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A Response to a Comment by G. Frenking and M. Hermann on: “The Quadruple Bonding in C₂ Reproduces the Properties of the Molecule”

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In a recent paper in this journal,^[1] we demonstrated by means of valence bond (VB) theory that the quadruple bond structure in C₂ reproduces the bond dissociation energy, the bond length, and the force constant of the molecule. We further demonstrated that other C₂ bonding models, with double π -bonding or double π -bonds with dative weak σ bonds, are either higher than the quadruply bonded structure or collapsing into it, during the variational procedure. The comment by Frenking and Hermann,^[2] which followed our publication apparently agrees now that C₂ has a fourfold bonding. Nevertheless, Frenking and Hermann still express concerns about two aspects of the quadruple bond:

a) According to Frenking and Hermann, our estimate of the intrinsic σ -bond strength relative to the nonbonded reference, the so-called quasiclassical state (QCS), must be highly overestimated because we used an average of two Slater determinants D_1 and D_2 (see Figure 1 a) for the QCS.^[1] They argue that D_2 must belong to two carbon atoms in their ³P atomic configurations, while D_1 represents the two atoms in their ⁵S states, and hence D_1 and D_2 must differ in their energies by 192.8 kcal mol⁻¹, which is twice the atomic promotion energy of carbon. As such, Frenking and Hermann^[2] feel that the energy averaging of D_1 and D_2 is behind the high intrinsic σ -bond strength that we derived, and request to see the individual energies of the two QCS determinants. b) As a supporting argument for their criticism in (a), Frenking and Hermann note that *the contribution of the configuration which has a genuine (electron-sharing) quadruple bond between carbon atoms [...] to the total wave function is only 13.7%*. This MO configuration is $2\sigma_g^2 1\pi_u^4 3\sigma_g^2$ and its low contribution to the wave function raises the effective bond order (EBO) only slightly above 2 (2.3

Figure 1. a) The QCS determinants for the σ bonds of the C₂ molecule. D'_1 and D'_2 are degenerate with D_1 and D_2 , respectively; the π bonds are present but not drawn here. b) The two σ bonds in the C₂ molecule.

or so) compared with the fundamental MO configuration, $2\sigma_g^2 1\pi_u^4 2\sigma_u^2$.^[2,3]

As this response to the Frenking and Hermann comment will show; i) D_2 does not correspond to the ³P–³P states of the two carbons in C₂, ii) the energy difference between D_1 and D_2 is only 65.6 kcal mol⁻¹, iii) the usage of the average energy of D_1 and D_2 is dictated by the wave function of C₂, iv) irrespective of whether one uses a QCS which is averaged over D_1 and D_2 or just the lower energy one D_2 , the resulting intrinsic bond strength of the σ bonds well exceeds 100 kcal mol⁻¹, and v) EBO does not count properly the number of bonds in C₂. However, if one takes into account the intrinsic nature of the σ orbitals, based on a correct assignment of their respective types (bonding/non-bonding/anti-bonding), the number of bonds in C₂ becomes the same whether one uses MO-based CASSCF or VB wave functions, and the two points of view can be reconciled as hoped by Frenking and Hermann^[2] in their comment.

Since the heart of Frenking and Hermann’s comment questions our estimation of the “in situ” total σ -bond strength in C₂, we begin by recalling how the energy of a QCS can serve as a reference state for calculating such a quantity without effectively dissociating the bonded fragment.^[4] Let us start by considering the textbook case of two electrons in two atomic orbitals centered on two different atoms, for example, two hydrogen atoms, H_a and H_b in Equation (1), where the normalization factor is omitted for simplicity. The wave function

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$\Psi_{\text{bond}}(H_2)$ in Equation (1) is the original Heitler and London wave function, which is at the origin of the Valence Bond theory ansatz,^[5] and which describes a covalent bond. It is given as a combination of two Slater determinants where the bar indicates spin β and lack of bar indicates spin α :

$$\Psi_{\text{bond}}(H_2) = |H_a \bar{H}_b| - |\bar{H}_a H_b| = H_a^\dagger H_b^\dagger \leftrightarrow H_a^\dagger H_b^\dagger \quad (1)$$

Combining the same two determinants, with an opposite sign to the one in Equation (1), leads to a triplet state which is roughly as repulsive as much as the singlet state is attractive at any distance from equilibrium to infinity. Therefore, the energy of only one of these two degenerate determinants is nearly constant at any distance from infinity up to the equilibrium distance.^[4] As such, taking only one of these determinants (and hence, decoupling the left-right exchange of the two electrons) defines a nearly non-bonding QCS, Equation (2).

$$\Psi_{\text{QCS}}(H_2) = |H_a \bar{H}_b| \equiv H_a^\dagger H_b^\dagger \quad (2)$$

Thus, the difference in energy between $\Psi_{\text{bond}}(H_2)$ and $\Psi_{\text{QCS}}(H_2)$ provides a so-called in situ (or intrinsic) bond-interaction energy of dihydrogen. The advantage of using this technique, compared with just dissociating the molecule, is that it allows us to probe the bond strength of any individual bond of any multiply bonded species, by decoupling the electrons of the respective bond of interest to the respective QCS and finding the intrinsic bond strength as the energy difference between the bond state $\Psi_{\text{bond}}(H_2)$ and the QCS $\Psi_{\text{QCS}}(H_2)$. The QCS approach has been shown to lead to reasonable bond strengths in many other cases.^[4]

Let us now turn to a case displaying two σ bonds, one between the hybrid atomic orbitals (HAOs) σ_1 and σ_{4a} , the other one between σ_2 and σ_3 (Figure 1b). This is precisely the situation of the σ system in the fourfold bonded structure that dominates the properties of the ground state of the C_2 molecule. As in our original work,^[1] here too we only decoupled the two σ bonds to measure their individual in situ energy, while the π bonds were left intact; so these latter bonds will be omitted in the following, for the sake of simplicity. The overall singlet wave function corresponding to the two σ bonds is shown in Equation (3) without a normalization factor, and cartooned in Figure 1b. It is seen that the covalent wave function corresponding to these two σ bonds is a combination of four QCS determinants *having equal weights*! Note that there are two types of QCS determinants. The first two determinants, D_1 and D_1' , have two identical spins on each carbon and are degenerate. The third and fourth determinants D_2 and D_2' , have opposite spins on the same atoms. Consequently, they are also degenerate but different in energy than D_1 and D_1' .

$$\begin{aligned} \Psi_{2\text{-bond}}(C_2) &= |(\sigma_1 \bar{\sigma}_4 - \bar{\sigma}_1 \sigma_4)(\sigma_2 \bar{\sigma}_3 - \bar{\sigma}_2 \sigma_3)| \\ &= |\sigma_1 \bar{\sigma}_4 \sigma_2 \bar{\sigma}_3| + |\bar{\sigma}_1 \sigma_4 \bar{\sigma}_2 \sigma_3| - |\sigma_1 \bar{\sigma}_4 \bar{\sigma}_2 \sigma_3| - |\bar{\sigma}_1 \sigma_4 \sigma_2 \bar{\sigma}_3| \\ &= D_1 + D_1' + D_2 + D_2' \end{aligned} \quad (3)$$

It follows that $\Psi_{2\text{-bond}}(C_2)$ displays 50% alternate spins between σ_1 and σ_{2a} , and another 50% between σ_3 and σ_4 . There-

fore, a physically correct QCS reference must display this symmetric distribution of the alternate vs. identical spins, along with the decoupling of the σ_1 - σ_4 and σ_2 - σ_3 bonds. This is precisely achieved by the normalized sum ($D_1 + D_2$), since D_1 displays full σ_1 - σ_2 and σ_3 - σ_4 parallel spins, whereas D_2 fully alternate spins. Here is the fundamental reason (explained already in a previous paper^[4c]), requested by Frenking and Hermann, for the usage of average energies of the two QCS determinants D_1 and D_2 as the reference in situ non-bonding energy for the σ system of C_2 , expressed explicitly in Equation (4).

$$E_{\text{QCS}}(C_2) = 0.5[E(D_1) + E(D_2)] \quad (4)$$

Let us now consider the whole fourfold-bonded structure for C_2 , including the π bonds. In the original paper,^[1] we indicated that the QC states are defined with the π bonds treated as delocalized MOs. It follows that the $p(\pi)$ electrons on each carbon have each 50% identical and 50% opposite spins. By contrast, Frenking and Hermann seem to ignore the two π bonds in our QC state(s) and claim or think that the two $p(\pi)$ electrons that are not shown have identical spin on each carbon atom. Based on this erroneous statement, Frenking and Hermann assume that each carbon atom has a 5S state in D_1 and a 3P state in D_2 . This is not correct, as in reality the carbon atoms in D_1 and D_2 have nothing to do with a pure state with fixed spins, be it of the 3P or 5S type.^[6] However, even if D_1 and D_2 are not pure states, we can still determine to which one of the $^3P/^5S$ states are they akin to. In D_1 , the two σ HAOs of each carbon, for example, σ_1 and σ_{2a} , have identical spin. If one expands their product in terms of configurations involving only pure 2s and 2p orbitals, terms of the type $2s^2$ and $2p^2$ cancel out due to the Pauli principle, and what remains in the expansion is the sole $2s^1 2p^1$ configuration. Since the $2p(\pi)$ AOs are pure 2p ones, D_1 displays four orthogonal singly occupied AOs on each carbon and is therefore akin (not identical, though) to a 5S - 5S state. This agrees with Frenking and Hermann's assumption, even if they erroneously assign identical spins to the electrons in the $2p(\pi)$ AOs; these spins are α and β .

On the other hand, quite different is the status of the D_2 determinant. Here, each carbon bears a pair of non-orthogonal HAOs (σ_1, σ_2 on one carbon, σ_3, σ_4 on the other), *which have different spins*.^[6] In such a case, expanding a product of two σ HAOs of the same carbon would lead to a combination of $2s^2$, $2p^2$ and $2s^1 2p^1$ atomic configurations, with coefficients depending on the shapes of the σ HAOs and their mutual overlaps. For example, if the two HAOs on the same carbon are close to pure 2s and 2p, respectively, their product is $2s^1 2p^1$ and D_2 will be akin to 5S - 5S . Alternatively, in the improbable situation where the two HAOs would be both close to pure 2s, then D_2 would be akin to 3P - 3P , and so on. How then to decide which pure carbon state D_2 is akin to? A very simple way is to consider the energy of D_2 relative to D_1 . If D_2 is a 3P - 3P type, then it should reside approximately $192.8 \text{ kcal mol}^{-1}$ below D_1 , as assumed by Frenking and Hermann who considered pure atomic states. If on the other hand, D_2 is a 5S - 5S type, then it should be quasi-degenerate with D_1 . *Actually, the*

calculation shows that (at the equilibrium C_2 distance) D_2 lies only $65.6 \text{ kcal mol}^{-1}$ below D_1 , showing that D_2 is clearly closer to a 5S – 5S state than to a 3P – 3P one. This is in sharp contrast to Frenking and Hermann's statement.

Besides, Frenking and Hermann^[2] propose to recalculate the $D_{2\sigma}^{\text{in-situ}}$ value for the σ intrinsic bond strength, by taking either D_1 or D_2 as reference states instead of their average. As can be seen from Scheme 1, owing to the rather small energy difference between D_1 and D_2 , this would modify the previously calculated in situ bond strength by only $\pm 32.8 \text{ kcal mol}^{-1}$ and would not affect the qualitative conclusions. Thus, even if we abandon the physically proper averaged QCS and use only D_2 as the reference state, still the value of $D_{2\sigma}^{\text{in-situ}}$ will amount to $123.8 \text{ kcal mol}^{-1}$, thus, making a strong contribution to the bonding of the molecule.

Scheme 1. Evaluated σ -bond strengths (in kcal mol^{-1}) of C_2 , using the lowest quasiclassical state, D_2 (left), or the average of D_1 and D_2 (right).

Of course, we are aware of the “seeming paradox” that C_2 is found to have a higher bond strength than acetylene, as measured by the in situ estimation, while its bond dissociation energy (BDE) is smaller. However, as has been noted by Frenking and Hermann themselves,^[3a] a meaningful estimation of the “bond strength” in a molecule may differ from the BDE. Indeed, a bond strength is estimated by reference to fragments A and B in states reflecting their actual electronic configurations in the molecule. On the other hand, a BDE is always calculated by reference to the separate A and B in their ground states. Since the two carbon atoms, in the C_2 molecule, each display four odd electrons in four atomic orbitals and hybrids, the bonded carbon atoms in the molecule are in a state akin to a 5S – 5S . However, as we showed in the original paper,^[1] at longer C–C distances the states of the carbon atoms within the stretched molecule collapse to a state akin to 3P – 3P , with a bonding crossover transpiring near $R_{CC}=1.85$ – $1.9 \text{ \AA}$. This is the reason why the bond strength of C_2 , which is estimated at the equilibrium distance and by reference to a 5S state, is found to be significant and larger than that of acetylene. By contrast, the BDE of C_2 which is estimated by reference to the lower 3P state, is weaker than that of acetylene. This is quite simple, and VB theory gets both quantities right.^[1,7]

Another aspect in Frenking and Hermann's comment^[2] is their argument that the contribution of the configuration which has “a genuine (electron sharing) quadruple bond [...] is

only 13.7%”. This claim is based on an analysis of a standard CASSCF wave function, in which the Hartree–Fock configuration $2\sigma_g^2 2\sigma_u^2 1\pi^4$ is considered to lack any σ bonding, while the $2\sigma_u^2 \rightarrow 3\sigma_g^2$ excitation, which has a weight of 13.7%, would be the only one displaying (double) σ bonding. In their analysis, the assumed absence of σ bonding in the Hartree–Fock configuration is based on the formal antibonding nature of the $2\sigma_u$ MO, which would exactly compensate for the bonding nature of the $2\sigma_g$ one. This oversimplified reasoning^[2] ignores the fact that the $2\sigma_u$ MO is certainly much less antibonding than the $2\sigma_g$ one is bonding, as a simple inspection of orbital shapes would show (see Figure 4a of our paper^[1]), and as has been noted by other authors.^[8] More rigorously, the bonding/antibonding nature of an MO can be quantitatively estimated by the overlap population (OP) of its two constituent fragments. Within elementary MO theory, the OP is $+S/(1+S)$ for a bonding MO (S being the overlap between the two constituting fragments), $-S/(1-S)$ for an antibonding MO, and zero for a fully non-bonding one. A positive OP thus denotes in-phase (bonding) overlap of the fragments, whereas a negative OP denotes out-of-phase overlap and antibonding character. Of course, the bonding/antibonding character of an MO is related to the magnitude of the OP. Now, as shown in Table 4 of our original paper,^[1] the OP of the $2\sigma_u$ MO, while quite basis-set-dependent, is always very weakly negative, and even becoming slightly positive in the cc-pV6Z basis set! By contrast, the OP of the $2\sigma_g$ MO is constant and always large, denoting strong bonding character. It is therefore totally unjustified to deny any σ bonding character to the $2\sigma_g^2 2\sigma_u^2 1\pi^4$ configuration, owing to the dubious nature of the $2\sigma_u$ MO. In fact, by discarding $2\sigma_u^2$ from the bond order calculation, one finds a $BO=3$ for the Hartree–Fock configuration^[8,9] and slightly more than 3 (≈ 3.14) if the contribution of 13.7% for the $2\sigma_g^2 1\pi_u^4 3\sigma_g^2$ configuration to the CASSCF wave function^[2] is taken into account. In this manner the apparently disparate VB and MO pictures converge to a single picture. Another way to reconcile the two pictures was shown by Zhang et al,^[10] who transformed the σ orbitals in the CASSCF wave function and obtained a wave function with more than three bonds.

In the same context, one of the misleading analogies that has been used^[2,3a,11] is between the σ bonding in C_2 and the one in Be_2 . In both cases the $2\sigma_g$ and $2\sigma_u$ orbitals are filled, and hence a naïve bond order application would lead to the conclusions that both molecules have little or no σ -bonding. Indeed, Be_2 is barely bound. So by analogy to Be_2 , C_2 could be deemed to have a residual weak σ -bonding if at all.^[3a,11] However, our calculated OPs for C_2 and Be_2 at their equilibrium distance (cc-pVTZ basis set and CASSCF(4,8) and (8,8) for Be_2 and C_2 , respectively) show that the $2\sigma_u$ orbital of C_2 is virtually non-bonding ($OP=-0.076$) and does not reduce at all the effect of the strong bonding character of $2\sigma_g$ ($OP=0.415$). By contrast, the $2\sigma_u$ orbital in Be_2 is clearly strongly antibonding ($OP=-0.385$), and overrides the bonding character of the $2\sigma_g$ orbital ($OP=0.316$). Therefore, the use of the alleged analogy^[2a,11] between C_2 and Be_2 is clearly misleading. It follows that, whatever the arguments that can be raised to explain the quasi-non-bonding nature of the $2\sigma_u$ orbital in C_2 , it remains that this MO

cannot be counted as an antibonding one in a bond order estimation.

In summary, we have provided in the present response the numerical data as well as explanations for the key points raised in Frenking and Hermann's comment. As summarized in Figure 1 a, these show that, owing to the nature of the ground state wave function at equilibrium distance, our choice of an averaged reference state to estimate the strength of the σ bonds in C_2 is the most logical one. As shown in Scheme 1, the results also demonstrate that even taking the reference state advocated by Frenking and Hermann would not change at all our conclusion that C_2 is quadruply bonded with a double π bond and a double σ bond of significant strength.

Finally, we show that if the bonding/antibonding natures of the MOs of C_2 are rigorously quantified, both MO-CASSCF and VB calculations lead to the same picture,^[10] namely that C_2 has a quadruple bond and thereby it breaks the glass ceiling of triple bonding.^[1]

We thank Frenking and Hermann for their comment which, jointly with the present response, should hopefully reconcile the formerly conflicting points of views.

Keywords: bond order • bond strength • bonding analysis • C_2 • promotion energy • quadruple bonds • valence bonds

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