Latent harmony in dicarbon between VB and MO theories through orthogonal hybridization of $3\sigma_g$ and $2\sigma_u$

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Besides the classic double bond scheme, several novel schemes have been proposed to describe the nature of the chemical bond in dicarbon (C$_2$), including a quadruple bond and a singlet diradical state. The results from a symmetry-broken CASSCF(8,8)/aug-cc-pVTZ study present a harmony between MO and VB theories, based on the orthogonal hybridization of the $3\sigma_g$ and $2\sigma_u$ orbitals together with the other six pristine valence orbitals. This scheme achieves the same bonding energy, $R_{C\cdots C}$, $\omega_u$ and one electron density as that from the eight pristine valence orbitals. A quadruple bond scheme, identical to Prof. Shaik's result from VB theory, is achieved with the 4th bond energy in the range of 12.8–27.6 kcal mol$^{-1}$. Meanwhile, the weight of a singlet open-shell configuration is the highest among all the possible configurations.

Introduction

Dicarbon (C$_2$) is a simple molecule with just two atoms. However, it has aroused many fundamental questions, fascinating mysteries and active discussions in chemistry.$^{1-6}$ It is a colourless gas and is very unstable. A tiny quantity of C$_2$ can be prepared from electric arc strikes, and a good amount of C$_2$ can exist in comets, stellar atmospheres, blue hydrocarbon etc. The C–C bond length ($R_{C\cdots C}$) is 1.243 Å in its $^1\Sigma_g^+$ ground state, and the corresponding vibration frequency ($\omega_u$) is 1855 cm$^{-1}.^{1,2,7}$ At least another 12 excited states have been observed experimentally and the $R_{C\cdots C}$ values are found to be in a large range of 1.23 Å to 1.53 Å.$^{2,4,10}$ Among them, two $R_{C\cdots C}$ values bear shorter bond lengths in the excited states ($^1\Sigma_g^+$ and $^3\Sigma_g^-$) than in the ground state. Similar shorter bond lengths in the excited states have also been reported in its cation and anion (C$_2^+$ and C$_2^-$).$^{8-11}$ The $R_{C\cdots C}$ of the dicarbide ion (C$_2^2-$) in crystalline calcium carbide and lithium carbide is shorter than 1.20 Å,$^{12,13}$ which is generally accepted as a traditional triple bond (1σ + 2π bonds) analogue of N$_2$.

It is worthy of note that the ground $R_{C\cdots C}$ distance of C$_2$ is 1.243 Å, shorter than the length of any classic C≡C double bond (1σ + 1π bond), such as in ethylene.$^{14}$ Hence, Prof. Shaik$^{15}$ pointed out that suspended π bonds may be responsible, since they prefer shorter lengths than σ bonds. The essential point of this assumption is that the occupied number of the 2σ$_u$ antibond is approximately equal to that of the 2σ$_g$ bond. However, 2σ$_u$ is a weak antibonding orbital due to a lower occupied number, which can not counteract the stronger bonding of σ$_g$. Furthermore, the $\omega_u$ value of C$_2$ is higher than that of ethylene. Hence, soon after, the nature of the C$_2$ bond was said to approach that of a triple bond (C≡C)$.^{16,17}$ Based on the characteristics of a triple bond in C$_2$, a scheme of a triple bond plus weak coupling by a pair of opposite spinning electrons was proposed in valence bond (VB) theory.$^{18}$ The opposite spinning electron coupling energy was found to be $\sim$12–20.2 kcal mol$^{-1}$ (ref. 19 and 20) at various levels of the theory. In this context, the corresponding 4th bonding scheme of C$_2$ (Fig. 1c) was proposed with VB theory.$^{19}$

A quadruple bond in C$_2$ is certainly reasonable based on quantum mechanics,$^{19,20}$ similar to that in [1.1.1]-propellane.$^{21}$ However, whether it is the best picture to describe the ground state of C$_2$ or not has aroused many active discussions.$^{21,22,26}$ According to traditional molecular orbital (MO) theory, the

![Fig. 1](attachment:image.png)

Fig. 1 The configurations of MO's double bond, MO's quadrupole bond and VB's quadruple bond schemes in C$_2$. The difference in the order of the occupied orbitals is highlighted with red lines.

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quadruple bond configuration of C₂ can be achieved by doubly exciting 2σₓ electrons to the 3σₓ orbitals. However, a calculation at the CASSCF(8,8)/cc-pVTZ level indicates that the weight of the double bond state (Fig. 1a) is 71.0% while the weight of the 2σₓ → 3σₓ quadruple bond counterpart (Fig. 1b) is only 13.6%. On the other hand, the weak 4p bond (the inset in Fig. 1c) was proposed by inequivalent hybridization of the 3σₓ and 2σₓ occupied states, covering only MO double and quadruple bond configurations, which does not seem perfect. Even in an egalitarian mode, the corresponding bond order of C₂ is between two and three. What is the dominant configuration if orthogonal hybridization of 3σₓ and 2σₓ is utilized and 100% weight of multi-configurational self-consistent field (MCSCF) is covered in the calculation? Is there any other configuration that can possess a higher weight in the ground state (1Σ⁺) of C₂ among all the possible configurations?

Results and discussion

As we know, the ground state of C₂ is generally accepted as double π bonds in MO theory (shown in Fig. 1a). However, the quasi-degeneracy of the 2σₓ, 3σₓ and 1πₓ orbitals is well known in C₂ and its ions, which results in many low-lying excited states of C₂, C₂⁻ and C₂⁺. The antiferromagnetic diradical characteristic of C₂ has also been proposed by the finite-difference pseudopotential method, local spin analysis and VB theory. Silicon resides in the same column of the periodic table as carbon. The singlet diradical characteristic on a silicon (100) surface is well known. Moreover, dicarbon is a very unstable molecule with a short lifetime, which is easy to dimerize into C₄ for instance.

As mentioned above, CASSCF(8,8)/aug-cc-pVTZ was used in our study because C₂ has multi-reference configurations in nature. In the beginning, the level was benchmarked for the 1Σ⁺ ground state (KK2σₓ¹1πₓ¹1πₓ¹2σₓ¹2σₓ¹) and four low-lying (1Πₓ, 3Σ⁺, 3Πₓ and 1Πₓ) excited states. All the potential energy curves are plotted in Fig. 2. Furthermore, the important data of these optimized states contrasting to the experimental data are listed in Table 1.

The calculated R_C–C and ω_C values of the 1Σ⁺ state are close to the experimental values. For example, the bonding energy of the 1Σ⁺ state is −142.5 kcal mol⁻¹, which is almost equivalent to the ideal R_C–C bonding breakage of C₂ based on the heats of formation. The R_C–C differences of the other four states compared to the experimental data are only less than 0.02 Å. These results clearly show that the results from the CASSCF(8,8)/aug-cc-pVTZ level are reliable. In the ground state, 3σₓ is a weak bond with a one electron density of ~0.4e. It contributes somewhat to the stabilization of C₂. Hence, a triple bond scheme of C₂ is also reasonable. However, the one electron density of the 2σₓ orbitals is ~1.6e, which is ~1.2e higher than that of the 3σₓ orbital. If the populations of all the other three valence orbitals (1πₓ₁, 1πₓ₂ and 3σₓ) are included, the relative 2σₓ antibond electrons are still ~1.0e higher. In this context, the quadruple bond scheme is hard to be accepted by naive application of MO theory.

Based on the traditional valence MOs, it is hard to interpret the singlet diradical characteristic of the C₂ ground state, while it has been shown through the finite-difference pseudopotential method and LSA analysis. Even though a singlet diradical state (KK2σₓ¹1πₓ¹2σₓ¹3σₓ¹) was achieved, it is still a 3Πₓ state. The diagram of 2σₓ¹3σₓ¹ occupation is shown in the left part of Fig. 3. As a result, the MO and VB theories fall into an apparent contradiction. In our opinion, this just indicates that opposite spinning electrons do not locate around the C–C bonds, which is in accordance with Prof. Shaik’s proposal. However, the difficulty with the VB interpretation of the full configuration interaction (CI) wave function may be due to the nonorthogonal transform and the neglect of ~15% weight of the configuration state functions (CSFs). Can VB quadruple bond schemes be reliable through the reformed valence MO orbitals? Is it feasible to describe the singlet diradical characteristic of C₂ through the reformed valence MO orbitals simultaneously?

We hereby propose another scheme through hybrid orbitals of the 2σₓ and 3σₓ orbitals to φ_2σₓ + 3σₓ(q₁) and φ_2σₓ − 3σₓ(q₂), which was used as the initial active orbital for the CASSCF calculation. It is worthy of note that the q₁ and q₂ orbitals ensure that the single-occupied electrons are located outside of the C–C bond (right part of Fig. 3a). Besides, the other six primitive valence orbitals were maintained. Subsequently, the potential energy curve of the ground state of C₂ was re-scanned at the same level with our orbitals. Compared with Prof. Shaik’s strategy, the eight CAS orbitals were all orthogonal and the SCFs covered 100% of the weight. As expected, the new results show that the bonding energy, R_C–C, ω_C and one electron density are all the same as the values from the eight primitive valence orbitals (in the first column of Table 1). This is reasonable because the final result is only determined by the one electron densities in the original natural orbitals and the corresponding gradient analysis when all the CSFs are included in the simulations. CASSCF(8,8) and VBSCF(1764) span the same space of 1764 configurations in MO and VB theories, separately. Theoretically, the same electron correlation energy and bonding energy can be achieved if the same orbitals are adopted in the

![Fig. 2 Plots of C₂ potential energy curves of 1Σ⁺ state and four (1Πₓ, 3Σ⁺, 3Πₓ and 1Πₓ) excited states at CASSCF(8,8)/aug-cc-pVTZ level. The bonding energy is relative to two isolated 3P carbon atoms at CASSCF(4,4)/aug-cc-pVTZ level. The vertical transition energies from 1Σ⁺ state are also shown.](image-url)
and the weights of the corresponding CSF weights, which are a function of the one electron density of the ground state in Table 1. The most important theoretical data of the five states, including \( R_{\text{C-C}} \) (\( \text{Å} \)) and vibrational frequencies (\( \omega_{\text{v}} \), cm\(^{-1} \)), together with their experimental data (shown in bracket) are shown in Fig. 4. The weight of the highest configuration (KK2\( \sigma^1_2 \pi^1_{u2} \pi^1_{g1} \pi^1_{g2} \sigma^1_{u3} \)\( \pi^1_{g3} \)) is 73.7%, around 2.7% higher than that of Prof. Frenking’s (KK2\( \sigma^1_2 \pi^1_{u2} \pi^1_{g1} \sigma^1_{u3} \)). The results elucidate that the spin-localization of the 2\( \sigma_u \) electrons is, indeed, outside of the C-C bond, in accordance with the VB view.\(^{15,16}\) If the bonding nature is estimated by the highest weight configuration, the ground state of C2 is inclined to be a singlet diradical due to a little higher weight than the traditional double bond configuration.

However, with our understanding from VB theory, the first three configurations have to be added up, since there is a combination of a major covalent structure (C\(^1\)–C\(^1\)), and two minor ionic ones (C\(^-\)–C\(^+\) and C\(^-\)–C\(^-\)). They all belong to the 4\(^{th}\) bond. To our surprise, the total weight of the three highest configurations is equal to the weight sum of the classic MO double and quadruple bond configurations (Fig. 3b), namely the initial value in Prof. Shaik’s nonorthogonal scheme. Hence, the corresponding covalent component of the 4\(^{th}\) bond is 84.8% (close to the weight of the 1\( \Pi_u \) and 3\( \Sigma_u^+ \) states). The opposite spin coupling energy between \( \Phi_L \) and \( \Phi_R \) can not be achieved directly in our orthogonal schemes. If the vertical excited energy from the 3\( \Sigma_u^+ \) to 1\( \Pi_u \) states (\( \Delta E_{\text{relax}} \) is 1.253 \( \text{Å} \)) is the input active orbitals and their corresponding CSF weights, which are affected by the input orbital styles. The five highest weight configurations of our scheme are shown in Fig. 4. Left: CASSCF orbitals, including \( \phi_u \) and \( \phi_d \). Right: The corresponding five most important configurations of a full-valence CASSCF(8,8)/aug-cc-PVTZ calculation of C2, showing the coefficients and the weights of the configurations.

### Table 1

<table>
<thead>
<tr>
<th>State</th>
<th>( R_{\text{C-C}} ) (( \text{Å} ))</th>
<th>( \Delta E_{\text{relax}} ) (kcal mol(^{-1} ))</th>
<th>( \omega_{\text{v}} ) (cm(^{-1} ))</th>
<th>Dominant Configuration</th>
<th>Other Configurations</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^1\Sigma_g^+ )</td>
<td>1.255 (1.243)</td>
<td>–142.5 (–142)</td>
<td>1839 (1855)</td>
<td>KK2( \sigma^1_2 \pi^1_{u2} )</td>
<td>KK2( \pi^1_{u2} \sigma^1_{u3} )</td>
</tr>
<tr>
<td>( ^3\Pi_u )</td>
<td>1.330 (1.312)</td>
<td>–131.8</td>
<td>1599 (1641)</td>
<td>KK2( \sigma^1_2 \pi^1_{u2} )</td>
<td>KK2( \pi^1_{u2} \sigma^1_{u3} )</td>
</tr>
<tr>
<td>( ^3\Sigma_u^+ )</td>
<td>1.224 (1.230)</td>
<td>–114.9</td>
<td>1975 (2084)</td>
<td>KK2( \sigma^1_2 \pi^1_{u2} )</td>
<td>KK2( \pi^1_{u2} \sigma^1_{u3} )</td>
</tr>
<tr>
<td>( ^3\Sigma_u^- )</td>
<td>1.384 (1.369)</td>
<td>–113.1</td>
<td>1436 (1470)</td>
<td>KK2( \sigma^1_2 \pi^1_{u2} )</td>
<td>KK2( \pi^1_{u2} \sigma^1_{u3} )</td>
</tr>
<tr>
<td>( ^1\Pi_u )</td>
<td>1.338 (1.318)</td>
<td>–104.7</td>
<td>1553 (1608)</td>
<td>KK2( \sigma^1_2 \pi^1_{u2} )</td>
<td>KK2( \pi^1_{u2} \sigma^1_{u3} )</td>
</tr>
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Simulation. Unfortunately, orthogonal orbitals are adopted in the former, but the nonorthogonal orbitals are adopted in the latter.\(^{18}\)

The difference between our and Prof. Frenking’s CASSCF schemes\(^{21}\) is the input active orbitals and their corresponding CSF weights, which are affected by the input orbital styles. The five highest weight configurations of our scheme are shown in Fig. 3. Equivalent hybridized orbitals of \( \phi_u \) and \( \phi_d \) from 2\( \sigma_u \) and 3\( \sigma_g \) localized around a single C atom (a) and the corresponding potential occupied styles before and after hybridization (b).
state of the carbon atom is a starting point. That is the reason why the C–C bonding breakage of C\textsubscript{2} is smaller than that of ethylene (−172 kcal mol\textsuperscript{−1}). In our simulation, the highest EBO is 2.74 for the \(^{2\Sigma^+}\) state, because of the occupied number of 0.976 in the \(3\sigma_g\) orbitals. Some distribution of \(3\sigma_g\) locates between the two carbon atoms. A similar contribution is from the lower occupied number of 1.031e in the \(2\sigma_u\) orbitals. Hence, its \(R_{C–C}\) value is ~0.03 Å shorter than the \(R_{C–C}\) value of the ground state, and the corresponding \(\omega_e\) value is the highest.

In the end, we would like to say a little more about the nature of the chemical bond in C\textsubscript{2} with an ancient Chinese poem about Mountain Lu written by Su Shi: “It’s a range viewed in face and peaks from the side. Assuming different shapes viewed from far and wide. Of the Mountain Lu we cannot make out the true face. For we are lost in the heart of the very place.”\textsuperscript{39} We are shown that the shape and scenery of Mountain Lu are different from different perspectives. Similarly, the understanding of “the most rigorous theory”\textsuperscript{23} for C\textsubscript{2} perhaps depends on the various viewpoints of chemists.

### Conclusions

In summary, a quadruple bond scheme identical to Prof. Shaik’s result from VB theory is achieved, which is related to its \(R_{C–C}\) length. Meanwhile, the weak 4th bond or the singlet diradical state of the carbon atom is a starting point. That is the reason why the C–C bonding breakage of C\textsubscript{2} is smaller than that of ethylene (−172 kcal mol\textsuperscript{−1}). In our simulation, the highest EBO is 2.74 for the \(^{2\Sigma^+}\) state, because of the occupied number of 0.976 in the \(3\sigma_g\) orbitals. Some distribution of \(3\sigma_g\) locates between the two carbon atoms. A similar contribution is from the lower occupied number of 1.031e in the \(2\sigma_u\) orbitals. Hence, its \(R_{C–C}\) value is ~0.03 Å shorter than the \(R_{C–C}\) value of the ground state, and the corresponding \(\omega_e\) value is the highest.

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### Methodology

Based on the calculations in previous references,\textsuperscript{21,23} the precision achieved by CASSCF(8,8), which covers the CSFs excited including all the valence electron orbitals, is as good as full CI, since it is commonly recognized that the weights of the inner \(1\sigma_g^21\sigma_u^2\) orbitals are always 100% in full CI simulations. The configurations of the C\textsubscript{2} electronic states are constructed directly from combinations of natural atomic orbitals in our simulations, because natural orbitals, as a particularly efficient choice, possess the unique advantage of minimizing the mixing effect of the 2s–2p orbitals in carbon and eliminating the diversification of LCAO-MOs in MCSCF simulations.\textsuperscript{33–34} All the calculations were performed mainly based on the GAUSSIAN 09 program package.\textsuperscript{35}

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### Notes and references

30 S. Su, Written on the wall at West Forest Temple. This version is translated by Xu Yuanchong.