polarization, etc.) and defines dispersion interactions explicitly [29].

4.2 Valence Bond calculations

All VB calculations were performed using the *ab initio* program TURTLE, implemented in the GAMESS-UK package [30]. As VB describes bonding in molecules as the pairing of spins, in order to obtain all VB structures and their weight, all possible configurations of the molecule were needed; a program (GENCONF) that could generate all configurations was indeed used. After stating the number of core and valence orbitals, all possible electronic configurations of the atoms and the orbital overlap matrix, GENCONF gave all configurations for the molecule. These were then used to perform the VB calculations in TURTLE, which automatically generates also all possible spin-configurations.

During the analysis, the basis set used was 6-31G, which is a smaller one than that used in the geometry optimizations, as the overall calculation is more complex and time-consuming. This basis set includes, for the core orbitals, six primitive Gaussian functions; for the valence orbitals, two basis functions each, one comprised of three primitives and one of one primitive only. Moreover, the VB orbitals are optimised with Perturbation Theory, used in order to excite the electrons from double to unoccupied orbitals.

Furthermore, the calculations for CO and CO₂ were performed using *Localized VB*; this was made explicit when the atomic orbitals were attributed to each atom specifically, thus not allowing the mixing of any. For C₃O₂, instead, *Fragment Orbitals VB* was used, where the -CO moieties were treated as one fragment, thus simplifying the overall description of the molecule. Moreover, in order to obtain hybrid orbitals, as in the case of CO₂ and C₃O₂, the orbitals were mixed by creating combinations of the $2p_z$ and the $2s$ orbitals, made explicit, once again, when defining the atomic orbitals corresponding to each atom. In the case of CO₂ and C₃O₂, the calculations were performed including only a few configurations to describe the molecules, in order to diminish their expense; namely, the structures with

carbon in the 1D and 5S states, which represent, respectively, the covalent and dative bonding descriptions of the molecules.

5 Results

5.1 Geometry optimization

Table 4 displays the optimized geometries of the three molecules analyzed. The results for carbon monoxide and dioxide appear to be in good agreement

Table 4: *Optimized geometries for CO, CO₂ and C₃O₂, displaying the bond lengths (pm) and bond angles.*

Molecule	Bond length	Bond angle
CO	1.1344	
CO ₂	1.1649	180°
C ₃ O ₂	C-C	180°
	C-O	1.1659

with values found in literature and previously mentioned in Section 2 [15, 16]. In the case of carbon suboxide, while the results for the bond length are in line with the ones previously reported [20], the bond angle was found to be 180°. In particular, in order to find the optimized geometry for carbon suboxide, several calculations were ran with different initial structures; the one with lowest energy, however, was found to be the linear structure, and thus was used to perform the VB calculations.

5.2 Carbon monoxide, CO

Carbon monoxide was represented by generating configurations through the program GENCONF: 59 different spin-configurations were found, which originated from 46 different configurations. Firstly, the final Valence-Bond energy of the molecule is -112.773996 Hartree, which is lower than the HF energy calculated ($E_{HF}=-112.667187$ Hartree). This is indeed expected, as the VB calculation is more complex, including, in this case, a total of 281 determinants, compared to the single Slater-determinant used in HF. VB proposes a more complete picture of the molecule, which allows to get closer to its real ground state energy.

Table 5 displays the main different electronic configurations with the respective weights. The $2p_{xyz}$ orbitals are abbreviated to the xyz notation, and different colours for each orbitals have been used in order to underline the coupling of the electrons between the carbon and the oxygen (green for the x , purple for the y and red for the z orbital); the same colour preference is preserved when visualizing the orbitals, as well as for the results displayed in the next sections. There are two main structures - one covalent and one ionic - each represented by three different electronic configurations, two of which have the same weight; this can be explained by looking at the orbital

occupations. In fact, when the $2p_z$ orbital is involved in the bonding, the configuration has a greater weight. The $2p_z$ orbitals are the ones along the internuclear axis, thus forming a σ bond, which presents a greater orbital overlap than when the $2p_{x,y}$ orbitals form a π bond.

It is important to notice the overall importance of the two structures: the covalent configurations add up to a total weight of 0.4555, while the ionic one to 0.3705. It is typically expected that the purely covalent structure has a weight of about 75% [23], which is higher than in this case; however, there are few more configurations with low weights (<0.03) that have not been reported in Table 5, but that contribute as well to the total covalent structure.

Table 5: *Weights of the main electronic configurations for carbon monoxide with respective energies (Hartree). Different colours indicate the spin-coupling between the carbon and oxygen electrons.*

		Electronic configuration	Weight of the structure	Energy of the structure
C, O				
1	C	$1s^2 2s^2 x^1 y^1 z^0$	0.1317	-112.122051
	O	$1s^2 2s^2 x^1 y^1 z^2$		
2	C	$1s^2 2s^2 x^1 y^0 z^1$	0.1619	-112.362635
	O	$1s^2 2s^2 x^1 y^2 z^1$		
3	C	$1s^2 2s^2 x^0 y^1 z^1$	0.1619	-112.362635
	O	$1s^2 2s^2 x^2 y^1 z^1$		
+C, O⁻				
4	C	$1s^2 2s^2 x^1 y^0 z^0$	0.1117	-111.998420
	O	$1s^2 2s^2 x^1 y^2 z^2$		
5	C	$1s^2 2s^2 x^0 y^1 z^0$	0.1117	-111.998420
	O	$1s^2 2s^2 x^2 y^1 z^2$		
6	C	$1s^2 2s^2 x^0 y^0 z^1$	0.1471	-112.136451
	O	$1s^2 2s^2 x^2 y^2 z^1$		
			E_{HF}	-112.667187
			E_{VB}	-112.773996

Moreover, the Table displays the energies of each structure, which are in line with the respective weights: the greater contributors to the bonding, structure n. 2 and 3 have the lowest energies, while n. 4 and 5 the highest. As the weights of these structures are the same, it is also expected that they have the same energies; the two remaining structures, n. 1 and 6, have values in between the other ones. Figure 5 displays a visualization of the orbital scheme for carbon monoxide, in particular the structures n. 1, 2 and 3 from Table 5. In structure n. 1, represented in Figure 5.A, the electrons of the $2p_x$ and $2p_y$ of the oxygen and carbon are coupled together, and the

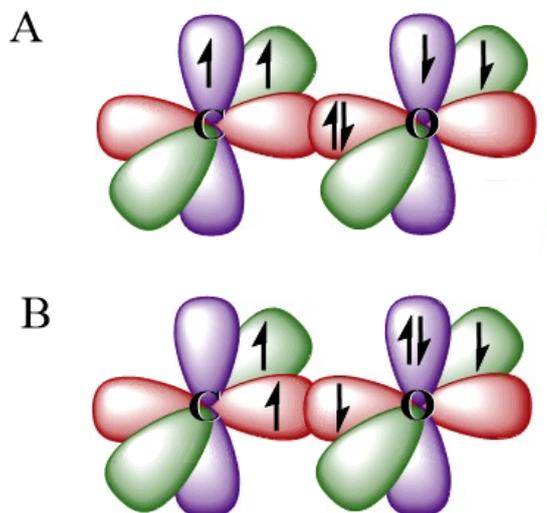


Figure 5: *Visualization of the orbital scheme for A structure n.1; B structures n.2,3.*

$2p_z$ (in red) of the oxygen is doubly occupied. Firstly, it is important to specify that the electrons represented with the arrows up or down do not correspond necessarily to spin α and β , it is simply a convention to underline the coupling between the electrons of the two atoms (thus, they could be both down on the carbon and both up on the oxygen). Secondly, the fact that the $2p_z$ of the oxygen is doubly occupied, while that of carbon is empty, implies the presence of a dative bond: the $2p_z$ of the oxygen will overlap with that of carbon, thus allowing the electrons to delocalize over the two orbitals. In particular, as this occurs over the internuclear axis, the oxygen behaves as a σ donor. In Figure 5.B, instead, structures n. 2 and 3 are represented: the key idea here is that the doubly occupied orbital of the oxygen now is no longer the one along the internuclear axis, but either in the $2p_x$ or $2p_y$ orbital (in this case, the purple orbital is either the $2p_x$ or $2p_y$). Therefore, the dative bond is now characterized by π symmetry.

The description reported is indeed confirmed by the results shown in Table 6, where the overlap coefficients between the orbital of the atoms are displayed. The largest overlap is indeed that between the $2p_z$ orbitals of the carbon and oxygen, where either a covalent or a dative σ bond is present. The overlap between the $2p_x$ and $2p_y$ orbitals is the same, due to the degeneracy of the two; their overlap is smaller than that of the $2p_z$ one, as the orbitals are no longer along the internuclear axis and can only interact through π bonding. Moreover, the Table shows a small overlap between the

Table 6: *Overlap of the orbitals of carbon monoxide. The greatest coefficients are highlighted in red.*

Orbital 1	Orbital 2	Overlap
C(2s)	O(2s)	0.1313
	O(z)	0.2506
C(x)	O(x)	0.2956
C(y)	O(y)	0.2956
C(z)	O(2s)	0.2506
	O(z)	0.5423

2s orbital of the oxygen and both the 2s and 2p_z of the carbon.

From the above analysis, it would appear that the most precise way to depict carbon monoxide is by using dative bonds, as represented in Figure 6: structure A represents the first 3 configurations reported in Table 5, with two covalent and one dative bond; structure B represents the last 3 configurations reported, that is, the ionic one, which comprises of one covalent bond and two dative bonds. While structure A matches the general known representation of the molecule [14], no other reference to support the structure depicted in B was found in previous literature studies; nonetheless, the approach to derive structure A and B was the same, and therefore they should be considered equally valid.

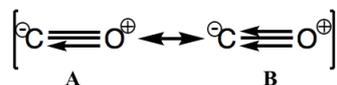


Figure 6: *Representation of the two main carbon monoxide structures: A two covalent and one dative bonds; B one covalent and two dative bonds.*

5.3 Carbon dioxide, CO₂

The calculations for carbon dioxide were heavier and more time-consuming than those for carbon monoxide. The results from the calculation which included only a few structures are displayed in Table 7. By using the program GENCONF, only two states of the carbon were here included, the ⁵S (with the oxygens in the ³P state), and the ¹D state (as well as for the oxygens). The former case is expected to be the most contributing one to the overall structure of the molecule, as the carbon is in its excited hybridized state, forming two double bonds with the oxygens; the latter case represents the expected configurations if the molecule was classified as a carbene. In total, 27 configurations were included, generating 144 structures, described by 648

determinants.

Table 7: *Weights of the main electronic configurations for carbon dioxide with respective energies (Hartree). Different colours underline the spin-coupling between the carbon and oxygen electrons.*

		Electronic configuration	Weight of the structure	Energy of the structure
1	C	$1s^2(\text{sp})_a^1(\text{sp})_b^1x^1y^1$	0.3823	-187.088185
	O ₁	$1s^22s^2x^2y^1z^1$		
	O ₂	$1s^22s^2x^1y^2z^1$		
2	C	$1s^2(\text{sp})_a^1(\text{sp})_b^1x^1y^1$	0.3825	-187.088214
	O ₁	$1s^22s^2x^1y^2z^1$		
	O ₂	$1s^22s^2x^2y^1z^1$		
3	C	$1s^2(\text{sp})_a^2(\text{sp})_b^0(x/y)^2z^0$	0.1864	-185.905991
	O ₁	$1s^22s^2x^2y^2z^0$		
	O ₂	$1s^22s^2(y/x)^2z^2$		
			E_{HF}	-187.514888
			E_{VB}	-187.173695

Firstly, it needs to be remembered that the carbon $2s$ and $2p_z$ orbitals were hybridized by creating linear combinations when defining AOs. The first two structures shown in the Table indeed correspond to the hybridized 5S state of the carbon. Moreover, the two structures have approximately the same weight and energy, as the only difference is the spin-coupling of the $2p_{x,y}$ orbitals between carbon and the first and second oxygen. As the $2p_{x,y}$ orbitals are degenerate, it would be expected that they present the same results; the slight difference implies that the symmetry of the molecule is, to some extent, lost, as no symmetry constriction was imposed in the input. Structure n. 3 represents the combined weights from two structures, which only differ in the $2p_{x,y}$ orbital occupation of the carbon and the second oxygen. These are the two structures which correspond to the dative representation of carbon dioxide (in other words, if it were to be considered a carbone): two lone pairs on the carbon, one lone pair on each oxygen, and one dative bond from each oxygen to the carbon (see Figure 4). Although it needs to be reminded that the weight reported actually comes from two different structures with equal weight (0.0931 each), it still represents a rather significant contribution to the overall bonding scheme of carbon dioxide. The energy of these two combined structure was found to be the same, as reported in the Table; the energy value is now much higher than that of the previous two structures, thus supporting the fact that they contribute less to the overall structure of the molecule, as more energetically unfavorable.

Figure 7 displays a visualization of the bonding scheme for carbon diox-

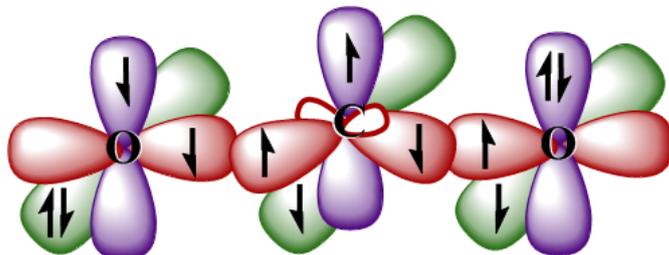


Figure 7: Visualization of the orbital scheme for structures *n. 1* and *2* of carbon dioxide; the carbon atom now retains two equivalent *sp* orbitals, each of which overlaps with the $2p_z$ orbital of the oxygens.

Table 8: Overlap of the orbitals of carbon dioxide. The greatest coefficients are highlighted in *red*.

Orbital 1	Orbital 2	Overlap
C(sp) _a	O ₁ (2s)	0.2950
	O ₁ (z)	0.6228
	C(sp) _b	0.1334
C(sp) _b	O ₂ (2s)	0.2887
	O ₂ (z)	0.6265
C(x)	O _{1,2} (x)	0.3167
C(y)	O _{1,2} (y)	0.3187

ide, built in the same way as for carbon monoxide; once again, the arrows up or down do not represent necessarily the α or β spins, but are used in order to clarify the spin-couplings between the carbon and the oxygens. The two *sp* hybrid orbitals of carbon are represented in *red*, both coupled with a $2p_z$ orbital from each oxygen. The Figure allows to represent the first two structures reported in Table 7, as the *purple* orbital can be either the $2p_x$ or the $2p_y$. From this representation it is possible to notice the presence of one σ and one π bonds between the carbon and each of the oxygens. Moreover, further information regarding the orbital scheme can be given by Table 8, which reports the overlap between the different orbitals of the molecule. Firstly, it can be seen that there is a small overlap between the *sp* orbitals of carbon, each of which also greatly overlaps (overlap >0.62) with the $2p_z$ of the oxygens, thus confirming the presence of a σ bond. A smaller overlap (overlap ~ 0.317 , half of the latter one), in fact, can be seen between the other $2p_{x,y}$ orbitals, where the π bonds are; the overlaps have, in this case, approximately the same value, as the two *x*, *y* orbitals are degenerate, however, the small difference indicates, as previously mentioned and thus here

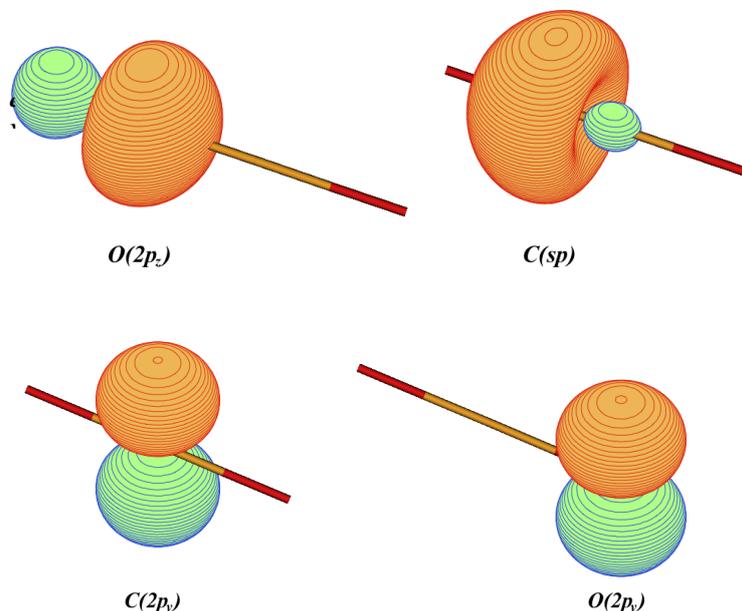


Figure 8: Visualization of the orbital $2p_z$ of the oxygen and the sp orbital of carbon (above); the $2p_y$ orbitals of both the carbon and the oxygen (below).

confirmed, that symmetry is, to some extent, lost. Figure 8 displays the orbitals forming a σ (above) and a π (below) bond: the $2p_z$ of the oxygen and the sp orbital of the carbon in the former case, the $2p_y$ of the carbon and of the other oxygen in the latter case. The images were taken from the molecule visualizer MOLDEN, where the output of the calculation allowed to visualize all optimized atomic orbitals. When forming the σ bond, it is possible to notice that the two orbitals point toward each other with the same colour, indicating a constructive overlap of the two. Secondly, it can be seen that in the case of the sp and $2p_z$ the orbitals slightly delocalize over the neighboring atom, while in the other case the delocalization is much smaller, as was already confirmed by the orbital overlaps reported in Table 8.

From the above analysis, the most appropriate way to depict carbon dioxide is with two covalent bonds between the atoms, with each of the oxygen atoms retaining one lone pair, confirming the initial hypothesis of the linear structure of this molecule.

5.4 Carbon suboxide, C_3O_2

The same approach as for carbon dioxide was used for analyzing carbon suboxide as well: one calculation was performed including only a few structures

which would be expected to be the most important ones. Firstly, as previously mentioned, the *Fragment Orbitals VB* method was used to describe the molecule. In order to do so, the results from the carbon monoxide calculations were used to observe the orbital symmetry and to derive a bonding scheme: the first 6 orbitals of the molecule are always doubly occupied, while the two remaining electrons can be placed either in an orbital with σ , π_x or π_y symmetry. The electronic configurations where the fragment is either in its $^3\Pi$ or $^1\Sigma$ states and with carbon in, respectively its 3P or 1D states were included. A total of 16 structures were taken into account, generating 68 configurations described by 292 determinants; the results are displayed in Table 9. To simplify the display of the results, only the valence orbitals of the -CO moieties are explicit, it is implied that there are 6 doubly occupied orbitals in the electronic configuration as well.

Table 9: *Weights of the main electronic configurations for carbon suboxide with respective energies (Hartree). Different colours underline the spin-coupling between the carbon and oxygen electrons.*

		Electronic configuration	Weight of the structure	Energy of the structure
1	C	$1s^2(\text{sp})_a^1(\text{sp})_b^1x^1y^1$	0.1518	-262.938454
	CO ₁	$\sigma^1\pi_x^0\pi_y^1$		
	CO ₂	$\sigma^1\pi_x^1\pi_y^0$		
2	C	$1s^2(\text{sp})_a^2(\text{sp})_b^2x^0y^0$	0.2161	-261.810597
	CO ₁	$\sigma^0\pi_x^0\pi_y^2$		
	CO ₂	$\sigma^0\pi_x^2\pi_y^0$		
3	C	$1s^2(\text{sp})_a^2(\text{sp})_b^0x^0y^2$	0.5526	-262.065298
	CO ₁	$\sigma^2\pi_x^0\pi_y^0$		
	CO ₂	$\sigma^0\pi_x^2\pi_y^0$		
			E_{VB}	-262.983383

There are 3 main structures, with rather different weights. The first one is the only one that includes the 5S state of the carbon, with hybridized sp orbitals (hybrids formed by linear combination of the $2s$ and $2p_z$ orbitals), coupled in a symmetric way with both the -CO components; thus, it would be represented with two double bonds between the carbon atoms. However, it is structure n. 3 that has the greatest weight, >0.5 ; here, each occupied valence orbital is doubly occupied, both for carbon and the -CO fragments, suggesting that this configuration can be represented by dative bonds, rather than covalent ones. Considering that the -CO fragments also present vacant orbitals, it seems appropriate to draw dative bonds from the central carbon towards the -CO moieties as well: the carbon does not necessarily need to retain the two lone pairs on itself, but can backdonate them to the adjacent atoms (Figure 9).



Figure 9: *Schematic representation of the dative bonds of carbon suboxide, from structure n. 2 and 3.*

Structure n. 2 can also be represented in the same way, although the orbital occupation is different from that of n. 3: the two π orbitals of the -CO are now doubly occupied, as well as the sp orbitals from the carbon. The fact that this configuration has a lower weight than that of n. 3 is unexpected, because it seems that, in configuration n. 2 there are two symmetric σ bonds from the carbon towards the fragments; in n. 3, on the other hand, the orbital occupation is asymmetric and thus also the bonding is. This implies that the symmetry of the molecule is broken, influencing the results and, specifically, the weight of the structures. To further support this statement, the symmetric structures of the ones reported should be expected to be present as well, with an equivalent weight (for example, the symmetric structure of n. 3, would have $(sp)_b$ doubly occupied), but they were not included in the results. Another unexpected result is the energy of structure n. 1, which is the lowest of the reported ones; one possible explanation is that the presence of the σ bonds is more energetically favored. The weight of this structure is, however, lower than the other two, revealing that energy of structures is not a direct indicator of its contribution to the overall structure of the molecule.

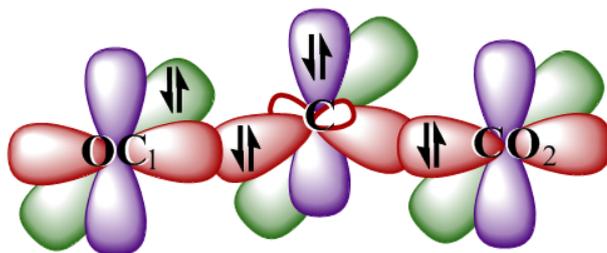


Figure 10: *Visualization of the orbital scheme for structures n. 3 of carbon suboxide; the carbon atom now retains two equivalent sp orbitals, each of which overlaps with the $2p_z$ orbital of the oxygens.*

Figure 10 visualizes the orbital scheme for structure n. 3, the greatest contributor to the bonding of the molecule. The two lone pairs of the carbon can be seen respectively in one of the sp and in the $2p_y$ orbitals; both -CO fragments donate their lone pair either by π (-CO₁) or by σ (-CO₂)

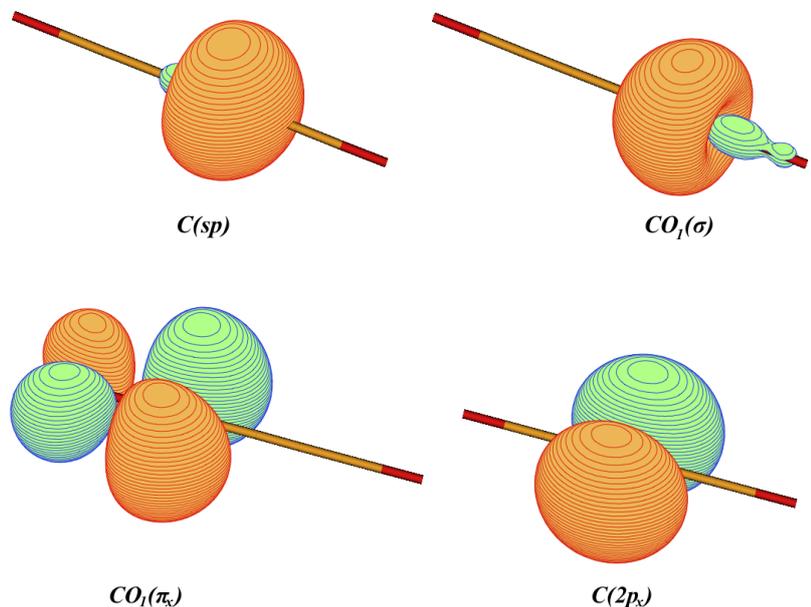


Figure 11: Visualization of the orbital: sp and σ orbitals of the central carbon atom and the $-CO_1$ fragment, respectively (above); π and $2p_x$ of the $-CO_2$ fragment and the central atom, respectively (below).

donation, thus originating in dative bonds rather than covalent ones. This picture is confirmed by looking at the overlap coefficients reported in Table 10. The first two results shown here are those between the sp of the carbon and the σ orbitals of the fragments, with a value double that of all other coefficients. The remaining ones reflect the data that are displayed in Table 9: overlap between orbitals with the same symmetry. As for carbon dioxide, it can be noted here as well that the coefficients should have exactly the same values for degenerate orbitals, as well as between the central carbon atom and the two $-CO$ fragments; the slight differences (~ 0.01) indicate that symmetry is lost throughout the calculation: not even here, in fact, were specified symmetry constrictions in the input. Further support to the overlap coefficients is given by Figure 11, where the orbitals images from MOLDEN are shown. Once again, a certain degree of delocalization of the orbitals towards the neighboring atom with which the spin-coupling or bond will be formed is seen. In this Figure, the sp hybridized orbital of the central carbon forms a bond with the σ from the $-CO$ moiety (above), and the x orbital interactions are shown as well (below).

The analysis of the results for carbon suboxide indicate, as was hypoth-

Table 10: *Overlap of the orbitals of carbon suboxide. The greatest coefficients are highlighted in red.*

Orbital 1	Orbital 2	Overlap
C(sp) _a	CO ₁ (σ)	0.7581
C(sp) _b	CO ₂ (σ)	0.7598
C(x)	CO ₁ (π_x)	0.3589
	CO ₂ (π_x)	0.3619
C(y)	CO ₁ (π_y)	0.3548
	CO ₂ (π_y)	0.3566

esized, that the most appropriate way to represent the molecule is by using bond arrows, which underline that the electrons come from each of the -CO fragments, but that, as was not predicted, the carbon also participates in the donation of electrons towards the -CO fragments. From this VB analysis, although dative bonds should be used to describe the bonds of carbon suboxide, it can not be concluded that the molecule can be classified as a carbene.

6 Conclusions

In this study, Valence Bond calculations of three molecules, carbon monoxide, dioxide and suboxide, was performed to attempt to define the types of bonds between the atoms.

A full-VB description was carried out for carbon monoxide only, as for the two other molecules the calculations were heavier and time-consuming. For this molecule, a triple-bond structure was found to be the most important one, characterized by two covalent and one dative bonds, inducing a negative charge on the carbon and a positive one on the oxygen. Another rather contributing structure to the overall picture of the molecule was found to be an ionic one, still characterized by three bonds, two of which are now dative.

The calculations for carbon dioxide and suboxide included only few of all possible configurations of the molecules, the ones that were expected to be the most important one. For carbon dioxide, the generally known picture with a linear, double-bond structure with the carbon being *sp* hybridized was indeed confirmed to be the most relevant one. In particular, two degenerate spin-configurations that obey this description were found, where either the $2p_x$ or $2p_y$ of the oxygens and carbon couple together.

The most reviling result was that of carbon suboxide: an appropriate way to depict the molecule is by treating the two -CO as fragments donating electrons to the central carbon atom, which, as well, donates its electrons to the vacant -CO orbitals. In particular, the configuration in which one of the two -CO behaves as a σ donor and the other as a π donor was found to be more stable and more important than the configuration where both -CO behave as π donors.

In conclusion, from the study conducted, it seems that none of the molecules investigated can be classified as carbones.

References

- [1] W. von E. Doering and A. Kentaro Hoffmann. The addition of dichlorocarbene to olefins. *Journal of the American Chemical Society*, 76(23):6162–6165, 1954.
- [2] J. B. Van Doren. Valence and the structure of atoms and molecules (lewis, g. n.). *Journal of Chemical Education*, 44(1):A82, 1967.
- [3] A. Haaland. Covalent versus dative bonds to main group metals, a useful distinction. *Angewandte Chemie International Edition in English*, 28(8):992–1007, 1989.
- [4] D. Himmel and I. Krossing. Dative bonds in main-group compounds: A case for fewer arrows! *Angewandte Chemie International Edition*, 53(2):370–374, 2014.
- [5] F. Ramirez. Hexaphenylcarbodiphosphorane. *Journal of the American Chemical Society*, 83(16):3539–3540, 1961.
- [6] G. Frenking. Dative bonds in main-group compounds: A case for more arrows! *Angewandte Chemie International Edition*, 53(24):6040–6046.
- [7] R. Tonner and G. Frenking. Divalent carbon(0) compounds with n-heterocyclic carbene ligands—theoretical evidence for a class of molecules with promising chemical properties. *Angewandte Chemie International Edition*, 46(45):8695–8698.
- [8] G. E. Hardy and J. I. Zink. Structure and triboluminescence of polymorphs of hexaphenylcarbodiphosphorane. *Journal of the American Chemical Society*, 100(25):8001–8002, 1978.
- [9] P. J. Quinlivan and G. Parkin. Flexibility of the carbodiphosphorane: Structural characterization of a linear form. *Inorganic Chemistry*, 56(10):5493–5497, 05 2017.
- [10] G. Frenking and Hermann. Donor-acceptor bonding in novel low-coordinated compounds of boron and group-14 atoms c-sn. *Chem. Soc. Rev.*, 45:1129–1144, 2016.
- [11] H. Schmidbaur. Replique: A new concept for bonding in carbodiphosphoranes? *Angewandte Chemie*, 119(17):3042–3043, 2007.
- [12] G. Frenking and R. Tonner. Carbodicarbenes divalent carbon(0) compounds exhibiting carbon carbon donor acceptor bonds. *Wiley Interdisciplinary Reviews: Computational Molecular Science*, 1(6):869–878, 2011.

- [13] M. Hopffgarten and G. Frenking. Energy decomposition analysis. *Wiley Interdisciplinary Reviews: Computational Molecular Science*, 2(1):43–62.
- [14] G. Burton. *Chemical Ideals*. 1994.
- [15] K. P. Huber and G. Herzberg. *Molecular Spectra and Molecular Structure— IV. Constants of Diatomic Molecules*. Van Nostrand Reinhold, New York, 1979.
- [16] Gerard Herzberg. *Electronic spectra and electronic structure of polyatomic molecules*. 1966.
- [17] G. Frenking and M. Hermann. *Gilbert Lewis and the Model of Dative Bonding*, pages 131–156. Springer International Publishing, Cham, 2016.
- [18] J. Koput. An ab initio study on the equilibrium structure and ccc bending energy levels of carbon suboxide. *Chemical Physics Letters*, 320(3):237 – 244, 2000.
- [19] P. R. Bunker. Carbon suboxide as a semirigid bender. *Journal of Molecular Spectroscopy*, 80(2):422 – 437, 1980.
- [20] A. Ellern, T. Drews, and K. Seppelt. The structure of carbon suboxide, in the solid state. *Zeitschrift für anorganische und allgemeine Chemie*, 627(1):73–76.
- [21] G. N. Lewis. The atom and the molecule. *Journal of the American Chemical Society*, 38(4):762–785, 1916.
- [22] Marcin Zielinski. *Atoms in Valence Bond. Method, implementation and application*. PhD thesis, Universiteit Utrecht, 2012.
- [23] S. Shaik and P. C. Hiberty. *Valence Bond Theory, Its History, Fundamentals, and Applications: A Primer*, chapter 1, pages 1–100. Wiley-Blackwell, 2004.
- [24] P. Atkins and R. Friedman. *Molecular quantum mechanics*. 2005.
- [25] A. F. Sax. Chemical bonding: The orthogonal valence-bond view. *International Journal of Molecular Sciences*, 16(4):8896–8933, 04 2015.
- [26] J. Verbeek and J. H. Van Lenthe. On the evaluation of non-orthogonal matrix elements. *Journal of Molecular Structure: THEOCHEM*, 229:115 – 137, 1991. Advances in valence bond theory.
- [27] Hiberty P. C. Analysis of molecular orbital wave functions in terms of valence bond functions for molecular fragments. i. theory. *International Journal of Quantum Chemistry*, 19(2):259–269, 1981.

- [28] T.H. Dunning. Gaussian basis sets for use in correlated molecular calculations. i. the atoms boron through neon and hydrogen. *The Journal of Chemical Physics*, 90(2):1007–1023, 1989.
- [29] R. T. McGibbon and A. G. Taube. Improving the accuracy of moller-plesset perturbation theory with neural networks. *The Journal of Chemical Physics*, 147(16):161725, 2017.
- [30] M. F. Guest, I. J. Bush, H. J. J. van Dam, P. Sherwood, J. M. H. Thomas, J. H. van Lenthe, R. W. A Havenith, and J. Kendrick. The gamess-uk electronic structure package: algorithms, developments and applications. *Molecular Physics*, 103(6-8):719–747, 2005.