A Valence Bond Study of the Oxygen Molecule

CARSTEN P. BYRMAN AND JOOP H. VAN LENTHE
Theoretical Chemistry Department, Debye Institute, Utrecht University, Padualaan 14,
3584 CH Utrecht, The Netherlands

Received February 10, 1995; accepted June 23, 1995

ABSTRACT

Ab initio valence bond calculations are performed for the three lowest states of the oxygen molecule ($^3\Sigma_g^-, ^1\Delta_g$, and $^1\Sigma_g^+$). One objective of the present study was to make a contribution to previous valence bond discussions about the oxygen "double" bond. Further, we study the origin of a small barrier in the potential energy surface of the ground state. Two compact models are employed to maintain the clear picture that can be offered by the valence bond method. The first model has only the Rumer structures that are essential for bonding and a proper dissociation. The second model, in addition, has structures which represent excited atoms. These prove to be important for the dissociation energies. For both models, the orbitals are fully optimized. The spectroscopic data obtained are significantly better than are the (few) valence bond results on O$_2$ that have been published and have the quality of multiconfiguration self-consistent field calculations in which the same valence space is used. The "hump" in the potential energy surface of the ground state is shown to arise from a spin recoupling. The free atoms correspond to a spin coupling that is incapable of describing the formation of bonds. Only at short distances, an alternative spin coupling provides bonding and the repulsive curve is converted into an attractive one. Our results on this subject support a valence bond explanation previously given by McWeeny [R. McWeeny, Int. J. Quantum Chem. Symp. 24, 733 (1990)]. © 1996 John Wiley & Sons, Inc.

Introduction

The oxygen molecule is an interesting molecule for advocates of the valence bond (VB) theory. The correct prediction of its ground state has been the subject of much discussion since the 1930s [1–9]. It was once thought of as a case in which the VB method failed even qualitatively to account for the experimental facts. Wheland (1937) was the first who showed that the VB method is capable of providing the correct answer [3]. However, his lengthy VB analysis did not receive much acclaim since the molecular orbital (MO) approach offered an easier explanation. It took a long time before quantitative VB studies appeared. Moss et al. in 1975 presented results obtained using the general-
ized valence bond (GVB) method for the ground and first excited states [6]. The orbitals were grouped into nonorthogonal pairs (strong orthogonality) and the perfect-pairing restriction was given up, to ensure a proper dissociation. Their GVB wave functions, however, did not have the proper molecular symmetry. Good dissociation energies were only obtained after a configuration interaction (CI) with the orthogonalized GVB orbitals, but, as a consequence, the simplicity of the VB model was lost. McWeeny has recently made a new contribution and judged the VB description to be no less natural than that provided by the MO theory [7]. He calculated the ground state at the experimental equilibrium distance using a minimal basis and concluded that the double bond arises from a resonance involving two dominant ionic structures. McWeeny also calculated the potential energy curves of the lower triplet and singlet states using a double-zeta basis [8]. Harcourt used McWeeny’s data to show that the one-electron transfer resonance between each covalent structure and a pair of ionic structures contributes most to the bonding energy [9]. These studies focused on the main ionic structures and did not consider, e.g., other covalent structures. They were primarily aimed at providing an easy qualitative VB explanation of the stability of the triplet ground state. McWeeny also calculated the potential energy surfaces, is a fine tool to study this [5, 7]. The emphasis throughout this article will be on the \( ^3\Sigma^+ \) ground state.

### Description of the States

In this section, we present and motivate our choice of structures. This will be done in three stages: First, we present for each state the structures that are dominant near the equilibrium geometries. Second, the (additional) structures that are necessary to achieve a proper dissociation are discussed. Last, attention is paid to structures that cannot contribute in the dissociation limit, but may become important as the atoms approach. McWeeny’s notation is adopted to give a symbolic representation of the chemical (Rumer) structures [7, 8]. Dots and circled dots symbolize singly and doubly occupied \( 2p \) orbitals, respectively. A connection between dots indicates an electron–pair bond. Dots that are not connected are coupled to a triplet. The \( z \)-axis is chosen as the internuclear axis. The \( s \) orbitals, which are considered to be doubly occupied, will be omitted from the figures.

A VB description of a molecule begins with the separate atoms. It will be assumed throughout that the oxygen atoms have the electronic configuration

\[
1s^22s^22p^4.
\]

The \( 1s \) and \( 2s \) orbitals will not be considered explicitly, because they are always doubly occupied in our single-configuration description of the atoms and, therefore, do not determine the symmetries of the molecular states. Four electrons can be permuted over the \( 2p \) orbitals in six different ways. Combining the atomic configurations results in 36 possible molecular permutations, which can be used to construct covalent structures by assigning a specific spin coupling to the unpaired electrons. Ionic structures will be excluded from our discussion. They will be taken care of via a full orbital optimization: It can be shown that delocalization of the orbitals is, at least mathematically, analogous to the admission of ionic structures [12]. Since we want a compact description of the states, we are interested only in those structures that are vital for bonding and/or a proper dissociation. These can be selected using chemical knowledge and symmetry considerations. We cannot expect our models to reproduce the experimental dissociation energies very accurately, because we make use of only the valence
space. A valence space full-CI calculation performed by Guberman showed that the best theoretical value attainable for the ground state is about 75% of the experimental value [11]. The results for the excited states may be expected to be even less accurate.

The lower states follow quite naturally from a qualitative VB treatment of the molecule. Realizing the importance of a central σ bond, we choose the 2p_z orbitals to be singly occupied. Thus, there remain four permutations that have to be considered (no attention has been paid to the molecular symmetries yet). The overlap between the singly occupied orbitals can be used as a criterion to select the structures that will be dominant at short internuclear distances. If nonorthogonal orbitals are coupled to a singlet (Heitler–London) and orthogonal orbitals to a triplet (Hund), a pair of singlet and a pair of triplet structures result [7]. These perfect-pairing structures are represented in Figure 1. They must clearly contribute to the lower states of the oxygen molecule, because other structures do not offer bonds and/or have an electrostatically unfavorable distribution of the electrons. The states of interest can be formed from them by taking the suitable linear combinations. The \( ^3\Sigma_g^- \) ground state corresponds to the \( "+" \) combination of the triplet structures, reflecting the gerade symmetry of the state (the \( "-" \) combination results in a \( ^3\Delta_u \) state, which will not be considered any further in the present study). The \( ^1\Delta_g \) and \( ^1\Sigma_g^+ \) states can be constructed from the singlet structures by taking the \( "-" \) and the \( "+" \) combination, respectively. Of course, these signs assume a specific order of the orbitals in the mathematical expressions of the wave functions. Note that the singlet structures depicted compose only one component of the twofold degenerate \( ^3\Delta_g \) state. At this point, it is not obvious whether the ground state is a triplet or a singlet: a singlet ground state would have a covalent \( \pi \) bond, while a triplet would have two three-electron \( \pi \) bonds. Since a covalent, Heitler–London type of bond is generally considered to be twice as strong as a three-electron bond, a definitive choice cannot be made without a further analysis [4].

Both the ground state and the two excited states dissociate into \( ^3P \) (ground state) oxygen atoms. So, only the configurations that have four singly occupied \( 2p \) orbitals, two on each atom, have to be considered for a proper dissociation. Since the configurations of Figure 1 fulfill this requirement, there is no need for other configurations. The structures represented, however, are not sufficient. This is often the case with perfect-pairing structures: Their spin coupling is ideally suited for the molecule, but not for the atoms. A correct dissociation is possible if the structures of Figure 2 are added to the wave functions. Together with the structures of Figure 1, they form a complete set, which means that for these configurations other conceivable structures can be expressed as a linear combination of them. It is clear from the spin-coupling scheme that these structures, although indispensable in the dissociation limit, will be of small importance around the equilibrium geometries, because they do not possess bonds between the atoms.

So far, only configurations that are able to dissociate into two \( ^3P \) oxygen atoms have been considered. The other configurations, or rather combinations of them, dissociate into at least one excited atom, which can have the term symbol \( ^1D \) or \( ^1S \). No other atomic states arise from the \( 2p^4 \) configuration [13]. Experimentally, the singlet atoms lie 1.967 and 4.188 eV, respectively, above the triplet atom [14]. They can both be combined with a \( ^3P \) atom to a \( ^3\Sigma_g^- \) molecular state. Likewise, two \( ^1D \) atoms are able to form a \( ^1\Delta_g \) or a \( ^1\Sigma_g^+ \) state. Since these "excited" configurations may interact with the states under consideration, we cannot simply neglect them. If we take both symmetry and electrostatic arguments into account, we arrive at the structures of Figure 3. These structures do not contribute in the dissociation limit, but may become important as the atoms approach.
Computational Details

Two models of the states were calculated: a proper dissociation model (PD), which had the structures of Figures 1 and 2, and a proper reference model (PR), which in addition had the structures of Figure 3. The "proper reference" model was named after an (orthogonal) model of Lie and Clementi, to which it bears some resemblance [10]. All orbitals were optimized and allowed to delocalize, i.e., to use the basis functions of the neighboring atom. The applied EZPP basis set, (10, 6, 2) → [5, 3, 2], was an extended zeta basis augmented by two sets of spherical harmonic d functions [15]. Rumer spin functions were used to have a one-to-one match with the structures of the figures [16]. The starting orbitals were optimized for the separate \(^3P\) atoms (the \(p_x\) and \(p_y\) orbitals were restricted to be equivalent). The \(p_z\) orbitals were chosen orthogonal to all \(s\) orbitals, which were, in turn, orthogonal to each other. These orthogonalities are not a restraint, because the \(s\) orbitals are doubly occupied in all configurations. The actual reason for these orthogonalizations is that they reduce CPU time, because the algorithm used to compute the nonorthogonal matrix elements benefits from all orthogonalities that are among the orbitals [17, 18]. The \(^1\Delta_x\) and \(^1\Sigma^+_g\) states only differ in the relative signs of the structures (cf. Figs. 1–3). The \(^1\Sigma^+_g\) state, being higher in energy, was calculated by taking each cycle the second-lowest eigenvector of the \(H\)-matrix in the basis of structures.

The calculations were performed with the VB/VBSCF program TURTLE, which is described in detail elsewhere [19, 20]. This program is able to
optimize orbitals for a wave function with an arbitrary number of configurations, structures, and amount of nonorthogonality, only limited by the size of the problem. This so-called valence bond self-consistent field method (VBSCF) can be regarded as a generalization of the multiconfiguration self-consistent field (MCSCF) method and puts no restrictions on the form of the wave function [21].

Results and Discussion

SPECTROSCOPIC CONSTANTS

No convergence problems were encountered and the iterative process reached self-consistency within 10 cycles (stop criterion: energy converged up to 10^{-6} Hartrees). The potential energy curves calculated with the PR model are given in Figure 4. The curves of the PD model show the same characteristics. Examining the figure, two peculiarities draw attention: At long interatomic distances, the curve of the ground state lies above the curves of the two excited states and it shows a small maximum. We will look at this hump in more detail in the section The Hump in the Potential Surface of the Ground State, but first present the derived spectroscopic constants.

In Table I, the spectroscopic constants calculated are given. The vibrational frequencies are calculated from the quadratic term of a sixth-degree polynomial fit around the equilibrium geometry. The wave functions at the equilibrium geometries, expressed in the normalized structures of Figures 1–3, are shown in Table II, together with the corresponding energies. Although there are very accurate MO studies of the oxygen molecule available, e.g., by Partridge et al. [22], we will compare our results with previous MCSCF studies in which the same valence space is used (up to and including 3\sigma^*). This is a fair and interesting comparison, because the MCSCF method can be regarded as the orthogonal equivalent of the VBSCF method.

It can be seen from Table I that the PD function is comparable to the HFPD function of Lie and Clementi, and the PR function, to their HFPR function [10]. The latter is essentially the same as Guberman's CPD function [11]. The analogy between the orthogonal and nonorthogonal models goes further than producing the same numbers. Evidently, none of the models can describe the dissociation process quantitatively: The dissociation energies are much too small. Our results could be improved by adding other structures based on the atomic valence orbitals, at the expense of a

FIGURE 4. The intermediate region of the potential curves calculated with the PR model.
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TABLE I
VBSCF compared to MCSCF: spectroscopic constants.

<table>
<thead>
<tr>
<th></th>
<th>( R_a ) (bohr)</th>
<th>( D_a ) (eV)(^a)</th>
<th>( \omega_a ) (cm(^{-1}))</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( ^3\Sigma_g^- )</td>
<td>2.286</td>
<td>2.832 (54%)</td>
<td>1550</td>
<td>PD</td>
</tr>
<tr>
<td>( ^1\Delta_g )</td>
<td>2.330</td>
<td>2.128 (50%)</td>
<td>1376</td>
<td>PD</td>
</tr>
<tr>
<td>( ^3\Sigma_g^+ )</td>
<td>2.383</td>
<td>1.505 (42%)</td>
<td>1202</td>
<td>PD</td>
</tr>
<tr>
<td>( ^3\Pi_g )</td>
<td>2.303</td>
<td>3.672 (70%)</td>
<td>1549</td>
<td>PR</td>
</tr>
<tr>
<td>( ^1\Pi_g )</td>
<td>2.330</td>
<td>2.799 (66%)</td>
<td>1445</td>
<td>PR</td>
</tr>
<tr>
<td>( ^1\Sigma_g^+ )</td>
<td>2.367</td>
<td>2.036 (57%)</td>
<td>1320</td>
<td>PR</td>
</tr>
<tr>
<td>Lie and Clementi(^b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( ^3\Sigma_g^- )</td>
<td>2.276</td>
<td>2.90 (56%)</td>
<td>1556.1</td>
<td>HFPD</td>
</tr>
<tr>
<td>( ^3\Sigma_g^+ )</td>
<td>2.2816</td>
<td>3.80 (73%)</td>
<td></td>
<td>HFPR</td>
</tr>
<tr>
<td>Guberman(^c)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( ^3\Sigma_g^- )</td>
<td>2.3152</td>
<td>3.7187 (71%)</td>
<td>1539.2</td>
<td>CPD</td>
</tr>
<tr>
<td>( ^3\Sigma_g^+ )</td>
<td>2.3198</td>
<td>3.8893 (75%)</td>
<td>1530.8</td>
<td>Valence space full-CI</td>
</tr>
<tr>
<td>Experimental(^d)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( ^3\Sigma_g^- )</td>
<td>2.283</td>
<td>5.214</td>
<td>1580</td>
<td></td>
</tr>
<tr>
<td>( ^3\Sigma_g^+ )</td>
<td>2.297</td>
<td>4.232</td>
<td>1484</td>
<td></td>
</tr>
<tr>
<td>( ^1\Sigma_g^+ )</td>
<td>2.319</td>
<td>3.578</td>
<td>1433</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Percentages of the experimental values.
\(^b\) An MCSCF study with a \((13,8,2) \rightarrow [7,4,2]\) basis. The HFPD wave function has the Hartree–Fock configuration and all configuration-state functions (CSFs) needed for a proper dissociation. The HFPR function, in addition, has those CSFs that are necessary for a so-called proper reference function \([10]\).
\(^c\) An MCSCF study with a \((9,5,2) \rightarrow [3,2,1]\) basis. The CPD function equals the HFPR function and consists of six configurations (10 CSFs). The valence space full-CI has 24 configurations (48 CSFs) \([11]\).
\(^d\) From \([22]\).

more complicated wave function, but we expect that a significant improvement requires a further nonorthogonal CI involving also the virtual orbitals. This expectation is based on Guberman’s valence space full-CI calculation of the ground state, which only yielded 75% of the experimental dissociation energy. We also performed some test calculations in which the singly and doubly occupied \( p_x \) and \( p_y \) orbitals were allowed to be different, to introduce some extra correlation. Then, instead of 10 orbitals, both models have 14 orbitals. This yielded, both at \( R_a \) and at \( R_c \), a lower total energy, but only slightly improved the dissociation energy of the ground state, viz., by 0.04 eV for the PD model and by 0.09 eV for the PR model. An attempt has been made to describe the three states

TABLE II
Energies and wave functions at the (calculated) equilibrium geometries.

<table>
<thead>
<tr>
<th></th>
<th>( E ) (Hartree)</th>
<th>( \Psi^a )</th>
<th>No. structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>PD</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( ^3\Sigma_g^- )</td>
<td>-149.708941</td>
<td>0.65967( \Psi_1 ) + 0.03595( \Psi_2 )</td>
<td>6</td>
</tr>
<tr>
<td>( ^1\Delta_g )</td>
<td>-149.683083</td>
<td>0.75665( \Psi_1 ) + 0.07023( \Psi_2 )</td>
<td>4</td>
</tr>
<tr>
<td>( ^3\Sigma_g^+ )</td>
<td>-149.660194</td>
<td>0.75666( \Psi_1 ) + 0.07445( \Psi_2 )</td>
<td>4</td>
</tr>
<tr>
<td>PR</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( ^3\Sigma_g^- )</td>
<td>-149.739830</td>
<td>0.52189( \Psi_1 ) + 0.02375( \Psi_2 ) + 0.21350( \Psi_3 )</td>
<td>8</td>
</tr>
<tr>
<td>( ^1\Delta_g )</td>
<td>-149.707718</td>
<td>0.61357( \Psi_1 ) + 0.04923( \Psi_2 ) + 0.13289( \Psi_3 )</td>
<td>8</td>
</tr>
<tr>
<td>( ^3\Sigma_g^+ )</td>
<td>-149.679702</td>
<td>0.64618( \Psi_1 ) + 0.05637( \Psi_2 ) + 0.11703( \Psi_3 )</td>
<td>8</td>
</tr>
</tbody>
</table>

\(^a\) The wave functions are expressed in the normalized structures of Figures 1–3. Structures that belong to the same figures have equal coefficients by symmetry.
on an equal footing by using the same number of structures in the PR model (cf. Table II). However, correlation turns out to be much more important for the excited states. The calculated vibrational frequencies ($\omega_u$) are all too small. This is what one would expect for variational and correctly dissociating models: Their curves are shallower than are the experimental ones. The ground state shows a behavior which we had not anticipated: The frequency calculated with the PD model is rather good and is slightly reduced on going to the PR model.

The ionic structures that were concluded to be essential for $\pi$ bonding by McWeeny [7] are implicitly present in our models. In his calculations of the ground state, McWeeny used localized $\pi$ orbitals. One can demonstrate that allowing the orbitals to delocalize is, in a first-order approximation, equal to the admission of ionic structures. This is consistent with the VBSCF optimization method [21]. The chemical meaning that one might assign to ionic structures is therefore dependent on the model used. If we strictly localize the $\pi$ orbitals and add the ionic structures of McWeeny to the structures of Figures 1 and 2, the energy at 2.286 bohr is 14.412 mHartrees above our result obtained with the PD model. So, in this particular case, delocalization is more efficient than is the inclusion of ionic structures and it renders a wave function that is more compact. Ionic structures or, equivalently, delocalized orbitals are indispensable for bonding. The omission of them leads to unbound states. This is not exceptional and, e.g., also applies for $F_2$. In a classical, i.e., localized, VB model, these molecules belong to a category that owe their stability neither to the covalent nor to the ionic components, but rather to very large resonance energies between these and are accordingly called charge-shift binders in the terminology of Shaik et al. to characterize the type of resonance involved [23].

**THE PREDICTION OF A TRIPLET GROUND STATE**

The MO theory predicts in a simple way that the oxygen molecule has a paramagnetic ground state. After the assumption that the relative order of the molecular orbitals in a correlation diagram is ...$1\sigma^+$, the successive application of the Aufbau principle, the Pauli principle, and Hund's rule directly leads to a triplet. Although easy in MO theory, this seems to be more difficult in VB theory. A simple VB approach appears to predict a singlet, because a singlet state has two covalent bonds, one $\sigma$ and one $\pi$, as one is apt to expect for a molecule with a (net) double bond. Such an approach, however, ignores or underestimates resonance, another so significant concept of the VB theory in understanding chemical bonding. What is important in a qualitative VB analysis is that one considers the pairs of structures instead of the individual structures of Figure 1. Moss et al. assumed that the individual structures account for the correct prediction of a triplet ground state: The structures of the singlet states $(D_{2h})$ were reasoned to be unfavorable compared to those of the triplet state $(D_{2d})$, because of the large repulsive interactions between the adjacent doubly occupied $p$ orbitals [6]. The best configuration of $O_2$ was expected to be one with a doubly occupied $p_x$ and $p_y$ orbital. For this reason, they performed their GVB calculations of the triplet and singlet state in $D_{2d}$ symmetry, leading to the correct experimental order. We believe that this reasoning is erroneous: A GVB calculation in $D_{2h}$ symmetry, using their DZP basis, predicts a singlet ground state. So, the singlet structures of Figure 1 have a lower energy than that of the triplet structures. The correct order is only predicted if wave functions of the proper symmetry are used. This is also apparent from the energies (in Hartree) of the individual structures of our PD wave functions: $-149.667473 \left( ^1\Delta \right)$, $-149.666987 \left( ^1\Sigma^+ \right)$, and $-149.647745 \left( ^1\Sigma^- \right)$. Even if the orbitals are optimized for the individual structures instead of the total wave function, a singlet ground state is predicted (no distinction can then be made between the $^1\Delta$ and $^1\Sigma^+$ states). This demonstrates once more the importance of resonance for the ground state. To make a prediction of the order of the states, a further qualitative analysis would have to make assumptions about certain resonance integrals. This would resemble the discussion of Wheland, who used complex orbitals for this. Of course, making such assumptions is precisely what one does when applying Hund's rule, but the qualitative VB description is more lengthy, which probably explains the disregard paid to the VB theory in this matter. Both qualitative descriptions of a molecule, MO and VB, are based on just the valence orbitals. Since such descriptions account for only a small part of the total bonding energy, e.g., a Hartree–Fock calculation of the $O_2$ ground state yields about 27% [24], it is not unlikely that a wrong order of states is predicted with both methods. Further, the relative
order of the molecular orbitals in a correlation diagram is not always clear. We mention the difficulties associated with the ground states of the isovalent molecules C2 (Σ+ g) and Si2 (Σ+ g) [25, 26]. Although this detracts nothing of the merits of Hund’s rule, it makes the rivalry between the two methods of small importance.

**THE HUMP IN THE POTENTIAL SURFACE OF THE GROUND STATE**

The maximum observed in the potential energy surface of the ground state is small but significant. The PD curve has a maximum of 1.6 mHartrees at 4.10 bohr. The PR curve has a smaller maximum, which is shifted to the right: 1.2 mHartrees at 4.25 bohr. This hump has been observed in both MO and VB studies and several explanations, physical and nonphysical, have been given for it. It was present in the GVB calculation of Moss et al., but absent in the studied range (< 6.0 bohr) of their GVB–CI calculation [6]. From their analysis of the exchange terms, they argued that the 1Δg state should be the lowest at large separation, but they were reticent about the hump in the GVB potential energy curve of the ground state. In their MCSCF study of several homonuclear diatomics, Lie and Clementi ascribed the hump, 1.5 mHartrees at 4 bohr, to an avoided curve crossing [10]. They also checked the possibility of a quadrupole–quadrupole interaction, but from 10 to 4 bohr, the energy rose much faster than R−5, an indication that the hump is of a different nature. In a comparable MCSCF calculation, Guberman reported a hump of 0.9 mHartree at 4.5 bohr and had another explanation [11]: He attributed it to the overlap of the 2p, orbital on one center with the doubly occupied 2s orbital on the other center. The Pauli principle requires the 2p, orbital to become orthogonal to the adjacent 2s orbital and is therefore distorted from the optimum atomic one at large distances. Guberman, however, concluded it to be an artifact of his calculation, for the hump disappeared in more elaborate MCSCF calculations. McWeeny explained the hump from a VB point of view [8]. At infinity, both atoms have an intratatomic triplet coupling. As the atoms approach, only the molecular singlet states correspond to bonding and the triplet curve rises. At a certain distance, the intratatomic triplet coupling is broken and the ground state is increasingly well represented by the structures of Figure 1. To the authors’ knowledge, there is no agreement yet where this hump originates from and whether it is a calculational artifact. For this reason, we pay special attention to it.

To study the origin of the hump, we have to examine more closely the contributions of the different structures along the potential energy surface of the ground state. We will use the simpler PD model for this purpose and split it into two parts: one part which represents the molecule and one part which represents the atoms. The molecule is well described by the triplet structures of Figure 1. At 2.286 bohr, these two structures result in an (optimized) energy of −149.708053 Hartrees, which is only 0.9 mHartree above the minimum of the PD curve (cf. Table II). These structures together have the proper molecular symmetry, but do not have any interaction at infinity and do not dissociate into ground-state atoms. The separate atoms can be described by a fixed combination of the triplet structures of Figures 1 and 2, but it is more convenient to choose one set of equivalent structures, which by symmetry have equal coefficients. The corresponding curves, which bear the labels “molecule” and “atoms,” are given in Figure 5, together with the compound curve, i.e., the PD curve. The PD function is a linear combination of the atomic and the molecular functions. The latter have a fixed spin coupling over the whole range of distances.

Except for the region 4.4–3.4 bohr, the PD curve closely follows the atomic and the molecular curves. In this intermediate region, a dramatic change in the spin coupling occurs and the PD curve can be called neither atomic nor molecular. The atomic triplet coupling is not appropriate to describe the formation of bonds as the atoms approach. It does, however, offer the lowest energy. The PD curve is therefore bound to follow the rising atomic curve until the molecular curve crosses. This results in a maximum. The position and height of the maximum will be determined by the moment of crossing. For example, if the polarization functions are removed from the applied EZPP basis, which affects mainly the molecular curve, the moment of crossing is at a shorter distance and the hump is, consequently, higher (2.1 mHartrees at 4.05 bohr). On going from the PD model to the PR model, the description of the molecule is improved, which explains the observed change in the position and height of the maximum. We have checked several basis sets, and except for a minimal STO-6G basis, all calculations showed a small hump. Although the underlying mechanism is the same, we would not call
the hump the result of an avoided crossing, because there is no crossing between two observable states. Our results are consistent with the VB explanation previously given by McWeeny [8]. We cannot conclude that the hump is "real": it may disappear in more elaborate calculations.

FIGURE 5. The PD function is decomposed into a function that represents the separate atoms and a function that represents the molecule. Near 4.1 bohr, there is a dramatic change in the spin coupling: The repulsive PD function then becomes attractive, which causes a small hump in the potential surface.

Conclusions

The three lowest states (3Σ−, 1Σ+, and 1Σ+) of the oxygen molecule were studied by two VB models based on the atomic valence orbitals. In both models, a minimal number of structures were used to maintain compact wave functions. Consequently, the quality of the calculations was not good enough to reproduce the experimental dissociation energies but equaled that of MCSCF studies using only the valence space. However, having covered most of the bonding energy, we feel justified to draw some conclusions about the nature of the oxygen double bond. The VB method with its compact wave functions is excellently suited for this.

The oxygen molecule in the ground state is described by the VB theory as a molecule having a covalent σ bond and two three-electron π bonds. Two covalent structures are essential to describe these three-electron bonds properly. The very large resonance between these structures accounts for the correct order of the states at the equilibrium geometry. Neglecting this resonance erroneously results in a singlet ground state. The singlet states have a favorable covalent π bond, but do miss the very large resonance. Ionic structures or delocalized orbitals are indispensable for bonding in all three states. This is, however, not unique for the oxygen molecule and applies to a broader class of molecules. The inclusion of ionic structures does not alter the relative order of the states in a classical VB calculation; Wheland was already right about this in 1937. Structures that represent excited atoms proved to be important for the dissociation energies.
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The barrier in the potential surface of the ground state originates from a spin recoupling. The atomic triplet coupling that describes the separate atoms is unable to describe the formation of bonds. Until a dramatic spin recoupling occurs, which marks the transition from two separate atoms to a bound molecule, the potential curve is repulsive. Then, an alternative molecular triplet coupling provides bonding. This results in a small hump. It requires more elaborate calculations or experiments to conclude whether the hump is exaggerated or an artifact of the calculation.

References