THEORETICAL EVIDENCE FOR "BENT BONDS" IN THE CO_2 MOLECULE

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Ab initio correlated wavefunction results for the CO_2 molecule are presented, which strongly suggest that the carbon–oxygen double bonds in the molecule are better represented in terms of a pair of "bent bonds" than by a combination of a σ-bond and a π-bond.

1. Introduction

The physical interpretation of many-electron wavefunctions is an important, yet sometimes difficult and often controversial, aspect of computational quantum mechanical studies. Thus, there is the frequent temptation to avoid the discussion of the wavefunction and restrict one's attention to the values of computed observables. Although this course may avert some contentious discussion, it certainly also evades a significant responsibility of the theorist.

A general N-electron wavefunction can always be written in the form of a linear combination of determinantal functions,

$$\Psi = \sum_i c_i \Phi_i , \qquad (1)$$

where each determinant is made up of a collection of N spin-orbitals, ϕ_i, from a complete set. In the treatment of molecular problems it is common to consider only one term of the infinite expansion given in eq. (1), which is the well-known "molecular orbital" approximation. Within this approximation, a great deal of effort has been expended on the interpretation of the wavefunction. However, the outstanding success of a variety of resulting concepts (e.g., the orbital symmetry rules) in enhancing our understanding of molecules and their interaction attest to the fact that the pursuit of an interpretation for the wavefunction is not a futile exercise. Fortunately for molecular orbital theory the general character of the canonical molecular orbitals, ϕ_i, arrived at by rather diverse computational techniques (from ab initio to semi-empirical methods) is very much the same. This has allowed a general consensus to form regarding the molecular orbital interpretation of many-electron wavefunctions *

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By contrast, when one improves the wavefunction by taking more than one term in eq. (1), one is faced with both an embarrassing number of possible options on how to proceed and the concomitant choice of possible interpretations. The routine computational treatment of multi-determinant wavefunctions is rather recent as compared to the routine computation of molecular orbitals. These two facts indicate why it should not be surprising that there is, as yet, no consensus regarding the interpretation of multi-determinant wavefunctions. A few criteria which might be applied in the choice of an interpretive approach could include the following: (1) the simplicity of the interpretation; (2) the coincidence of the interpretive approach with familiar physical and chemical concepts derived from experiment; and (3) the economy of the approach in devising compact and accurate approximations to wavefunctions. Two examples of such interpretive schemes are the valence-bond (VB) approach [12–16] and the atoms-in-molecules (AIM) approach [17–21]. In the present work we adopt the valence-bond interpretive framework.

2. Computational methods

The calculations we describe have been carried out within the generalized valence-bond perfect pairing (GVB PP) method [22] (see also refs. [15,16]). We use a valence double-zeta plus polarization basis set [23] and correlate all of the valence electron pairs. Thus there are 256 determinants in the expansion of eq. (1) and there are sixteen ϕ_i^{GVB} describing the valence electrons of CO_2, with each determinant in the expansion containing eight doubly occupied ϕ_i^{GVB}. For comparison we also present the results of a Hartree–Fock molecular orbital calculation using the same basis set. In this calculation there is only one determinant with a set of eight doubly occupied ϕ_i^{MO} describing the valence electrons.

In both GVB PP calculations we describe below, the above aspects are identical. The calculations differ only in the symmetry restrictions imposed upon the orbitals ϕ_i^{GVB}. The canonical molecular orbitals, ϕ_i^{MO}, are symmetry adapted and for a linear molecule (such as CO_2) are of $\sigma, \pi, \delta, ...$ character. These symmetry orbitals are also frequently used in GVB calculations [24]. However, such symmetry restrictions in the GVB method are not necessary. Some time ago Hay et al. [25] tested the effects of removing symmetry restrictions for ethylene and acetylene, and found the variational ground state to be described by σ,π-bonds rather than bent bonds. Our results are in agreement with their conclusion although the two descriptions for acetylene are nearly degenerate. In the case of CO_2, however, when the symmetry restrictions are removed, a bent bond description is obtained which yields a lower energy for the molecule.

Table 1
Results for the CO_2 molecule

Method	Total energy (hartree)
Hartree–Fock	−187.674466
GVB PP [a)]	−187.765041
GVB PP [b)]	−187.776321

[a)] With σ,π-orbital symmetry restrictions.
[b)] With no restrictions.

Table 1 contains the computed total energies for the ground state of CO_2 at the experimental equilibrium geometry obtained from the following calculations: molecular orbital (Hartree–Fock), GVB PP with σ–π orbital symmetry restrictions and GVB PP without orbital symmetry restrictions.

3. Results and discussion

In fig. 1, we show that two π_y molecular orbitals responsible for the π-bond and the oxygen lone pair in the yz plane according to the molecular orbital interpretation (each orbital is occupied by two electrons). We note that the chemist's usual picture of a CO π-bond and an O lone pair is not entirely apparent from these orbitals. The GVB PP results for CO_2 in which the orbitals are constrained to have σ and π symmetry give the π-like PP orbitals (in the yz plane) shown in fig. 2. Although the σ-like PP orbitals are found to be

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[*] There has been considerable discussion regarding equivalent orbitals and localized orbitals [1–11] within the molecular orbital framework. However, the fact that they are all related by a unitary transformation which leaves the energy invariant, has not allowed a consensus to evolve on the most appropriate local viewpoint.

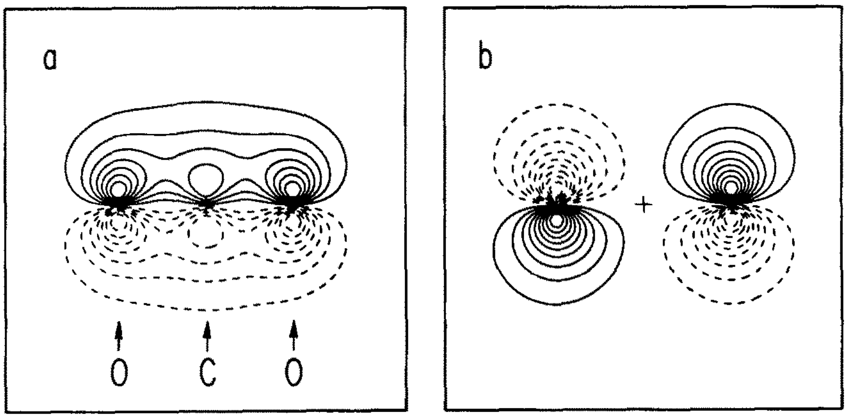

Fig. 1. The two π_y molecular orbitals of CO_2 in the yz plane. Each orbital contains two electrons. There is an equivalent set in the xz plane.

highly localized (not shown) into two CO bond pairs and two oxygen lone pairs, the π-like orbitals in fig. 2 are not easily identifiable as an oxygen lone pair and a C–O π-bond.

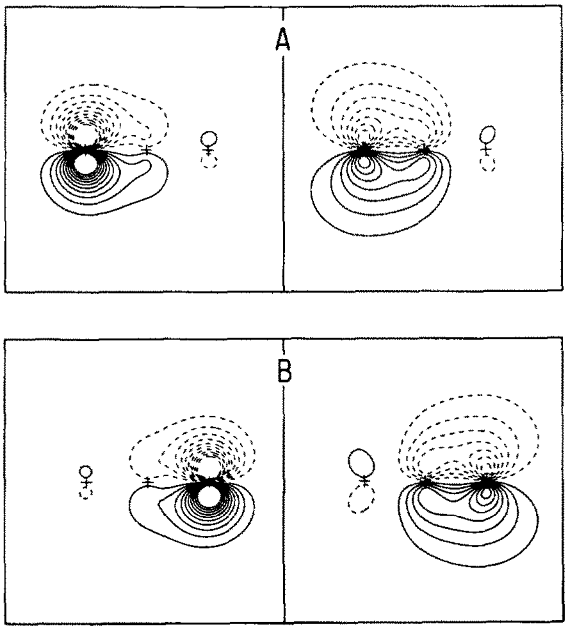

Fig. 2. The four GVB PP orbitals (in the yz plane) of π_y symmetry from a calculation with σ,π-symmetry constraints. Each orbital contains one electron and the two orbitals in each panel (A and B) are singlet-coupled into an electron pair. There is an equivalent set of orbitals in the xz plane.

If the σ, π symmetry restriction on the GVB PP orbitals is removed, the orbitals change dramatically, as shown in fig. 3. Each orbital contains one electron and the eight PP orbitals in the yz plane are displayed. This description of the many-electron wavefunction for CO_2 has an energy which is 0.3 eV lower than the GVB description in terms of σ and π orbitals (fig. 2). In panels A and B of fig. 3, one can observe the "bent" bonds which constitute one of the two equivalent sets of CO double bonds in CO_2. Panel A shows an oxygen hybrid orbital on the left and a carbon hybrid orbital on the right. These two orbitals overlap to form one bond component of a symmetric pair which yield a C–O double bond. The other component is shown in panel B. The bond formed by the overlapping of the two hybrids (panel A or panel B) has a shape reminiscent of the greek letter Ω, hence we refer to them as Ω-bonds when they occur in pairs or triplets in the description of double or triple bonds.

Panels C and D in fig. 3 show the oxygen lone pairs in the yz plane. Now, contrary to the results of molecular orbital theory and GVB PP with σ, π constraints on the orbitals, one obtains a set of orbitals clearly identifiable as lone pairs. In panel C are shown two PP orbitals which constitute one of the lone pairs. Again, there is one electron in each orbital and the "in–out" correlation in the pair is clearly seen, with the orbital to the right in the panel being closer to the oxygen nucleus and the orbital to the left in the panel being farther from the nucleus. Panel D shows the other equivalent lone pair in the yz plane.

A schematic representation of the many-electron

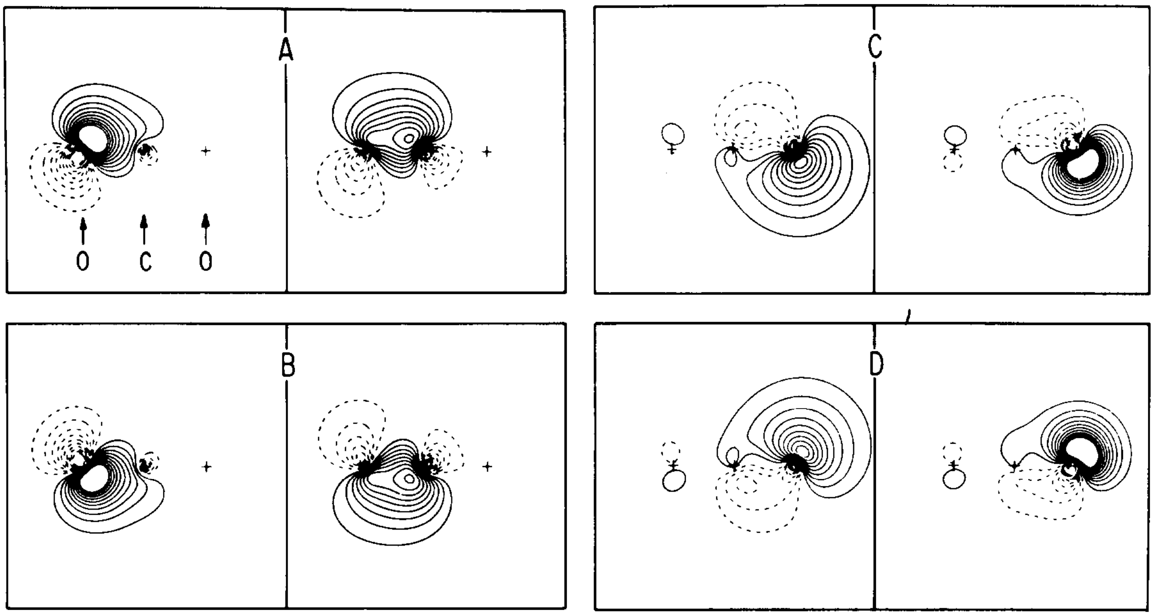

Fig. 3. The eight GVB PP orbitals in the *yz* plane of CO_2 from a calculation with no symmetry constraints on the orbitals. Each orbital contains one electron and the two orbitals in each panel (A, B, C, D) are singlet-coupled into an electron pair. Panels A and B are two equivalent "bent bonds" forming a CO double bond. Panels C and D are two equivalent lone pairs on the oxygen atom at the right. There is an equivalent set of eight PP orbitals in the *xz* plane.

wavefunction in terms of the computed GVB PP orbitals which give the lowest variationally determined total energy is shown in fig. 4. We note that this is one of two equivalent "resonance" structures which are needed to describe the correct symmetry of the overall wavefunction. When this resonance effect is taken into account via a resonating GVB calculation [26], it is found that the energy of the Ω-bond description is even lower relative to that of the corresponding $\sigma-\pi$ description. It is interesting to observe that many features of the description we find here from ab initio generalized valence bond calculations are similar to a qualitative discussion of bonding in CO_2 given by Pauling [14] over twenty-five years ago. The ascendancy of molecular orbital theory as the paradigm for describing molecular electronic structure in the intervening years has tended to obscure the fact that the valence bond language provides a simple framework for describing important electronic correlation effects which are ignored in a molecular orbital treatment.

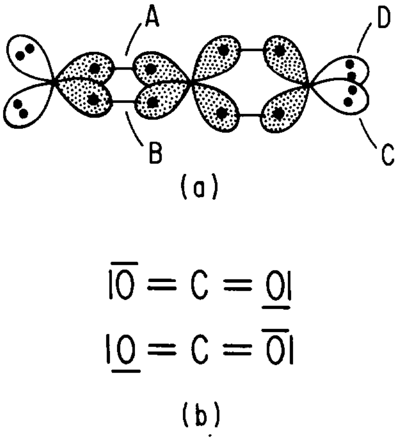

Fig. 4. (a) Schematic representation of the many-electron GVB PP wavefunction. The letters A–D denote the electron pairs whose orbitals are shown in the corresponding panels of fig. 3. This is one of two equivalent "resonance" structures; the other is obtained by rotating 90° about the internuclear axis. (b) Usual chemical representation of the two resonance structures.

4. Summary

We have presented the results of ab initio calculations which show that it is energetically favorable to form "bent bonds" in the CO_2 molecule [**]. To our knowledge, there has been no published discussion of such a situation for multiple bonds in any molecule. Our results are in many ways similar to a qualitative discussion presented by Pauling many years ago. A more detailed discussion of these aspects of CO_2 and of other molecules for which we have found Ω-bonds (bent multiple bonds) will be presented elsewhere.

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[**] Although this conclusion is based on resonating GVB PP calculations presented herein, it is also supported by CI calculations with resonance. Configuration interaction calculations designed to ease the most severe restrictions of the GVB PP wavefunction (by including alternate spin couplings, relaxing strong orthogonality between pairs and incorporating resonance) have been carried out for both the σ,π- and Ω-bond wavefunction descriptions. The Ω-bond description is unambiguously favored.

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