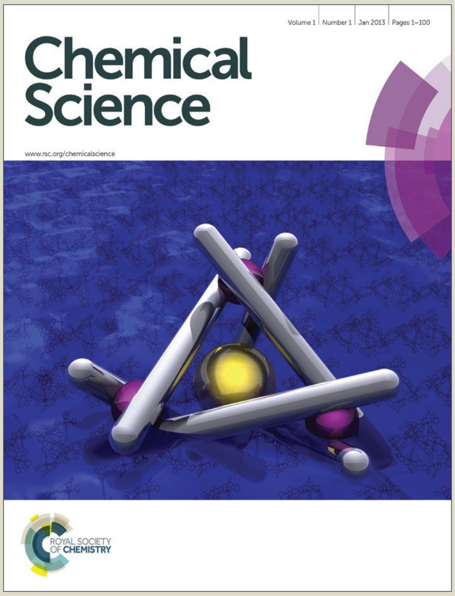
# Chemical Science

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemicalscience

Journal Name

ARTICLE

# Latent Harmony in Dicarbon between VB and MO Theories through Orthogonal Hybridization of $3\sigma_g$ and $2\sigma_u$

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

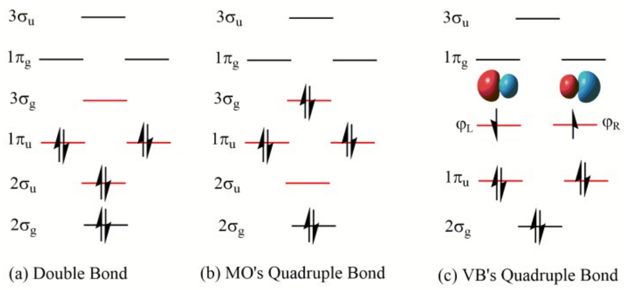
Ronglin Zhong,[a] Min Zhang [a,*], Hongliang Xu [a] and Zhongmin Su [a,*]

Besides the classic double bond scheme, several novel schemes have been proposed to describe the nature of the chemical bond in dicarbon ($C_2$), mainly including 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 $3\sigma_g$ and $2\sigma_u$ orbitals together with other six pristine valence orbitals. This scheme achieves the same bonding energy, $R_{C-C}$, $\omega_e$ and one electron density as from the eight pristine valence orbitals. Especially, 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. 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 very unstable. A tiny quantity of $C_2$ can be prepared from electric arc strikes, and a good bit of $C_2$ can exist in comets, stellar atmospheres and blue hydrocarbon flames, et al. The C-C bond length ($R_{c-c}$) is 1.243 Å in its ${}^1\Sigma_g^+$ ground state, and the corresponding vibration frequency ($\omega_e$) is 1855 $cm^{-1}$.[2, 7] At least another 12 excited states have been observed experimentally and $R_{c-c}$s is in a large range of 1.23 Å to 1.53 Å.[2, 4] Among them, two $R_{c-c}$s bear shorter bond lengths in the excited states (${}^3\Sigma_u^+$and ${}^1\Sigma_u^+$) than that 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 $R_{c-c}$ of 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 $R_{c-c}$ distance of $C_2$ is 1.243 Å, shorter than the length of any classic C=C double bond (1σ+1π bonds), 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 of this assumption is that the occupied number of $2\sigma_u$ antibond is approximately equal to that of $2\sigma_g$ bond. However, $2\sigma_u$ is a weak antibond orbital due to a lower occupied number, which can't counteract the stronger bonding of $2\sigma_g$. Furthermore, the $\omega_e$ of $C_2$ is higher than that of ethylene. Hence, soon after the nature of $C_2$ bond was approached to a triple bond (C≡C).[16, 17] Based on the character of a triple bond in $C_2$, a scheme of a triple bond plus a weak coupling by a pair of opposite spinning electrons was proposed in VB theory.[18] The opposite-spinning-electron coupling energy was investigated to be ~12-20.2 kcal.$mol^{-1}$ [19,20] at various levels of the theory. In this context, the corresponding 4th bonding scheme of $C_2$ (Fig. 1c) was proposed in VB theory.[19]



(a) Double Bond (b) MO's Quadruple Bond (c) VB's Quadruple Bond

**Figure 1.** The configurations of MO's double bond, quadruple bond and VB's quadruple bond scheme in $C_2$. The difference in order of occupied orbitals is highlighted in red lines.

The quadruple bond in $C_2$ is certainly reasonable based on quantum mechanics[19, 21], similar as in [1.1.1]-propellane[22]. However, whether it is the best picture to describe the ground state of $C_2$ or not has aroused many active discussions [21, 23-26]. According to the traditional MO theory, the quadruple bond configuration of $C_2$ can be achieved by double excited $2\sigma_u$ electrons to $3\sigma_g$ orbitals. However, the calculation at the CASSCF(8,8)/cc-pVTZ level indicates that the weight of double bond state (Fig. 1a) is 71.0% while the weight of $2\sigma_u \rightarrow 3\sigma_g$ quadruple bond counterpart (Fig. 1b) is only 13.6%.[21] On the other hand, the weak 4th bond (the insert in Fig. 1c) was proposed by inequivalent *hybridization* of $3\sigma_g$ and $2\sigma_u$ occupied states, covering only MO double and quadruple bond

---

[a] Institute of Functional Material Chemistry & Local United Engineering Lab for Power Battery, Faculty of Chemistry, Northeast Normal University, Changchun 130024, China. E-mail: mzhang@nenu.edu.cn (Prof. M. Zhang) zmsu@nenu.edu.cn (Prof. Z. Su)

† Ronglin Zhong and Min Zhang contributed equally.

configurations, which seems neither perfect. Even in an egalitarian mode, the corresponding bond order of $C_2$ is between two and three. What is the dominant configuration like if orthogonal hybridization of $3\sigma_g$ and $2\sigma_u$ is utilized and 100% weight of MCSCF is covered in the calculation? Is there any other configuration which can possess a higher weight in the ground state ($^1\Sigma_g^+$) of $C_2$ among all the possible configurations?

## Results and discussion

As we know, the ground state of $C_2$ is a *generally accepted* as double π bonds in MO theory (shown in Fig. 1a). However, the quasi-degeneracy of $2\sigma_u$, $3\sigma_g$ and $1\pi_u$ orbitals is well known in $C_2$ and its ions, which results in many low-lying excited states of $C_2$, $C_2^-$ and $C_2^+$.[1,2,4] The antiferro-magnetic diradical character of $C_2$ has also been proposed by finite-difference pseudopotential method, local spin analysis and VB theory.[24-26] Silicon resides in the same column of the periodic table with carbon. The singlet diradical character on silicon (100) surface has been well-known.[27,28] Moreover, dicarbon is a very unstable and short-life molecule which is easy to dimerize into $C_4$ for an instance.

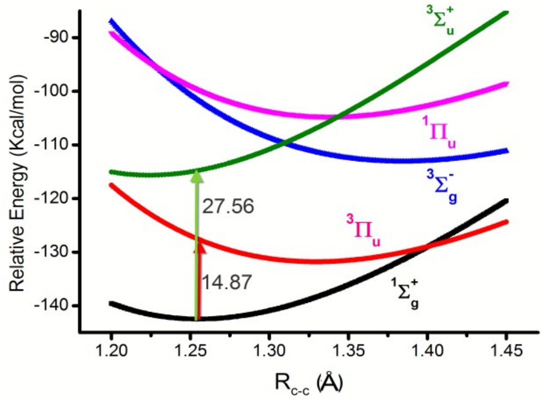


**Figure 2.** Plots of $C_2$ potential energy curves of $^1\Sigma_g^+$state and four ($^3\Pi_u$, $^3\Sigma_u^+$, $^3\Sigma_g^-$ and $^1\Pi_u$) excited states at CASSCF(8,8)/*aug*-cc-pVTZ level. The bonding energy is relative to two isolated $^3P$ carbon atoms at CASSCF(4,4)/*aug*-cc-pVTZ level. The vertical transition energies from $^1\Sigma_g^+$ state are also shown.

As mentioned above, the CASSCF(8,8)/*aug*-cc-pVTZ is used in our study because $C_2$ is multi-reference configurations in nature. In the beginning, the level is benchmarked for the $^1\Sigma_g^+$ ground state ($KK2\sigma_g^2 1\pi_{xu}^2 1\pi_{yu}^2 2\sigma_u^2$) and four low-lying ($^3\Pi_u$, $^3\Sigma_u^+$, $^3\Sigma_g^-$ and $^1\Pi_u$) 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 $\omega_e$ of $^1\Sigma_g^+$ state are close to the experimental values. For example, the bonding energy of $^1\Sigma_g^+$ state is -142.5 kcal.mol$^{-1}$, which is almost equivalent to the ideal $R_{C-C}$ bonding breakage of $C_2$ based on the heats of formation[23]. The $R_{C-C}$ differences of other four states to the experimental data are only less than 0.02 Å. These results clearly show that the result of CASSCF(8,8)/*aug*-cc-pVTZ level is reliable. In the ground state, $3\sigma_g$ is a weak bond with one electron density of ~0.4*e*. It contributes somewhat for the stabilization of $C_2$. Hence, a triple bond scheme of $C_2$ is also reasonable.[16,17] However, one electron density of the $2\sigma_u$ orbital is ~1.6*e*, which is ~1.2*e* higher than that in the $3\sigma_g$ orbital. If the populations of all the other three valence orbitals ($1\pi_g$ and $3\sigma_u$) are included in, the relative $2\sigma_u$ antibond electrons are still ~ 1.0*e* higher. In this context, the quadruple bond scheme is hard to be accepted by naive application of MO theory.

**Table 1.** The most important theoretical data of the five states, including $R_{C-C}$s (Å) and vibrational frequencies ($\omega_e$, cm$^{-1}$), together with their experimental data (shown in bracket)

| | $^1\Sigma_g^+$ | $^3\Pi_u$ | $^3\Sigma_u^+$ | $^3\Sigma_g^-$ | $^1\Pi_u$ |
|---|---|---|---|---|---|
| **$R_{C-C}$** (Å) | 1.255 (1.243) | 1.330 (1.312) | 1.224 (1.230) | 1.384 (1.369) | 1.338 (1.318) |
| ***ΔE*$_{relat.}$** (kcal/mol) | -142.5 (-142) | -131.8 | -114.9 | -113.1 | -104.7 |
| **$\omega_e$** (cm$^{-1}$) | 1839 (1855) | 1599 (1641) | 1975 (2084) | 1436 (1470) | 1553(1608) |
| **Dominant configuration** | $KK2\sigma_g^2$ $1\pi_{xu}^2 1\pi_{yu}^2 2\sigma_u^2$ | $KK2\sigma_g^2 2\sigma_u^2$ $1\pi_{xu}^2 1\pi_{yu}^\alpha 3\sigma_g^\alpha$ | $KK2\sigma_g^2 1\pi_{xu}^2$ $1\pi_{yu}^2 2\sigma_u^\alpha 3\sigma_g^\beta$ | $KK2\sigma_g^2 2\sigma_u^2$ $3\sigma_g^2 1\pi_{xu}^\alpha 1\pi_{yu}^\alpha$ | $KK2\sigma_g^2 2\sigma_u^2$ $1\pi_{xu}^2 1\pi_{yu}^\alpha 3\sigma_g^\beta$ |
| **EBO** | 2.15 | 1.90 | 2.74 | 1.92 | 1.90 |
| **weight** | 71.0% | 87.5% | 85.1% | 93.0% | 89.9% |
| **One electron density** | 0.014 ***e*** ($3\sigma_u$) | 0.020 ***e*** ($3\sigma_u$) | 0.016 ***e*** ($3\sigma_u$) | 0.026 ***e*** ($3\sigma_u$) | 0.027 ***e*** ($3\sigma_u$) |
| | 0.115 ***e*** ($1\pi_{yg}$) | 0.074 ***e*** ($1\pi_{yg}$) | 0.109 ***e*** ($1\pi_{yg}$) | 0.048 ***e*** ($1\pi_{yg}$) | 0.041 ***e*** ($1\pi_{yg}$) |
| | 0.115 ***e*** ($1\pi_{xg}$) | 0.098 ***e*** ($1\pi_{xg}$) | 0.109 ***e*** ($1\pi_{xg}$) | 0.048 ***e*** ($1\pi_{xg}$) | 0.097 ***e*** ($1\pi_{xg}$) |
| | 0.393 ***e*** ($3\sigma_g$) | 0.965 ***e*** ($1\pi_{yu}$) | 0.976 ***e*** ($3\sigma_g$) | 0.990 ***e*** ($1\pi_{xu}$) | 0.985 ***e*** ($1\pi_{yu}$) |
| | 1.602 ***e*** ($2\sigma_u$) | 1.045 ***e*** ($3\sigma_g$) | 1.031 ***e*** ($2\sigma_u$) | 0.990 ***e*** ($1\pi_{yu}$) | 1.023 ***e*** ($3\sigma_g$) |
| | 1.888 ***e*** ($1\pi_{yu}$) | 1.905 ***e*** ($1\pi_{xu}$) | 1.891 ***e*** ($1\pi_{yu}$) | 1.956 ***e*** ($2\sigma_u$) | 1.912 ***e*** ($1\pi_{xu}$) |
| | 1.888 ***e*** ($1\pi_{xu}$) | 1.910 ***e*** ($2\sigma_u$) | 1.891 ***e*** ($1\pi_{xu}$) | 1.966 ***e*** ($3\sigma_g$) | 1.933 ***e*** ($2\sigma_u$) |
| | 1.984 ***e*** ($2\sigma_g$) | 1.982 ***e*** ($2\sigma_g$) | 1.977 ***e*** ($2\sigma_g$) | 1.978 ***e*** ($2\sigma_g$) | 1.982 ***e*** ($2\sigma_g$) |

Based on the traditional valence MOs, it is hard to interpret the singlet diradical character of the $C_2$ ground state while it has been shown through finite-difference pseudopotential method and LSA analysis[25,26] Even a singlet diradical state ($KK2\sigma_g^2 1\pi_u^4 2\sigma_u^\downarrow 3\sigma_g^\uparrow$) was achieved, it is still a $^1\Sigma_u^+$ state. The diagram of $2\sigma_u^\downarrow 3\sigma_g^\uparrow$ 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, it just indicates that opposite-spinning electrons don't locate around the C-C bonds, which is in accord with Prof. Shaik's proposal. However, the difficulty with the VB interpretation of the full CI wave function may be posed by the nonorthogonal transform and neglect of ~15% weight of 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 character of $C_2$ through the reformed valence MO orbitals simultaneously?

We hereby propose another scheme through hybrid orbitals of $2\sigma_u$ and $3\sigma_g$ orbitals to $\phi_{2\sigma_u+3\sigma_g}$($\Phi_L$) and $\phi_{2\sigma_u-3\sigma_g}$ ($\Phi_R$), which is used as the initial active orbital of CASSCF calculation. It is worthy of note that the $\Phi_L$ and $\Phi_R$ orbitals ensure that the single-occupied electrons locate outside of C-C bond (right part of Fig. 3a) Besides, the other six pristine valence orbitals are kept. Subsequently, the potential energy curve of the ground state of $C_2$ is re-scanned at the same level with our orbitals. Compared with Prof. Shaik's strategy, the eight CAS orbitals are all orthogonal and the SCFs cover 100% weight. As expected, the new results show the bonding energy, $R_{C\text{-}C}$, $\omega_e$ and one electron density are all the same as the values from the eight pristine valence orbitals (in the first column of Table 1). It is reasonable because the final result is only determined by one electron densities in 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 simulation. Unfortunately, orthogonal orbitals are adopted in the former, but the nonorthogonal orbitals are adopted in the latter.[18]

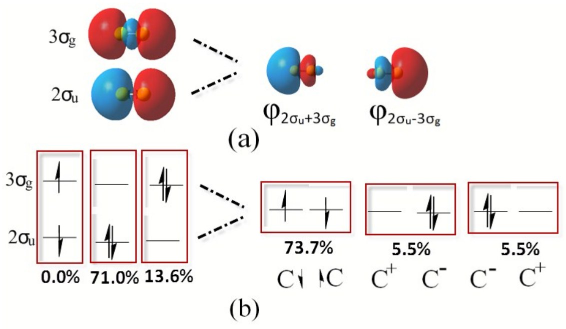


**Figure 3.** Equivalent *hybridized* orbitals of $\Phi_L$ and $\Phi_R$ from $2\sigma_u$ and $3\sigma_g$ localized around single C atom (a) and the corresponding potential occupied styles before and after hybridization (b)

The difference between our and Prof. Frenking's CASSCF schemes 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. The weight of the highest configuration ($KK2\sigma_g^{2}1\pi_{xu}^{2}1\pi_{yu}^{2}\Phi_L^{\downarrow}\Phi_R^{\uparrow}$) is 73.7%, around 2.7% higher than that of Prof. Frenking's one ($KK2\sigma_g^{2}1\pi_{xu}^{2}1\pi_{yu}^{2}2\sigma_u^{2}$). The results elucidate that the spin-localization of $2\sigma_u$ electrons is indeed outside of C-C bonding in accord with VB's view[18,19]. If the bonding nature is estimated by the highest weight configuration, the ground state of $C_2$ is inclined to be a singlet diradical due to a little higher weight than the traditional double bond configuration.

However, with understanding from VB theory, the first three configurations have to be added up, since there are a combination of a major covalent structure ($C^{\downarrow}–C^{\uparrow}$), and two minor ionic ones ($C^-–C^+$ and $C^+–C^-$). They all belong to the 4th bond. To our surprise, the total weight of three highest configurations is equal to the weights' sum of 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 4th bond* is 84.8% (close to the weight of $^3\Pi_u$ and $^3\Sigma_u^-$ state). The opposite-spin coupling energy between the $\Phi_L^{\downarrow}\Phi_R^{\uparrow}$ can't be achieved directly in our orthogonal schemes. If the vertical excited energy from $^1\Sigma_g^+$ to $^3\Pi_u$ sates ($R_{C\text{-}C}$ is 1.253 Å) is the minimum to break the coupling energy of $\Phi_L$ and $\Phi_R$, the relevant value is 12.8 ~ 15.1 kcal.mol$^{-1}$(depending on the calculated weight) which is also consistent with the VB's results. If the correct decoupled triplet state $^3\Sigma_u^+$ is utilized as the electron spin-flip energy, the maximum of the 4th bonding energy is 27.56 kcal.mol$^{-1}$. Hence, the VB's 4th bond based on Lewis electron pairing is reasonable. The results of our scheme implement an inherent harmony between VB and MO theories.

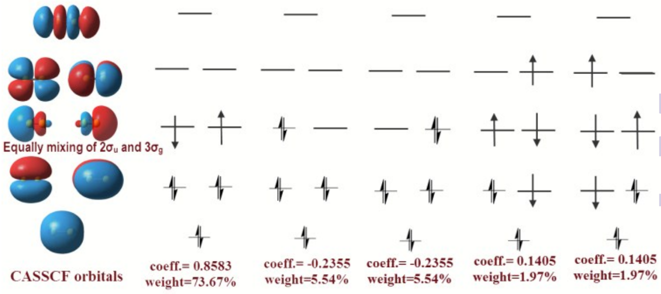


**Figure 4.** Left: CASSCF orbitals including $\Phi_L$ and $\Phi_R$. Right: The corresponding five most important configurations of a full-valence CASSCF(8,8)/*aug*-cc-PVTZ calculation of $C_2$, showing the coefficients and the weights of the configurations.

Furthermore, we focus on the Effective Bond Order (EBO) based on one electron density of the ground state in Table 1.[29] The EBO of $2\sigma_g$-$2\sigma_u$ is 0.191 and that of $3\sigma_g$-$3\sigma_u$ is 0.190. It is still a problem how to define their bond orders. No σ bond or 2 tiny-weak σ bonds. If no, it is a classic double bond scheme. If 2 tiny-weak σ, it is another quadruple bond scheme. Anyway, EBO results at least demonstrate that the two π bonds contribute most to bonding energy if the $^3P$ state of carbon atom as a starting point. That's the reason why the C-C bonding breakage of $C_2$ is smaller than that of an ethylene (-172 kcal/mol). In our simulation the highest EBO is 2.74 for the $^3\Sigma_u^+$ state, because the occupied number of 0.976 *e* in $3\sigma_g$ orbitals. Some distribution of $3\sigma_g$ locates between two carbons. Similar contribution is from the lower occupied number of 1.031 e in $2\sigma_u$ orbitals. Hence, its $R_{C\text{-}C}$ is ~0.03 Å shorter than the $R_{C\text{-}C}$ of the ground state and the corresponding $\omega_e$ is highest.

In the end, we would like to say a little more to the nature of the chemical bond in $C_2$ 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.*"[30] We are shown that the shape and scenery of Mountain Lu is different from different perspectives. Similarly, the understanding of "*the most rigorous theory*"[23] for $C_2$ 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 $R_{C\text{-}C}$ length. Meanwhile, the weak 4th bond or the singlet diradical character of $C_2$ is also easy to be understood, which is related to its instable/reactive nature. Our study conquers the shortcoming of traditional valence MO orbitals. It is worthy of note that $C_2$ must be multi-reference configurations in nature due to no energy difference among these projects, and the only difference is the dominant contribution in the total CSFs, and how to understand them.

## Methodology

Based on the calculation in the previous references[21, 23], the precision by CASSCF(8,8) which covered the CSFs excited included all valence electron orbitals is as good as Full CI, since it is a common recognition that the weights of the inner $1\sigma_g^2 1\sigma_u^2$ orbitals is always 100% from Full CI simulations. The configuration of $C_2$ electronic states are constructed directly from the combinations of natural atomic orbitals in our simulation, because natural orbitals, as a particularly efficient choice, possess the unique advantage to minimize the mixing effect of 2s-2p orbitals in carbon and eliminates the diversification of LCAO-MOs in the MCSCF simulations[31-34]. All the calculations were performed mainly based on GAUSSIAN 09 program package[35].

## Acknowledgements

This work was supported by the financial support from National Nature Science Foundation of China (No. 21203020 and 21131001), National Nature Science Foundation of Jilin Prov. (No.20150101006JC) and Thirteen Five-Year Sci-tech Research Guideline of the Education Department of Jilin Prov, China.

## Notes and references

1 R. S. Mulliken, *Phys. Rev.*, 1939, 56, 778-781.
2 R. Hoffmann, *Amer. Sci.*, 1995, 83, 309–311.
3 W. Weltner and R. J. Van Zee, *Chem. Rev.*, 1989, 89, 1713-1747.
4 M. Martin, *J. Photoch. Photobio. A*, 1992, 66, 263-289.
5 P. S. Skell and J. H. Plonka, *J. Am. Chem. Soc.*, 1970, 92, 5620-5624.
6 P. S. Skell, K. J. Klabunde and F. A. Fagone, *J. Am. Chem. Soc.*, 1972, 94, 7862-7866.
7 M. Douay, R. Nietmann and P. F. Bernath, *J. Mol. Spectrosc.*, 1988, 131, 250-260.
8 R. D. Mead, U. Hefter, P. A. Schulz and W. C. Lineberger, *J. Chem. Phys.*, 1985, 82, 1723-1731.
9 D. Forney, H. Althaus and J. P. Maier, *J. Phys. Chem.*, 1987, 91, 6458-6461.
10 M. Rösslein, M. Wyttenbach and J. P. Maier, *J. Chem. Phys.*, 1987, 87, 6770-6772.
11 J. P. Maier and M. Rösslein, *J. Chem. Phys.*, 1988, 88, 4614-4620.
12 M. Atoji, *J. Chem. Phys.*, 1961, 35, 1950-1960.
13 R. Juza, V. Wehle and H.-U. Schuster, *Z. Anorg. Allg. Chem.*, 1967, 352, 252-257.
14 E. D. Jemmis, B. Pathak, R. B. King and H. F. Schaefer Iii, *Chem. Commun.* 2006(20)**:** 2164-2166.
15 J. M. Galbraith, E. Blank, S. Shaik and P. C. Hiberty, *Chem.-Eur. J.*, 2000, 6, 2425-2434.
16 P. Pyykkö, S. Riedel and M. Patzschke, *Chem.-Eur. J.*, 2005, 11, 3511-3520.
17 D. R. Huntley, G. Markopoulos, P. M. Donovan, L. T. Scott and R. Hoffmann, *Angew. Chem. Int. Ed.*, 2005, 44, 7549-7553.
18 P. Su, J. Wu, J. Gu, W. Wu, S. Shaik and P. C. Hiberty, *J. Chem. Theory. Comput.*, 2010, 7, 121-130.
19 S. Shaik, D. Danovich, W. Wu, P. Su, H. S. Rzepa and P. C. Hiberty, *Nat. Chem.*, 2012, 4, 195-200.
20 D. Danovich, P. C. Hiberty, W. Wu, H. S. Rzepa and S. Shaik, *Chem.-Eur. J.*, 2014, 20, 6220–6232.
21 G. Frenking and M. Hermann, *Angew. Chem. Int. Ed.*, 2013, 52, 5922-5925.
22 W. Wu, J. Gu, J. Song, S. Shaik and P. C. Hiberty, *Angew. Chem. Int. Ed.*, 2009, 48, 1407-1410.
23 S. Shaik, H. S. Rzepa and R. Hoffmann, *Angew. Chem. Int. Ed.*, 2013, 52, 3020-3033.
24 L. T. Xu and T. H. Dunning, *J. Chem. Theory. Comput.*, 2014, 10, 195-201.
25 J. R. Chelikowsky, N. Troullier, K. Wu and Y. Saad, *Phys. Rev. B*, 1994, 50, 11355-11364.
26 E. Ramos-Cordoba, P. Salvador and M. Reiher, *Chem-Eur J*, 2013, 19, 15267-15275.
27 C. H. Choi, D.-J. Liu, J. W. Evans and M. S. Gordon, *J. Am. Chem. Soc.*, 2002, 124, 8730-8740.
28 X. Lu, M. Zhu, X. Wang and Q. Zhang, *J. Phys. Chem. B*, 2004, 108, 4478-4484.
29 B. O. Roos, A. C. Borin and L. Gagliardi, *Angew. Chem. Int. Ed.*, 2007, 46, 1469-1472.
*30* S. Su, *Written on the Wall at West Forest Temple. This version is translated by Xu Yuanchong*
31 P. O. Löwdin, *Phys. Rev.*, 1955, 97, 1474-1489.
32 P. O. Löwdin, *Phys. Rev.*, 1955, 97, 1490-1508.
33 P. O. Löwdin, *Phys. Rev.*, 1955, 97, 1509-1520.
34 E. R. Davidson, *Rev. Mod. Phys.*, 1972, 44, 451-464.
*35* M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, J. Vreven, T. , K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A Pople, *Gaussian 09w, Revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.*