

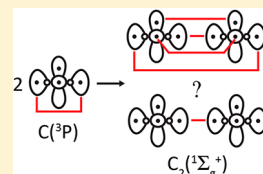
Insights into the Perplexing Nature of the Bonding in C_2 from Generalized Valence Bond Calculations

Lu T. Xu and Thom H. Dunning, Jr.*

Department of Chemistry, University of Illinois at Urbana–Champaign, 600 South Mathews Avenue, Urbana, Illinois 61801, United States

Supporting Information

ABSTRACT: Diatomic carbon, C_2 , has been variously described as having a double, triple, or quadruple bond. In this article, we report full generalized valence bond (GVB) calculations on C_2 . The GVB wave function—more accurate than the Hartree–Fock wave function and easier to interpret than traditional multiconfiguration wave functions—is well-suited for characterizing the bonding in C_2 . The GVB calculations show that the electronic wave function of C_2 is not well described by a product of singlet-coupled, shared electron pairs (perfect pairing), which is the theoretical basis for covalent chemical bonds. Rather, C_2 is best described as having a traditional covalent σ bond with the electrons in the remaining orbitals of the two carbon atoms *antiferromagnetically* coupled. However, even this description is incomplete as the perfect pairing spin function also makes a significant contribution to the full GVB wave function. The complicated structure of the wave function of C_2 is the source of the uncertainty about the nature of the bonding in this molecule.



1. INTRODUCTION

There is considerable interest in the nature of the bonding in the simplest carbon compound, diatomic carbon (C_2).¹ The C_2 molecule has been variously described as having a double bond,² a triple bond,³ or a quadruple bond⁴ (but see ref 5). Shaik, Rzepa, and Hoffman⁶ recently discussed the nature of the bonding in C_2 in an interesting, if inconclusive, dialogue. This article engendered a follow-up set of articles by Frenking and Hermann⁷ and Danovich et al.⁸ In spite of these studies and the resulting spirited discussions, the nature of the bonding in C_2 remains a puzzle.

In this paper generalized valence bond (GVB) theory is used to describe the electronic structure of C_2 . The GVB wave function evolves smoothly from that of the separated atoms to that of the molecule, while allowing the orbitals and spin function to optimally adjust to the presence of the other atom. The GVB wave function is more accurate than the Hartree–Fock (HF) wave function, including many of the important nondynamic correlation effects found in valence multiconfiguration SCF wave functions. In spite of this, the GVB wave function remains compact and readily interpretable. Thus, GVB theory provides an ideal means to characterize the nature of the bonding in C_2 .

As first put forward by Lewis,⁹ further elaborated by Langmuir,¹⁰ and finally placed on a firm theoretical foundation by Heitler and London,¹¹ a covalent bond arises from the sharing of a singlet-coupled, electron pair (see also ref 12 and references therein). For a molecule with multiple covalent bonds between atoms A and B, the wave function has an electron in a singly occupied orbital on atom A, φ_{Ai} , singlet coupled to an electron in a singly occupied orbital on atom B, φ_{Bj} for $i = 1 - N_{\text{bonds}}$. The wave functions of many molecules are well described by this type of wave function. For example,

for molecular nitrogen (N_2) the dominant configuration in the full GVB wave function is

$$\Psi_{\text{PP}} = \hat{a} \varphi_{\sigma_A} \varphi_{\sigma_B} \varphi_{\pi_{xA}} \varphi_{\pi_{xB}} \varphi_{\pi_{yA}} \varphi_{\pi_{yB}} \frac{1}{2\sqrt{2}} (\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha) (\alpha\beta - \beta\alpha) \quad (1)$$

This configuration has a coefficient of 0.96 in the GVB wave function of N_2 ,¹³ accounting for 92% of the wave function. The above spin function is referred to as the perfect pairing spin function. Thus, N_2 is well described as having one σ and two π bonds. On the other hand, there are well-known molecules where the wave function is not well described by a single, perfectly paired spin function. In the π electron system of benzene, the perfect pairing spin function has a coefficient of only 0.79 and, thus, accounts for just 62% of the wave function.¹⁴ In this case, multiple spin functions must be included in the wave function to adequately describe the bonding, e.g., the spin functions that describe the two Kekule structures.

As we shall show, the wave function of C_2 is not well-described by a product of singlet-coupled, shared electron pairs, a fact first noted by Raos et al.¹⁴ In this paper we report full GVB^{15,16} (or SCVB¹⁷) as well as CASSCF^{18,19} and MRCI + Q^{20,21} calculations on the C_2 molecule with a correlation consistent basis set close to the complete basis set limit (aug-cc-pVQZ).²² We also find that the wave function of C_2 is not well described by a product of singlet-coupled, shared electron pairs, the theoretical basis for the use of traditional covalent bonding constructs. Instead, we find that the wave function for C_2 at its equilibrium geometry is best described by a σ bond between

Received: October 3, 2013

the carbon atoms and an *antiferromagnetic* coupling of the electrons in the remaining orbitals. Although this type of bonding is rare in chemistry, it is similar to that found in Cr_2 .^{23,24} However, even this description is incomplete—the contribution of the perfect pairing spin function to the full GVB wave function of C_2 is significant. As a result, it is not possible to assign a specific bond order to C_2 .

2. METHODOLOGY

The GVB wave function for the ground state (^3P) of the carbon atom is

$$\Psi_{\text{GVB}}[\text{C}(^3\text{P})] = \hat{a}\phi_{1s}\phi_{1s}\phi_{2s_-}\phi_{2s_+}\phi_{2p_x}\phi_{2p_y}\alpha\beta\left(\frac{\alpha\beta - \beta\alpha}{\sqrt{2}}\right)\alpha\alpha \quad (2)$$

where we have kept the $1s$ core orbital doubly occupied. The singlet coupled ($2s_-$, $2s_+$) pair provides a more accurate description of the carbon $2s$ lone pair than the $2s^2$ configuration in the Hartree–Fock (HF) wave function—the energy of the GVB wave function, eq 2, is 10.9 kcal/mol lower than that of the HF wave function.²⁵

The form of the ($2s_-$, $2s_+$) lobe orbitals is

$$\phi_{2s_{\pm}} = \sqrt{\frac{c_1}{c_1 + c_2}}\phi_{2s} \pm \sqrt{\frac{c_2}{c_1 + c_2}}\phi_{2p_z} = c_{2s}\phi_{2s} \pm c_{2p}\phi_{2p_z} \quad (3)$$

where the coefficients (c_1 , c_2) in eq 3 are obtained from a two-configuration MCSCF calculation on the carbon atom ($c_1\phi_{2s}^2 - c_2\phi_{2p_z}^2$). For the carbon atom, $c_{2s} = 0.93$ and $c_{2p} = 0.36$; thus, the ($2s_-$, $2s_+$) lobe orbitals have substantial $2p$ character. The $2s$ lobe orbitals are nonorthogonal with an overlap of

$$S(2s_-, 2s_+) = \frac{c_1 - c_2}{c_1 + c_2} \quad (4)$$

For the carbon atom, $S(2s_-, 2s_+) = 0.74$. Although there is significant overlap between the two lobe orbitals, they are concentrated in different spatial regions: one more on the left side of the atom ($2s_-$), the other more on the right side of the atom ($2s_+$). The GVB valence orbitals of the carbon atom are plotted in Figure 1, along with the corresponding GVB orbital

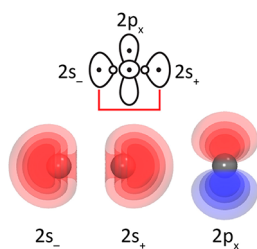


Figure 1. GVB orbital diagram for the ground, ^3P , state of the carbon atom along with contour plots of the valence ($2s_-$, $2s_+$, and $2p_x$) orbitals (the $2p_y$ orbital is identical to the $2p_x$ orbital except for orientation and is not plotted). Orbital pairs joined by a red line are singlet coupled. Contours are ± 0.1 , ± 0.15 , ± 0.2 , ± 0.25 .

diagram. As can be seen, the $2s_-$ and $2s_+$ lobe orbitals are well positioned to form bonds with other atoms, thereby naturally accounting for the tetravalence of carbon.

Given the GVB wave function for the carbon atom, it is straightforward to construct the GVB wave function for C_2 in the separated atom limit ($R = \infty$):

$$\Psi_{\text{GVB}}[\text{C}_2(X^1\Sigma_g^+)] = \hat{a}\phi_{2s_{-A}}\phi_{2s_{+A}}\phi_{2s_{-B}}\phi_{2s_{+B}}\phi_{2p_{xA}}\phi_{2p_{yA}}\phi_{2p_{xB}}\phi_{2p_{yB}}\Theta \quad (5)$$

In eq 5, the doubly occupied $1s$ core orbitals on each carbon atom have been omitted and the carbon atoms have been labeled as A (left) and B (right). The GVB orbitals in eq 5 are uniquely determined by the optimization process and are, in general, nonorthogonal but are orthogonal to the doubly occupied core orbitals (orbitals of different symmetry are, of course, orthogonal). The formation of the ground, $X^1\Sigma_g^+$, state of C_2 from $\text{C}(^3\text{P}) + \text{C}(^3\text{P})$ is represented schematically by the GVB orbital diagram in Figure 2 (the significance of the two representations for C_2 will be discussed below).

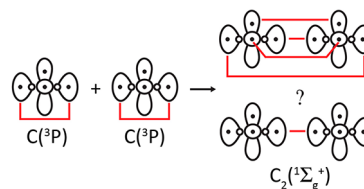


Figure 2. GVB orbital diagram illustrating the formation of $\text{C}_2(X^1\Sigma_g^+)$ from two $\text{C}(^3\text{P})$ atoms. For more details on the bonding in the resulting C_2 molecule, see the text. Orbital pairs joined by a red line are singlet coupled.

For 8 electrons in 8 singly occupied orbitals, there are 14 linearly independent ways to couple the electron spins.²⁶ Thus, the spin function, Θ , is a linear combination of these 14 spin couplings:

$$\Theta = \sum_{k=1}^{14} c_k \Theta_k \quad (6)$$

However, with the above orbital ordering, only one spin function is required at $R = \infty$:

$$\Theta_9 = \frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha)\frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha) \left\{ \frac{1}{\sqrt{12}}[2\alpha\alpha\beta\beta - (\alpha\beta + \beta\alpha)(\alpha\beta + \beta\alpha) + 2\beta\beta\alpha\alpha] \right\} \quad (7)$$

This spin function couples the electrons in the first two orbital pairs, ($\phi_{2s_{-A}}$, $\phi_{2s_{+A}}$) and ($\phi_{2s_{-B}}$, $\phi_{2s_{+B}}$), into singlets, the electrons in the following two orbitals ($\phi_{2p_{xA}}$, $\phi_{2p_{yA}}$) into a triplet, those in the next two orbitals, ($\phi_{2p_{xB}}$, $\phi_{2p_{yB}}$), also into a triplet, and then the two triplet spin functions are coupled into a singlet, yielding the $X^1\Sigma_g^+$ state of C_2 . For other orbital orderings, including the “molecular” and “quasi-atomic” orbital orderings discussed in section 3 below, more than one spin function is required to describe the wave function of C_2 at the separated atom limit (see also ref 14).

Because we use the orthonormal Kotani spin basis,²⁷ the contribution of a particular spin coupling to the GVB wave function, say, Θ_k in eq 6, is just $w_k = c_k^2$, with

$$\sum_{k=1}^{14} w_k = 1 \quad (8)$$

In eq 8, w_k is referred to as the spin coupling or spin function weight. It is possible to use other spin bases, e.g., the Rumer and Serber bases; these are discussed in ref 26 and, for C_2 , in ref 14.

In the full GVB method, the orbitals, $\{\varphi_i\}$, as well as the spin coupling coefficients, $\{c_k\}$, are optimized at each value of R with no constraints. As R decreases, the orbitals on one atom respond to the presence of the other atom by contracting or expanding, polarizing and/or hybridizing, delocalizing, etc. In addition, the $\{c_k\}$ change to reflect the changes in orbital spin couplings as the molecule is formed. The GVB wave function provides a more accurate description of the electronic structure of molecules than the HF wave function. The full GVB wave function includes the most important nondynamical correlation effects in the valence (s, p) CASSCF wave function^{18,19} and approaches it in accuracy.

The HF, GVB, CASSCF, and MRCI+Q^{20,21} calculations in this work were performed with the Molpro suite of quantum chemical programs.²⁸ The CASSCF wave function included all configurations arising from the (2s, 2p) orbitals. The MRCI+Q calculations included all single and double excitations from the CASSCF wave function. The dissociation energy, D_e , and equilibrium distance, R_e , for the MRCI+Q calculations was computed with the CASSCF+1+2 wave function, but the potential energy curve was obtained by averaging the lowest three states (two $^1\Sigma_g^+$ states and one $^1\Delta_g$ state). Augmented correlation consistent basis sets of quadruple- ζ quality (aug-cc-pVQZ) were used for the carbon atom.²⁰ This basis set has an acceptably small convergence error associated with the solution of the electronic Schrödinger equation.

The GVB calculations were carried out using the Molpro fully variational CASVB program with the Kotani spin basis.²⁸ Although we use the GVB notation to refer to the calculations presented here, the full GVB wave function is identical to the spin-coupled valence bond (SCVB) wave function of Gerratt, Cooper, Karadakov, Raimondi, and co-workers.¹⁷ The calculations reported herein were, in fact, made possible by the methodology developed by Thorsteinsson, Cooper, et al.²⁹ and implemented in the CASVB module in Molpro.

3. RESULTS AND DISCUSSION

The equilibrium energy (E_e), bond energy (D_e), and bond distance (R_e) of C_2 from Hartree–Fock (HF), GVB, CASSCF, and MRCI+Q calculations are summarized in Table 1, along

Table 1. Summary of Results of HF, GVB, and MRCI+Q Calculations on C_2 (Basis Set: aug-cc-pVQZ)^a

method	E_e	D_e	R_e
HF	−75.405 840	18.3	1.239
GVB	−75.594 679	112.6	1.244
val-CASSCF	−75.643 390	143.2	1.254
MRCI+Q	−75.803 136	142.8	1.247
exp ^{31,32}		145.2	1.24244

^a E_e is given in hartree, D_e in kilocalories per mole, and R_e in angstroms.

with the available experimental data.^{30,31} The calculated HF, GVB, and MRCI+Q potential energy curves are plotted in Figure 3. As can be seen, the GVB wave function provides a far more accurate representation of the C_2 molecule than the HF wave function, recovering nearly 80% of the bond energy predicted by the MRCI+Q calculations (112.6 versus 142.8 kcal/mol), whereas C_2 is barely bound at the HF level (18.3

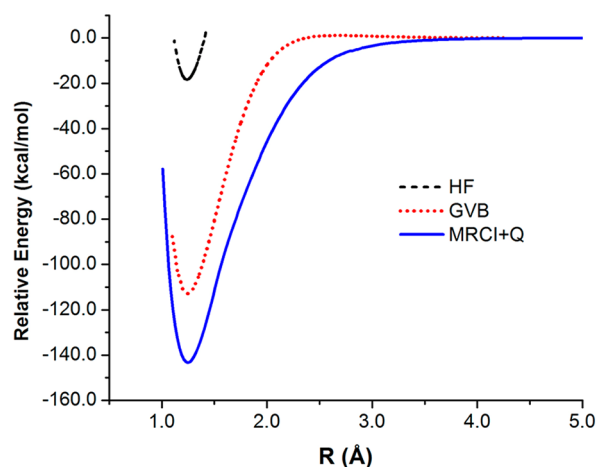


Figure 3. Plots of the HF, GVB, and MRCI+Q potential energy curves for the $X^1\Sigma_g^+$ state of C_2 . The MRCI+Q curve was obtained by averaging the lowest three states (two $^1\Sigma_g^+$ states and one $^1\Delta_g$ state).

kcal/mol). The GVB wave function also predicts a more accurate bond distance for C_2 (1.244 versus 1.242 Å), although the difference with the HF result (1.239 Å) is not as dramatic as for D_e .

As noted in the Introduction, the full GVB wave function accounts for the major nondynamical correlation effects in the atom or molecule. In the C atom, it accounts for the 2s–2p near degeneracy effect, and in the C_2 molecule, it includes all of the nondynamical correlation effects required to describe the dissociation of the molecule into its fragments. As a result, the GVB energy of the $C_2(X^1\Sigma_g^+)$ state at R_e is 118.5 kcal/mol lower than the HF energy and just 30.6 kcal/mol above the valence CASSCF energy. The energy of the MRCI+Q wave function, which includes both nondynamical and dynamical correlation effects, is another 100.3 kcal/mol below the CASSCF energy. Interestingly, in C_2 , inclusion of dynamical correlation effects beyond those in the valence CASSCF wave function has only a minor effect on both D_e and R_e (decreasing D_e by <0.5 kcal/mol and increasing R_e by <0.01 Å). These results clearly show that the GVB wave function provides a far more suitable basis for describing the bonding in C_2 than the HF wave function.

The essence of a GVB wave function is captured in the orbitals, $\{\varphi_i\}$; the coefficients/weights of the spin functions, $\{c_k, w_k\}$; and the orbital overlaps, $S_{ij} = S(\varphi_i, \varphi_j)$, all of which depend on the internuclear distance, R . In Figure 4, the GVB orbitals of C_2 are plotted as a function of $\Delta R = R - R_e$. The orbitals at $\Delta R = 2.0$ Å are essentially the same as those for two $C(^3P)$ atoms (compare these orbitals with those in Figure 1). As ΔR decreases, the “inner” σ bonding orbitals ($2s_{+A}, 2s_{-B}$) and the π orbitals ($2p_{xA}, 2p_{yA}, 2p_{xB}, 2p_{yB}$) polarize and delocalize onto the other atom, thus strengthening the bonding interaction between the two atoms. On the other hand, the “outer” σ orbitals ($2s_{-A}, 2s_{+B}$) largely retain their atomic forms.

The spin function also changes smoothly as R decreases, from that appropriate for $C(^3P) + C(^3P)$ to that for $C_2(X^1\Sigma_g^+)$; see Figure 5. For Figure 5 we employed the molecular orbital ordering: $2s_{+A}, 2s_{-B}, 2s_{-A}, 2s_{+B}, 2p_{xA}, 2p_{xB}, 2p_{yA}$, and $2p_{yB}$. Coupled with the perfect pairing spin coupling, the resulting wave function describes the formation of four electron pairs, ($2s_{+A}, 2s_{-B}$), ($2s_{-A}, 2s_{+B}$), ($2p_{xA}, 2p_{xB}$), and ($2p_{yA}, 2p_{yB}$). Except for the presence of the additional singlet-coupled pair ($2s_{-A}, 2s_{+B}$), the resulting wave function for C_2 corresponds to the

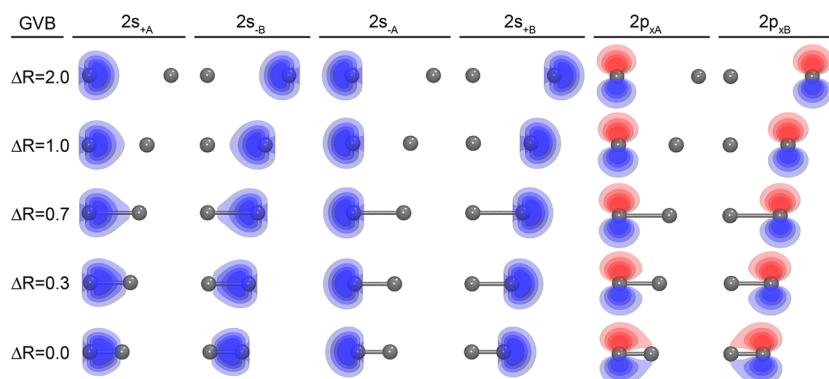


Figure 4. Plots of the GVB valence orbitals of the $C_2(X^1\Sigma_g^+)$ state at selected internuclear distances, $\Delta R = R - R_e$; $R_e = 1.247 \text{ \AA}$ (the $2p_{yA,B}$ orbitals are identical to the $2p_{xA,B}$ orbitals except for orientation and are not plotted). Although the orbitals are listed in the molecular ordering, they do not depend on the ordering used. Contours are ± 0.1 , ± 0.15 , ± 0.2 , ± 0.25 .

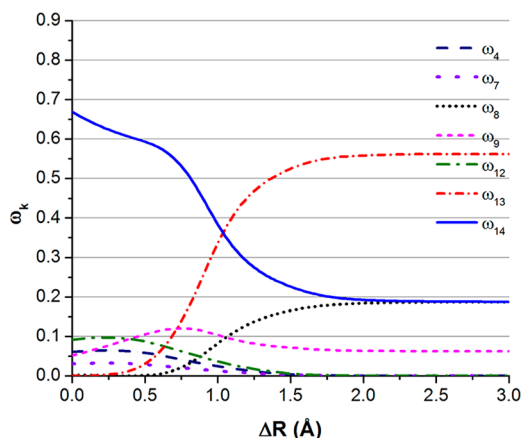


Figure 5. Plots of the spin coupling weights, w_k , of the major spin couplings for the full GVB wave function of the $C_2(X^1\Sigma_g^+)$ state as a function of $\Delta R = R - R_e$ ($R_e = 1.247 \text{ \AA}$). The molecular orbital ordering is used, and spin function no. 14 is the perfect pairing spin function.

dominant configuration for the N_2 molecule, eq 1, at its equilibrium geometry. Indeed, we find that, as ΔR decreases, the weight of the perfect pairing (PP) spin function ($w_{PP} = w_{14}$) increases, becoming the dominant spin coupling at R_e . But, at R_e $w_{PP} = 0.67$, a value which falls far short of that needed for C_2 to be well-described by the perfect pairing spin function—for N_2 , $w_{PP} = 0.96$. This is in full agreement with the results reported by Raos et al.¹⁴

The total energies, spin coupling coefficients, and dominant spin coupling weights for the ground state of C_2 at R_e are listed in Table 2. As noted above, the perfect pairing spin function has a coefficient c_{PP} ($= c_{14}$) of 0.82 and accounts for just 67% of the wave function. A further measure of the inadequacy of the perfect pairing configuration can be obtained by optimizing the GVB wave function with just the perfect pairing spin function ($\Theta_{PP} = \Theta_{14}$). This increases the energy of C_2 by more than 20 kcal/mol relative to the full GVB energy (see Table 2). Clearly, the wave function for C_2 is not well described by a product of singlet-coupled, shared electron pairs, i.e., C_2 does not have a set of traditional covalent σ and π bonds like N_2 .

Although the total GVB wave function does not depend on the ordering of the orbitals, the spin coupling coefficients do. A close examination of the spin coupling coefficients for the molecular ordering suggested that another orbital ordering

Table 2. GVB Energies and Spin Coupling Coefficients for the C_2 Molecule at the Equilibrium Geometry from the MRCI+Q Calculations ($R_e = 1.247 \text{ \AA}$)^a

	symbolic spin function ^b	molecular ordering	quasi-atomic ordering
E_{GVB}		−75.594 669	−75.594 669
spin coupling coefficients			
c_1	$\alpha\alpha\alpha\beta\beta\beta$	0.097525	0.157711
c_2	$\alpha\alpha\alpha\beta\alpha\beta$	−0.137702	0.203604
c_3	$\alpha\alpha\beta\alpha\alpha\beta$	0.097370	0.107699
c_4	$\alpha\beta\alpha\alpha\beta\beta$	−0.246447	−0.917702
c_5	$\alpha\alpha\beta\beta\alpha\beta$	0.097370	0.008343
c_6	$\alpha\alpha\beta\alpha\beta\alpha$	−0.068851	−0.065199
c_7	$\alpha\beta\alpha\alpha\beta\alpha$	0.174265	−0.063060
c_8	$\alpha\alpha\beta\beta\alpha\alpha\beta$	0.045922	−0.112928
c_9	$\alpha\beta\alpha\beta\alpha\alpha\beta$	−0.227698	−0.109222
c_{10}	$\alpha\alpha\alpha\beta\beta\alpha\beta$	−0.168650	0.000000
c_{11}	$\alpha\alpha\beta\alpha\beta\alpha\beta$	0.119254	−0.039597
c_{12}	$\alpha\beta\alpha\alpha\beta\alpha\beta$	−0.301835	−0.183359
c_{13}	$\alpha\alpha\beta\beta\alpha\beta\alpha\beta$	0.011905	0.022861
c_{14}	$\alpha\beta\alpha\beta\alpha\beta\alpha\beta$	0.817835	0.105863
$c_{PP} = c_{14}$ (%)		66.89	
$c_{qAt} = c_4$ (%)			84.22
$E_{GVB(PP)}, \text{ h}$	$\alpha\beta\alpha\beta\alpha\beta\alpha\beta$	−75.562 129	
$E_{GVB(PP)} - E_{GVB}, \text{ kcal/mol}$		20.42	
$E_{GVB(qAt)}, \text{ h}$	$\alpha\beta\alpha\alpha\alpha\beta\beta\beta$		−75.577 381
$E_{GVB(qAt)} - E_{GVB}, \text{ kcal/mol}$			10.85

^a c_{PP} and c_{qAt} are the coefficients of the perfect pairing and quasi-atomic spin functions. ^b The symbolic spin function defines the path taken in the Kotani branching diagram:²⁶ α refers to an upward path segment and β refers to a downward path segment. These paths uniquely define each Kotani spin function.

might yield a spin-coupling function with a significantly larger coefficient. In this new ordering, which we refer to as the quasi-atomic ordering, the first two orbitals are $(2s_{+A}, 2s_{-B})$ and the remaining orbitals are listed by center: first the orbitals on carbon atom A ($2s_{-A}, 2p_{xA}, 2p_{yA}$) and then the orbitals on carbon atom B ($2s_{+B}, 2p_{xB}, 2p_{yB}$). The coefficients of the spin functions at R_e are listed in the last column of Table 2 (the dependence of the spin coupling weights on ΔR for this orbital ordering is given in the Supporting Information). With this ordering the coefficient for spin function no. 4 is 0.918. If we optimize the GVB wave function with the quasi-atomic orbital

ordering and spin function ($\Theta_{\text{qAt}} = \Theta_4$), the energy increases by only 10.8 kcal/mol, just over half that for the perfect pairing spin function with the molecular ordering. Clearly, the electronic structure of C_2 is better described by the quasi-atomic spin function with the quasi-atomic ordering of the orbitals than by the perfect pairing spin function with the molecular orbital ordering.

The quasi-atomic spin function is

$$\begin{aligned} \Theta_4 = & \frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha)\frac{1}{6}\{3\alpha\alpha\alpha\beta\beta\beta + 3\beta\beta\beta\alpha\alpha\alpha \\ & + (\alpha\beta + \beta\alpha)[\beta\alpha\alpha\beta - \beta\beta\alpha\alpha - (\alpha\beta - \beta\alpha)\beta\alpha] \\ & + \beta\beta(\alpha\alpha\alpha\beta - \alpha\beta\alpha\alpha) + (\beta\beta\alpha\alpha - \alpha\alpha\beta\beta)\beta\alpha \\ & - (\alpha\alpha\beta + \alpha\beta\alpha + \beta\alpha\alpha)(\alpha\beta + \beta\alpha)\beta\} \end{aligned} \quad (9)$$

Although this spin function appears to be complicated, it has a simple interpretation: the electrons in the first two orbitals ($2s_{+A}, 2s_{-B}$) are coupled into a singlet, those in the next three orbitals ($2s_{-A}, 2p_{xA}, 2p_{yA}$) are coupled into a quartet, those in the last three orbitals ($2s_{+B}, 2p_{xB}, 2p_{yB}$) are also coupled into a quartet, and then the spins of the electrons in these last six orbitals are coupled to give an overall singlet state. This wave function corresponds to a traditional covalent σ bond between the two carbon atoms and an *antiferromagnetic* coupling of the electrons in the remaining orbitals. It describes an unusual type of bonding in chemistry, although it is similar to that for Cr_2 , where the electrons in the 4s orbitals are singlet coupled and the electrons in the 3d orbitals on each of the atoms are antiferromagnetically coupled.^{23,24}

However, the quasi-atomic orbital ordering with the quasi-atomic spin function still accounts for only 84% of the wave function at R_e , which indicates that additional spin functions are important in the C_2 wave function. In Figure 6, we plot the

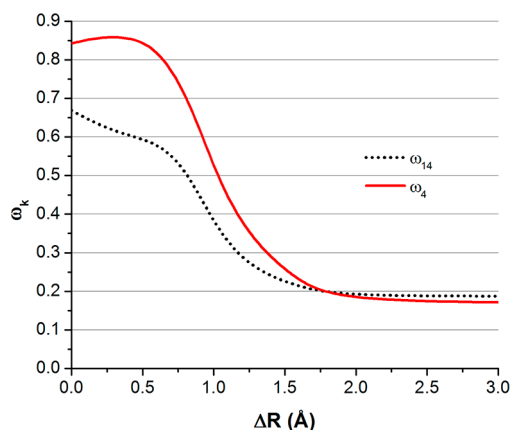


Figure 6. Plots of the dominant spin coupling weights for the molecular ($w_{\text{pp}} = w_{14}$) and quasi-atomic ($w_{\text{qAt}} = w_4$) orbital orderings for the full GVB wave functions of the $X^1\Sigma_g^+$ state of C_2 as a function of $\Delta R = R - R_e$; $R_e = 1.247$ Å. Because different orbital orderings are associated with the two spin couplings, they are not orthogonal and, thus, $w_{\text{pp}} + w_{\text{qAt}} \neq 1$.

weights of the dominant spin couplings for the molecular ($w_{\text{pp}} = w_{14}$) and quasi-atomic ($w_{\text{qAt}} = w_4$) orbital orderings as a function of ΔR . Both weights are less than 0.2 at $\Delta R = 3.0$ Å, because a linear combination of spin functions is required to describe the spin coupling of the electrons at the separated atom limit (see ref 14). As ΔR decreases, the weights of both the

quasi-atomic and perfect pairing spin couplings increase, with w_{qAt} increasing more rapidly than w_{pp} below $\Delta R = 1.5$ Å, but both remain important. As ΔR decreases further, there is a maximum in the curve for w_{qAt} at $\Delta R = 0.3$ Å with $w_{\text{qAt}}(\text{max}) = 0.86$.

The decrease in w_{qAt} at $\Delta R < 0.3$ Å is due to the fact that the antiferromagnetic coupling of the electrons becomes less and less favorable at short internuclear distances. At sufficiently small ΔR the ($2p_{xA}, 2p_{xB}$) and ($2p_{yA}, 2p_{yB}$) orbital pairs would prefer to be singlet coupled, representing the incipient formation of π bonds, rather than triplet coupling the ($2p_{xA}, 2p_{yA}$) and ($2p_{xB}, 2p_{yB}$) orbital pairs as in the quasi-atomic spin function. On the other hand, w_{pp} continues to increase with decreasing ΔR , although there is a marked change in slope around $\Delta R \approx 0.75$ Å. This change in slope may well be due to the onset of Pauli exchange-repulsion between the two σ pairs³² (see below). It appears that the curve for w_{pp} will eventually cross the curve for w_{qAt} but this crossing will not occur until $R \ll R_e$.

The above finding raises the question: Why is C_2 so poorly described by a wave function with the perfect pairing spin coupling? For the perfect pairing wave function with the molecular orbital ordering, C_2 has four singlet-coupled, shared electron pairs: ($2s_{+A}, 2s_{-B}$), ($2s_{-A}, 2s_{+B}$), ($2p_{xA}, 2p_{xB}$), and ($2p_{yA}, 2p_{yB}$). In spite of this seemingly favorable situation, the perfect pairing configuration is less favorable than the quasi-atomic configuration because of Pauli exchange-repulsion³³ between the two σ electron pairs: ($2s_{+A}, 2s_{-B}$) and ($2s_{-A}, 2s_{+B}$). In C_2 , the inner ($2s_{+A}, 2s_{-B}$) and outer ($2s_{-A}, 2s_{+B}$) σ pairs occupy similar regions of space and have substantial “unfavorable” interpair overlaps: $S(\varphi_{2s_{A-}}, \varphi_{2s_{B-}}) = S(\varphi_{2s_{B-}}, \varphi_{2s_{A+}}) = 0.39$ and $S(\varphi_{2s_{A-}}, \varphi_{2s_{B+}}) = S(\varphi_{2s_{A+}}, \varphi_{2s_{B-}}) = 0.17$ (the dependence of the overlaps, S_{ij} , on ΔR is given in the Supporting Information). So, despite the fact that C_2 would prefer to have the electrons in the inner σ pair and the two π pairs singlet coupled, this is not favorable because it requires that the electrons in the outer σ orbitals also be singlet coupled, which leads to unfavorable Pauli exchange-repulsion between the inner and outer σ pairs.

Various means have been proposed to calculate the Pauli exchange-repulsions between electron pairs, e.g., the energy decomposition analysis of Morokuma³⁴ (see also ref 35). In C_2 , the large unfavorable overlaps between the σ orbitals involved in the two singlet-coupled, electron pairs would be expected to lead to large exchange-repulsion energies. Krapp et al.³⁶ have, in fact, used Morokuma’s EDA scheme, paired with density function theory, to compute the Pauli repulsion forces in the $\text{C}_2(X^1\Sigma_g^+)$ state. They found that Pauli repulsion between the electrons in the σ orbitals, $\Delta E_{\text{Pauli}}(\sigma) = +252.2$ kcal/mol, outweighed the attractive σ orbital interactions, $\Delta E_{\text{orb}}(\sigma) = -201.7$ kcal/mol, resulting in net repulsion in the σ system. This repulsive interaction increases the energy of the perfect pairing configuration, thereby decreasing its contribution to the full GVB wave function.

4. CONCLUSION

Generalized valence bond (GVB) calculations show that the electronic structure of the ground state ($X^1\Sigma_g^+$) of C_2 is not well described by a product of singlet-coupled, shared electron pairs—the perfect pairing configuration, which is the theoretical basis for traditional covalent chemical bonds. Thus, C_2 does not possess a set of traditional covalent σ and π bonds. Instead, the full GVB calculations show that the molecule is best, although

still incompletely, described as having a traditional covalent σ bond with the electrons in the remaining orbitals on the two centers *antiferromagnetically* coupled. This is similar to the electronic structure of Cr_2 , where the electrons in the 4s orbitals are singlet coupled and those in the 3d orbitals are antiferromagnetically coupled.^{23,24} We refer to this as the quasi-atomic configuration.

However, the above description of the GVB wave function is incomplete—the perfect pairing configuration also makes a significant, if smaller contribution to the wave function. The magnitude of the perfect pairing contribution depends on the internuclear distance, R , with the weight of the perfect pairing configuration being less than that of the quasi-atomic configuration for most of the region of interest. For $\Delta R < 0.3 \text{ \AA}$ ($\Delta R = R - R_e$), the weight of the quasi-atomic configuration begins to decrease and, eventually, will be less than that for the perfect pairing configuration, but only at internuclear distances much less than the equilibrium internuclear distance, R_e .

The four singlet-coupled, shared electron pairs in the perfect pairing wave function is the basis for the claim by Shaik et al.⁴ that C_2 has a quadruple bond. In molecules where the shared electron pairs occupy distinct regions of space, four pairs would, in fact, correspond to four covalent bonds. However, this is not the case in C_2 . In this molecule, the shared electron pairs in the σ system strongly overlap with one another and Pauli repulsion between the two pairs negates any bonding interactions. That is, the Pauli Principle, through the exchange repulsion between electron pairs, complicates the correlation between shared electron pairs and chemical bonds if the electron pairs occupy orbitals that are concentrated in the same region of space.

In summary, for the internuclear distances of molecular interest, the GVB wave function of C_2 is a mixture of the quasi-atomic configuration and the perfect pairing configuration. The complicated nature of the wave function for C_2 provides a natural explanation for the fact that the properties of this molecule do not fit into the well-established pattern for the $\text{H}_n\text{C}_2\text{H}_n$ series and makes clear why it is not possible to assign a definitive bond order (double, triple, quadruple) to C_2 .

■ ASSOCIATED CONTENT

● Supporting Information

Plots of the variation of the orbital overlaps and spin coupling weights for the quasi-atomic orbital ordering with $\Delta R = R - R_e$ ($R_e = 1.247 \text{ \AA}$). This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: thdjr@illinois.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by funding from the Distinguished Chair for Research Excellence in Chemistry and the National Center for Supercomputing Applications at the University of Illinois at Urbana–Champaign. We thank the other members of our research group, in particular, Beth Lindquist, Tyler Takeshita, and David Woon, for their valuable comments on the material presented herein.

■ REFERENCES

- (1) Hoffmann, R. C_2 in all its guises. *Am. Sci.* **1995**, 83, 309–311.
- (2) Mulliken, R. S. Note on electronic states of diatomic carbon, and the carbon-carbon bond. *Phys. Rev.* **1939**, 56, 778–781.
- (3) Su, P.; Wu, J.; Gu, J.; Wu, W.; Shaik, S.; Hiberty, P. C. Bonding conundrums in the C_2 molecule: A valence bond study. *J. Chem. Theory Comput.* **2011**, 7, 121–130.
- (4) Shaik, S. S.; Danovich, D.; Wu, W.; Su, P.; Rzepa, H. S.; Hiberty, P. C. Quadruple bonding in C_2 and analogous eight-valence electron species. *Nat. Chem.* **2012**, 4, 195–200.
- (5) Schleyer, P. v. R.; Maslak, P.; Chandrasekhar, J.; Grev, R. S. Is a CC quadruple bond possible? *Tetrahedron* **1993**, 34, 6387–6390.
- (6) Shaik, S.; Rzepa, H. S.; Hoffmann, R. One molecule, two atoms, three views, four bonds. *Angew. Chem., Int. Ed.* **2013**, 52, 3020–3033.
- (7) Frenking, G.; Hermann, M. Critical comments on “One molecule, two atoms, three views, four bonds. *Angew. Chem., Int. Ed.* **2013**, 52, S922–S925.
- (8) Danovich, D.; Shaik, S.; Rzepa, H. S.; Hoffmann, R. A response to the “Critical comments on ‘One molecule, two atoms, three views, four bonds’”. *Angew. Chem., Int. Ed.* **2013**, 52, S926.
- (9) Lewis, G. N. The atom and the molecule. *J. Am. Chem. Soc.* **1916**, 38, 762–785.
- (10) Langmuir, I. The arrangement of electrons in atoms and molecules. *J. Am. Chem. Soc.* **1919**, 41, 868–934.
- (11) Heitler, W.; London, F. Interaction between neutral atoms and homonuclear binding according to quantum mechanics. *Z. Phys.* **1927**, 44, 455–472.
- (12) Ruedenberg, K.; Schmidt, M. W. Why does electron sharing lead to covalent bonding? A variational analysis. *J. Comput. Chem.* **2007**, 28, 391–410.
- (13) Xu, L. T.; Dunning, T. H., Jr. unpublished.
- (14) Raos, G.; Gerratt, J.; Cooper, D. L.; Raimondi, M. On the role of different spin bases within spin-coupled theory. *Mol. Phys.* **1993**, 79, 197–216.
- (15) Goddard, W. A., III Improved quantum theory of many-electron systems. II. The basic method. *Phys. Rev.* **1967**, 157, 81–93.
- (16) Goddard, W. A., III; Dunning, T. H., Jr.; Hunt, W. J.; Hay, P. J. Generalized valence bond description of bonding in low-lying states of molecules. *Acc. Chem. Res.* **1973**, 6, 368–376 and references therein.
- (17) Gerratt, J.; Cooper, D. L.; Karadakov, P. B.; Raimondi, M. Modern valence bond theory. *Chem. Soc. Rev.* **1997**, 87–100 and references therein.
- (18) Roos, B. O. The complete active space SCF method in a fock-based super-CI formulation. *Int. J. Quantum Chem.* **1980**, S14, 175–189 and references therein.
- (19) Ruedenberg, K.; Schmidt, M. W.; Gilbert, M. M.; Elbert, S. T. Are atoms intrinsic to molecular electronic wave functions? *Chem. Phys.* **1982**, 71, 41–49 and other papers in this series.
- (20) Werner, H.-J.; Knowles, P. J. An efficient internally contracted multiconfiguration-reference configuration interaction method. *J. Chem. Phys.* **1988**, 89, 5803–5814.
- (21) Langhoff, S. R.; Davidson, E. R. Configuration interaction calculations on the nitrogen molecule. *Int. J. Quantum Chem.* **1974**, 8, 61–72.
- (22) Dunning, T. H., Jr. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *J. Chem. Phys.* **1989**, 90, 1007–1023.
- (23) Goodgame, M. M.; Goddard, W. A., III. The “sextuple” bond of Cr_2 . *J. Phys. Chem.* **1981**, 85, 215–217.
- (24) Thomas, E. J., III; Murray, J. S.; O'Connor, C. J.; Politzer, P. The Cr_2 molecule: Some perspectives. *J. Molec. Struct. Theochem.* **1999**, 487, 177–182.
- (25) Clementi, E.; Veillard, A. Correlation energy in atomic systems. IV. Degeneracy effects. *J. Chem. Phys.* **1966**, 44, 3050–3053.
- (26) Pauncz, R. *The construction of spin eigenfunctions: An exercise book*; Springer: New York, 2000; pp 15–30.
- (27) (a) Kotani, M.; Siga, M. Note on the theory of electronic states of polyatomic molecules. *Proc. Phys.-Math. Soc. Jpn.* **1937**, 19, 471.

(b) Kotani, M. On the valence theory of the methane molecule. I. *Proc. Phys.-Math Soc. Jpn.* **1937**, *19*, 460–470.

(28) Werner, H.-J.; Knowles, P. J.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Celani, P.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Hetzer, G.; Korona, T.; Lindh, R.; Lloyd, A. W.; McNicholas, S. J.; Manby, F. R.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pitzer, R.; Rauhut, G.; Schütz, M.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T. *Molpro*, version 2009.1; University College Cardiff Consultants Ltd.: Cardiff, UK, 2009 and references therein.

(29) (a) Thorsteinsson, T.; Cooper, D. L.; Gerratt, J.; Karadakov, P. B.; Raimondi, M. Modern valence bond representations of CASSCF wavefunctions. *Theor. Chim. Acta* **1996**, *93*, 343–366. (b) Cooper, D. L.; Thorsteinsson, T.; Gerratt, J. Fully variational optimization of modern VB wave functions using the CASVB strategy. *Int. J. Quantum Chem.* **1997**, *65*, 439–451. (c) Cooper, D. L.; Thorsteinsson, T.; Gerratt, J. Modern VB representations of CASSCF wave functions and the fully-variational optimization of modern VB wave functions using the CASVB strategy. *Adv. Quantum Chem.* **1999**, *32*, 51–67. (d) Thorsteinsson, T.; Cooper, D. L. An overview of the CASVB approach to modern valence bond calculations. In *Quantum Systems in Chemistry and Physics. Vol. 1: Basic Problems and Model Systems*; Hernandez-Laguna, A., Maruani, J., McWeeny, R., Wilson, S.; Kluwer: Dordrecht, 2000; pp 303–326.

(30) Urdahl, R. S.; Bao, Y.; Jackson, W. H. An experimental determination of the heat of formation of C_2 and the C–H bond dissociation energy in C_2H . *Chem. Phys. Lett.* **1991**, *178*, 425.

(31) Douay, M.; Nietmann, R.; Bernath, P. F. New observations of the $A^1\Pi_u-X^1\Sigma_g^+$ transition (Phillips System) of C_2 . *J. Mol. Spectrosc.* **1988**, *131*, 250.

(32) Kitaura, K.; Morokuma, K. A new energy decomposition scheme for molecular interactions with the Hartree-Fock Approximation. *Int. J. Quantum Chem.* **1976**, *10*, 325–340.

(33) (a) Gillespie, R. J.; Popelier, P. L. A. *Chemical Bonding and Molecular Geometry*; Oxford University Press, Oxford, 2001. (b) Gillespie, R. J.; Robinson, E. A. Models of molecular geometry. *Chem. Soc. Rev.* **2005**, *34*, 396.

(34) Morokuma, K. Molecular orbital studies of hydrogen bonds. III. $C=O\cdots H-O$ hydrogen bond in $H_2CO\cdots H_2O$ and $H_2CO\cdots 2H_2O$. *J. Chem. Phys.* **1971**, *55*, 1236–1244.

(35) Söderhjelm, P.; Karlström, G.; Ryde, U. Comparison of overlap-based models for approximating the exchange-repulsion energy. *J. Chem. Phys.* **2006**, *124*, 244101 and references therein.

(36) Krapp, A.; Bickelhaupt, F. M.; Frenking, G. Orbital overlap and chemical bonding. *Chem.—Eur. J.* **2006**, *12*, 9196–9216.