

# The generalized valence bond description of O<sub>2</sub> \*

B. J. Moss, F. W. Bobrowicz<sup>†</sup>, and W. A. Goddard III

Arthur Amos Noyes Laboratory of Chemical Physics,<sup>‡</sup> California Institute of Technology, Pasadena, California 91125  
(Received 30 January 1975)

*Ab initio* calculations using the generalized valence bond (GVB) method have been carried out for the lowest triplet and singlet states of O<sub>2</sub> at internuclear distances ( $R$ ) between  $2a_0$  and  $6a_0$ . In contrast to other orbital descriptions, GVB leads correctly to ground state oxygen atoms as the bond length is increased to infinity. This proper behavior requires optimization of the spatial orbitals themselves and of the permutational coupling between them as well. Analysis of the results as a function of  $R$  is straightforward. Constructing a simple configuration interaction (CI) wavefunction using the GVB orbitals leads to excellent potential curves, accounting for 94% of the bond dissociation energy. The calculated adiabatic separation of the singlet and triplet states is 1.09 eV, which is 0.11 eV above the experimental  $T_e$ .

## I. INTRODUCTION

An early major success for the molecular orbital (MO) description of molecules was obtained for O<sub>2</sub> where Mulliken<sup>1</sup> predicted a triplet ground state and two very low-lying singlet states (1–2 eV), all later verified by experiment.<sup>2</sup> In contrast, a simple valence bond (VB) description



suggests a singlet ground state.<sup>3</sup> However, despite the useful description at small internuclear distance ( $R$ ), the MO wavefunction *cannot* lead to ground state oxygen atoms as the molecule is pulled apart. Indeed, at large  $R$  a simple VB wavefunction would be better.

Since we are interested in studying formation of various states of O<sub>2</sub> from O atoms, neither the MO nor VB methods are suitable. The simplest wavefunction leading to a proper description as O<sub>2</sub> dissociates is the generalized valence bond (GVB) wavefunction.<sup>4–6</sup> The GVB wavefunction is a generalization of the VB wavefunction in which the orbitals are solved for self-consistency (rather than taken as atomic). Alternately, the GVB method can be considered to be a generalization of the MO or Hartree-Fock (HF) method in which dominant pair-correlation effects are included self-consistently.

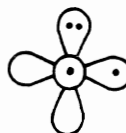
A special point in this paper is the self-consistent optimization of the permutation coupling of the orbitals (hereafter referred to as orbital coupling). In calculations on large molecules it has generally been convenient to couple various orbital pairs in either a singlet or triplet manner, as this greatly simplifies the variational equations.<sup>7</sup> However, in O<sub>2</sub> we find that the optimum orbital coupling changes markedly as the bond is stretched from the equilibrium bond length  $R_e$  to infinity and that these changes *must* be included to permit proper dissociation. In order to allow for this and yet retain computational tractability, a new formulation<sup>8</sup> of the GVB equations has been made to facilitate these studies.

## II. QUALITATIVE GVB DESCRIPTION OF O<sub>2</sub>

### A. Near $R_e$

In order to provide a framework for discussing the

calculations, we first consider the various ways of orienting the atomic orbitals of two oxygen atoms to form O<sub>2</sub>. The ground <sup>3</sup>P state of oxygen atom has the configuration  $(1s)^2(2s)^2(2p)^4$ . Ignoring the  $(1s)$  and  $(2s)$  electrons, we can visualize this as



(1)

where the two lobed figures such as

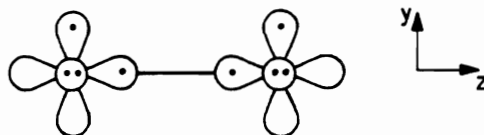


represent  $d$  orbitals in the plane, and

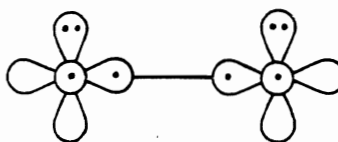


represents a  $p$  orbital pointing out of the plane. The dots indicate the number of electrons in each orbital.

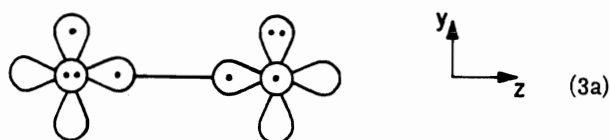
As there are three possible orientations of (1) (corresponding to the three components of a <sup>3</sup>P state), there are nine ways of pairing two ground state atoms. Including spin, this gives rise to a total of 81 possible states of O<sub>2</sub>. However, we are only interested in those states that can result in a strong bond. Thus, we will consider only those cases in which two singly-occupied orbitals are oriented so that a sigma bond can be formed:



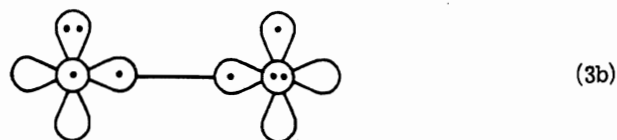
(2a)



(2b)



(3a)



(3b)

where the straight line connecting the orbitals comprising the sigma bond indicates that they are singlet-paired.

Configurations (2a) and (2b) are equivalent and each leads to triplet and singlet states with the singlet state being much lower (possessing  $\pi$  bond); thus we will consider only the singlet state in the following.

Configurations (3a) and (3b) are equivalent and each leads to a singlet and triplet state; in this case the unpaired orbitals [ $p_{y1}$  and  $p_{zr}$  of (3a)] are orthogonal so that the singlet and triplet states differ only in the exchange integral

$$E_{3a}^T = E_0 - K_{y1,zr} \quad (4)$$

$$E_{3a}^S = E_0 + K_{y1,zr}$$

and hence the triplet state must be lower.

In order to compare the energies of (2a) and (3a) we must also consider the doubly occupied  $\pi$  orbitals. In (2a) we form a  $\pi$  bond in the  $yz$  plane, but in the  $xz$  plane there are doubly occupied  $\pi_x$  orbitals on each oxygen, leading to large repulsive interactions. On the other hand, in (3a) each doubly occupied orbital overlaps a singly-occupied orbital. This allows the doubly occupied orbital to delocalize onto the adjacent center, leading to a significant reduction in the electron repulsion between the electrons in this orbital and in the kinetic energies while maintaining a low nuclear-attraction energy (that is, the doubly occupied orbital acquires bonding character). Because of the Pauli principle, the singly occupied orbital starting on the second center must become orthogonal to the delocalized doubly occupied orbital, leading to considerable antibonding character. However the net effect of the doubly occupied orbital dominates, leading to a net bonding of  $\sim 30$  kcal for each three-electron  $\pi$  bond.<sup>5,9</sup> In contrast, for (2a) each doubly occupied orbital must become orthogonal to the other (essentially because of the Pauli principle), leading to antibonding rather than bonding interactions.

From these considerations we expect the best configuration of O<sub>2</sub> to be (3) and for the triplet state to be the lower state of (3). Thus a VB-based analysis of O<sub>2</sub> does correctly predict a triplet ground state. Early VB analyses<sup>3</sup> neglected the important role of the doubly occupied  $\pi$  orbitals in arriving at a singlet ground state.

## B. Large $R$

At large  $R$ , we cannot assume that the  $p_z$  orbitals are paired into a  $\sigma$  bond as in (2) and (3). Instead we must [for (3a)] take the  $p_{y1}$  and  $p_{z1}$  orbitals to be triplet-coupled

and the  $p_{zr}$  and  $p_{xr}$  orbitals to be triplet-coupled. This allows us to form three states: a singlet, triplet, and quintet. In this case an analysis of the exchange terms yields permutational numbers<sup>10</sup> of  $+\frac{1}{2}$ , 0, and  $-1$  for the  $p_{z1}$  and  $p_{xr}$  orbitals of the singlet, triplet, and quintet states, respectively, as compared with  $+1$  for (3a). Thus at large  $R$  the singlet state should be lowest.

Clearly the permutational coupling changes significantly with  $R$  and variations in this quantity must be allowed.

In the Hartree-Fock method the permutational coupling is fixed; however, there are other even more serious limitations. In the conventional HF wavefunction for the ground state of O<sub>2</sub> there are seven doubly occupied and two singly occupied orbitals at all internuclear separations. However, each ground state O atom has three doubly occupied and two singly occupied orbitals. Hence the HF wavefunction leads to an excited description of the separated atoms.

The GVB approach is conceptually more consistent in that each electron can have a separate orbital. Thus, as the molecule is pulled apart, the orbitals can be equally distributed on the two centers. The GVB wavefunction for  $N$  electrons has the form

$$\psi_{\text{GVB}} = \alpha \{ [\phi_a(1) \phi_b(2) \cdots \phi_n(N)] \chi(1, 2, \cdots, N) \}, \quad (5)$$

where  $\alpha$  is the antisymmetrizer. The spin function  $\chi$ , which is an eigenfunction of  $\hat{S}^2$ , defines (through the antisymmetrizer) how the orbitals  $\{\phi\}$  are coupled permutationally. Optimization of (5) consists of self-consistently determining the optimal set of orbitals and the optimal form of  $\chi$ .<sup>6,11</sup>

Because of the complexity of spin eigenfunctions for many-electron systems, it is convenient to use diagrams to represent the ways in which various orbitals are coupled. The overall shape of a diagram indicates the number of electrons and the eigenstate of  $\hat{S}^2$  being considered. Internal partitions denote the specific coupling pattern involved. Two orbitals placed horizontally within a rectangle are singlet-paired, and two or more orbitals placed vertically within a rectangle are coupled to high spin. The standard (linearly independent) couplings for four-electron singlets and triplets are given in Fig. 1.

In O<sub>2</sub> at small  $R$ , we expect the two highly overlapping orbitals comprising the sigma bond to be singlet paired. Taking the internuclear axis to coincide with the  $z$  axis and ignoring the orbitals which are doubly occupied for  $R = \infty$ , the wavefunctions for the  $^1\Delta_g$  and  $^3\Sigma_g^-$  states [from (3a)] are

$$\psi_{^1\Delta_g}(R_e) = \begin{array}{|c|c|} \hline p_{z\ell} & p_{zr} \\ \hline p_{y\ell} & p_{xr} \\ \hline \end{array} \quad (6a)$$

$$\psi_{^3\Sigma_g^-}(R_e) = \begin{array}{|c|c|} \hline p_{z\ell} & p_{zr} \\ \hline p_{y\ell} & \\ \hline p_{xr} & \\ \hline \end{array} \quad (6b)$$

where we have labeled the self-consistent orbitals according to their atomic origin. At large internuclear distances, however, the orbitals on each center must be coupled as in the ground state atom. Since <sup>3</sup>P oxygen atom has two singly occupied orbitals triplet coupled, the wavefunctions at large *R* are

$$\psi_{1\Delta_g}(\omega) = \begin{array}{|c|c|} \hline p_{z\ell} & p_{zr} \\ \hline p_{y\ell} & p_{xr} \\ \hline \end{array} \quad (7a)$$

$$\psi_{3\Sigma_g^-}(\omega) = \sqrt{\frac{2}{3}} \begin{array}{|c|c|} \hline p_{z\ell} & p_{zr} \\ \hline p_{y\ell} & \\ \hline p_{xr} & \\ \hline \end{array} + \sqrt{\frac{1}{3}} \begin{array}{|c|c|} \hline p_{z\ell} & p_{xr} \\ \hline p_{y\ell} & \\ \hline p_{zr} & \\ \hline \end{array}$$

$$= \frac{1}{2} a \{ p_{x\ell} p_{y\ell} p_{zr} p_{xr} [\alpha\alpha(\alpha\beta + \beta\alpha) - (\alpha\beta + \beta\alpha)\alpha\alpha] \}. \quad (7b)$$

Therefore, the simplest wavefunction capable of correctly describing dissociation of these states must be a linear combination of these atomic and molecular couplings:

$$\psi_{1\Delta_g}(R) = C_m \begin{array}{|c|c|} \hline p_{z\ell} & p_{zr} \\ \hline p_{y\ell} & p_{xr} \\ \hline \end{array} + C_a \begin{array}{|c|c|} \hline p_{z\ell} & p_{zr} \\ \hline p_{y\ell} & p_{xr} \\ \hline \end{array} \quad (8a)$$

$$\psi_{3\Sigma_g^-}(R) = C_m \begin{array}{|c|c|} \hline p_{z\ell} & p_{zr} \\ \hline p_{y\ell} & \\ \hline p_{xr} & \\ \hline \end{array} + C_a \left\{ \sqrt{\frac{2}{3}} \begin{array}{|c|c|} \hline p_{z\ell} & p_{zr} \\ \hline p_{y\ell} & \\ \hline p_{xr} & \\ \hline \end{array} + \sqrt{\frac{1}{3}} \begin{array}{|c|c|} \hline p_{z\ell} & p_{xr} \\ \hline p_{y\ell} & \\ \hline p_{zr} & \\ \hline \end{array} \right\} \quad (8b)$$

The GVB wavefunction (5) for any *R* can always<sup>12</sup> be cast in the form of (8) [keep in mind that the atomic labels of (8) serve only to identify the orbitals, they are no longer forced to be purely atomic orbitals].

### III. CALCULATIONAL DETAILS

#### A. The Wavefunction

In the GVB method we can allow all orbitals to be singly occupied; however, the separated atoms each involve three doubly occupied orbitals so that the minimal GVB description is to allow six doubly occupied orbitals (four sigma and two pi) and four singly occupied orbitals (two sigma and two pi). As we found that splitting further pairs with GVB leads to only minor effects, this level of GVB [often denoted as GVB(2) indicating that all but four orbitals are doubly occupied] was used throughout this study.

As GVB calculations involving more than a very few electrons acquire immense computational complexity, two approximations are made in most GVB calculations. These approximations, which are actually restrictions, are perfect pairing and strong orthogonality.<sup>7</sup> The former approximation restricts the spin function in (6) to singlet couple as many orbital pairs as is possible for

a given eigenstate of  $\hat{S}^2$ . That is, for a state of spin *S*

$$\chi_{PP} = [\alpha(1)\beta(2) - \beta(1)\alpha(2)][\alpha(3)\beta(4) - \beta(3)\alpha(4)] \dots \quad (9)$$

with the last 2*S* spins being  $\alpha$ . The strong orthogonality restriction requires each orbital to be orthogonal to all other orbitals except for the other orbital in the same pair. As this perfect pairing (GVB-PP) wavefunction can be cast in a form requiring only simple HF-like variational equations for solution, GVB-PP calculations can easily be performed on relatively large numbers of electrons.<sup>7</sup>

While the perfect pairing restriction is often an excellent approximation, it is inadequate for cases where significant orbital coupling changes can be expected (e.g., chemical reactions). The case at hand clearly demonstrates this in that the GVB-PP wavefunctions (6) are unable to properly describe dissociation. To overcome this limitation, the GVB equations were reformulated, removing the perfect pairing restriction, but maintaining the requirement of strong orthogonality (orbitals are still grouped into nonorthogonal pairs, but are not required to be coupled in any specific manner). As this strongly orthogonal (GVB-SO) wavefunction retains much of the computational simplicity of GVB-PP, it too can readily handle fairly large numbers of electrons.<sup>8</sup> Because of symmetry the orbitals of the GVB(2) wavefunction of O<sub>2</sub> satisfy the strong orthogonality condition and use of this procedure leads to the (unrestricted) GVB wavefunction.

#### B. Basis Set

The calculations were carried out using the double-zeta (DZ) basis set [4*s*2*p*] of Dunning,<sup>13</sup> contracted from

#### FOUR-ELECTRON SINGLET

$$G1 \quad \begin{array}{|c|c|} \hline \phi_i & \phi_j \\ \hline \phi_k & \phi_\ell \\ \hline \end{array} = \frac{1}{2} \mathcal{A} \{ \phi_i \phi_j \phi_k \phi_\ell (\alpha\beta\alpha\beta - \alpha\beta\beta\alpha - \beta\alpha\alpha\beta + \beta\alpha\beta\alpha) \}$$

$$G2 \quad \begin{array}{|c|c|} \hline \phi_i & \phi_k \\ \hline \phi_j & \phi_\ell \\ \hline \end{array} = \frac{1}{\sqrt{12}} \mathcal{A} \{ \phi_i \phi_j \phi_k \phi_\ell (2\alpha\alpha\beta\beta - \beta\alpha\beta\alpha - \alpha\beta\beta\alpha - \alpha\beta\alpha\beta + 2\beta\beta\alpha\alpha - \beta\alpha\alpha\beta) \}$$

#### FOUR-ELECTRON TRIPLET

$$G1 \quad \begin{array}{|c|c|} \hline \phi_i & \phi_j \\ \hline \phi_k & \\ \hline \phi_\ell & \\ \hline \end{array} = \frac{1}{\sqrt{2}} \mathcal{A} \{ \phi_i \phi_j \phi_k \phi_\ell (\alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha) \}$$

$$G2 \quad \begin{array}{|c|c|} \hline \phi_i & \phi_k \\ \hline \phi_j & \\ \hline \phi_\ell & \\ \hline \end{array} = \frac{1}{\sqrt{6}} \mathcal{A} \{ \phi_i \phi_j \phi_k \phi_\ell (2\alpha\alpha\beta\alpha - \alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha) \}$$

$$G3 \quad \begin{array}{|c|c|} \hline \phi_i & \phi_\ell \\ \hline \phi_j & \\ \hline \phi_k & \\ \hline \end{array} = \frac{1}{\sqrt{12}} \mathcal{A} \{ \phi_i \phi_j \phi_k \phi_\ell (3\alpha\alpha\alpha\beta - \beta\alpha\alpha\alpha - \alpha\beta\alpha\alpha - \alpha\beta\alpha\alpha) \}$$

FIG. 1. Standard couplings for four-electron systems.

TABLE I. Energies from GVB and GVB-CI calculations on O<sub>2</sub> using the DZd basis. (Add the quoted number to -149 to obtain the total energies in hartrees.)

Internuclear distance ( <i>a</i> <sub>0</sub> )	<sup>3</sup> Σ <sub>g</sub> <sup>-</sup>		<sup>1</sup> Δ <sub>g</sub>	
	GVB	GVB-CI	GVB	GVB-CI
2.0	-0.62241	-0.71401	-0.57513	-0.66951
2.285616 <sup>a</sup>	-0.65978	-0.78030	-0.62773	-0.73923
2.5	-0.64978	-0.77278	-0.63437	-0.73559
3.0	-0.61954	-0.70471	-0.62084	-0.67998
3.5	-0.60156	-0.64204	-0.60821	-0.63387
4.0 <sup>a</sup>	-0.59847	-0.61167	-0.60353	-0.61346
4.5	-0.59976	-0.60480	-0.60210	-0.60665
5.0	-0.60064	-0.60362	-0.60155	-0.60433
6.0	-0.60107	-0.60313	-0.60118	-0.60298

<sup>a</sup>With the DZ basis the GVB energies of the <sup>3</sup>Σ<sub>g</sub><sup>-</sup> and <sup>1</sup>Δ<sub>g</sub> states are -149.60154 and -149.54193 at 2.285616 *a*<sub>0</sub> and -149.59797 and -149.60301 at 4.0 *a*<sub>0</sub>.

the [9s5*p*] Gaussian set of Huzinaga,<sup>14</sup> and augmented by five uncontracted *d* functions on each center, each having an exponent of 0.9.

This basis is often referred to as [4s2*p*1*d*] and denoted as DZd. The double-zeta set by itself is inadequate to describe the molecular bond formation, since with this basis the energy of the <sup>1</sup>Δ<sub>g</sub> state at 4 bohr is lower than that of both the <sup>3</sup>Σ<sub>g</sub><sup>-</sup> and <sup>1</sup>Δ<sub>g</sub> states at *R*<sub>0</sub> (see Table I).

## IV. RESULTS

### A. Orbitals and orbital coupling

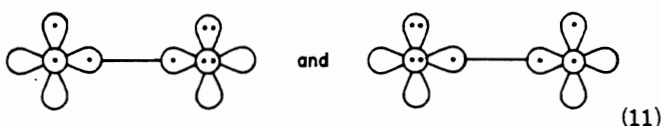
The orbitals from the GVB calculations on the <sup>3</sup>Σ<sub>g</sub><sup>-</sup> state are shown for various *R* in Fig. 2. The orbitals for the <sup>1</sup>Δ<sub>g</sub> state are essentially the same. As expected, the 1*s* orbitals (not shown) and the 2*s* orbitals remain localized as the atoms are brought together. The 2*p*<sub>*x*</sub> orbitals, which are paired to form a bond, do not change significantly until around *R* = 4*a*<sub>0</sub> = 2.1 Å. Because of the Pauli principle the O<sub>1</sub>2*p*<sub>*x*</sub> orbital must remain orthogonal to the O<sub>1</sub>2*s* doubly occupied orbital and this seems to be a dominant influence upon the changes in the shape of both orbitals. (Similar results of course apply to O<sub>2</sub>2*p*<sub>*x*</sub> and O<sub>2</sub>2*s*.) Orthogonalizing the O<sub>1</sub>2*p*<sub>*x*</sub> orbital to O<sub>1</sub>2*s* would lead to just the type of character built up in O<sub>1</sub>2*p*<sub>*x*</sub> as *R* decreases. The way to decrease this effect on O<sub>1</sub>2*p*<sub>*x*</sub> is to hybridize the O<sub>1</sub>2*s* orbital to the right (decreasing its overlap with O<sub>1</sub>2*p*<sub>*x*</sub>) and by *R* = 3*a*<sub>0</sub> we already see such changes in O<sub>1</sub>2*s*. As the internuclear separation decreases, the overlap between the 2*p*<sub>*x*</sub> orbitals continually increases, reaching a value of 0.24 at *R* = 4*a*<sub>0</sub> and a value of 0.80 at *R*<sub>0</sub>.

At *R* = 4*a*<sub>0</sub>, the four π orbitals are still basically atomic. Indeed, significant changes in these orbitals do not occur until around 3*a*<sub>0</sub>. At this point, the doubly occupied O<sub>1</sub>2*p*<sub>*x*</sub> and O<sub>1</sub>2*p*<sub>*y*</sub> orbitals begin to delocalize in a bonding manner onto the other center. The singly occupied O<sub>1</sub>2*p*<sub>*x*</sub> and O<sub>1</sub>2*p*<sub>*y*</sub> orbitals also delocalize, but do so in an antibonding manner in order to remain orthogonal to the doubly occupied orbitals. By *R*<sub>0</sub>, these orbitals are almost equivalently delocalized onto both centers.

In the HF description the π orbitals are of π<sub>u</sub> (bonding) and π<sub>g</sub> (antibonding) symmetries. The GVB orbitals at *R*<sub>0</sub> are close to this description, but as *R* increases we see that the optimum orbitals become more and more localized. The problem in the HF description can be seen by expanding the π<sub>g*x*</sub> and π<sub>g*y*</sub> orbitals in terms of atomic components,

$$\begin{aligned} \pi_{g_x}(1)\pi_{g_y}(2) &= (l_x + r_x)(l_y + r_y) \\ &= \underbrace{(l_x l_y + r_x r_y)}_{\text{ionic}} + \underbrace{(l_x r_y + r_x l_y)}_{\text{covalent}}. \end{aligned} \quad (10)$$

Thus use of symmetry functions as in HF leads to equal amounts of ionic and covalent character in the wavefunction. Putting in the other π electrons shows that the HF wavefunction is a superposition of the covalent configurations (3a) and (3b) along with the ionic configurations



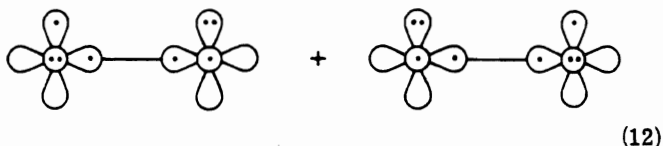
(including the HF description of the σ bond leads to additional ionic configurations).

Changes in the coupling between the orbitals are also straightforward and in line with our qualitative expectations. Results of analysis of the GVB wavefunctions in terms of the atomic and molecular couplings of (8) are shown in Fig. 3. As we see, concurrent with increasing overlap between the 2*p*<sub>*x*</sub> orbitals, molecular coupling becomes of ever increasing importance as *R* is decreased from infinity to *R*<sub>0</sub>. As expected, at *R*<sub>0</sub> molecular coupling vastly predominates over any residual atomic coupling. Comparing these curves, we note that the degree of "molecular" coupling in the triplet always exceeds that of the singlet state. The reason for this is that while the exchange interactions between the singly occupied π orbitals in (6b) are favorable, these same interactions are quite unfavorable in (6a). (This was the same reason used to conclude that the <sup>3</sup>Σ<sub>g</sub><sup>-</sup>, and not the <sup>1</sup>Σ<sub>g</sub><sup>-</sup>, was the ground state of O<sub>2</sub>.)

The optimum orbitals for the <sup>3</sup>Σ<sub>g</sub><sup>-</sup> state at *R*<sub>0</sub> are grouped together in Fig. 4.

### B. Spatial symmetry and CI

In the GVB method we use a simple orbital product such as in (5) and optimize the orbitals and orbital coupling. The result as shown in Figs. 2 and 4 is to obtain orbitals localized more on the left or right side of the molecule. This is fine except that closer examination shows that this wavefunction corresponds to symmetry *D*<sub>2*d*</sub> rather than *D*<sub>∞*h*</sub>. The origin of this difficulty can be spotted in (3a) and (3b), neither of which describes *D*<sub>∞*h*</sub> symmetry. To obtain proper symmetry functions we must combine (3a) and (3b) as



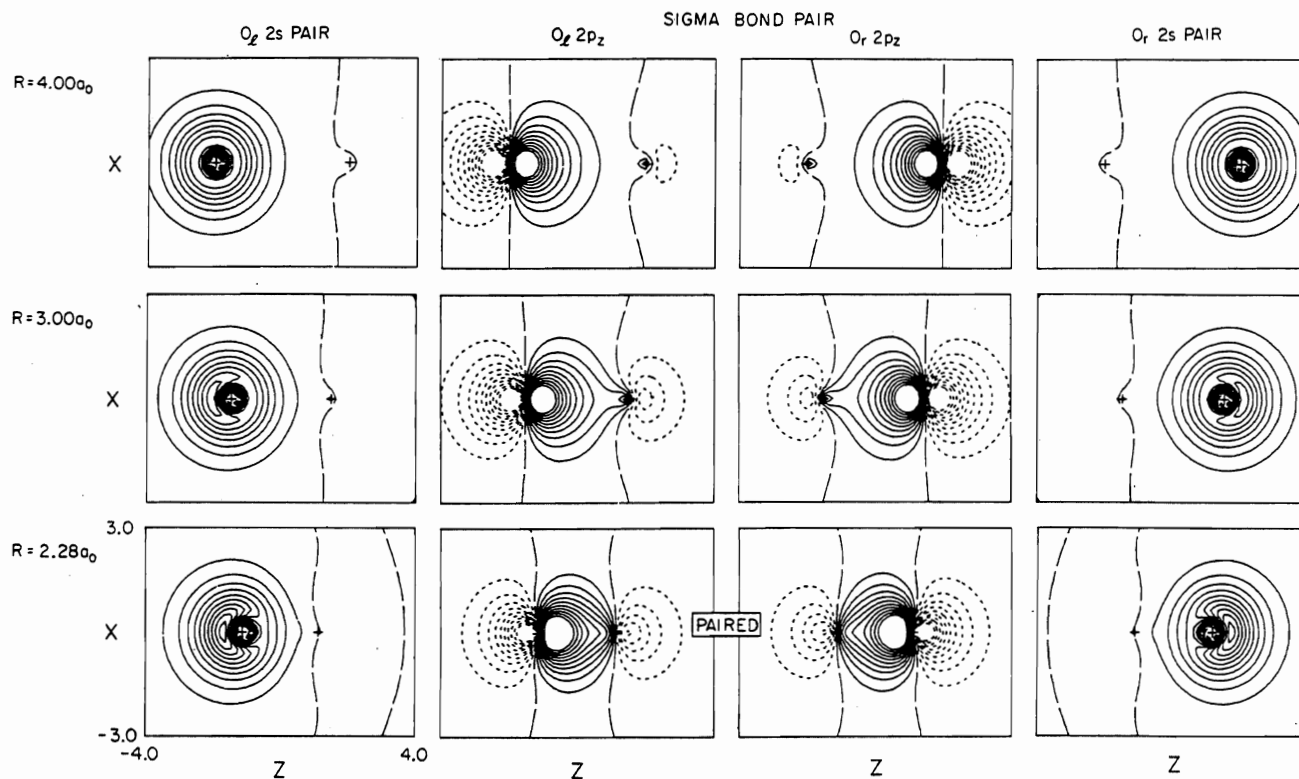
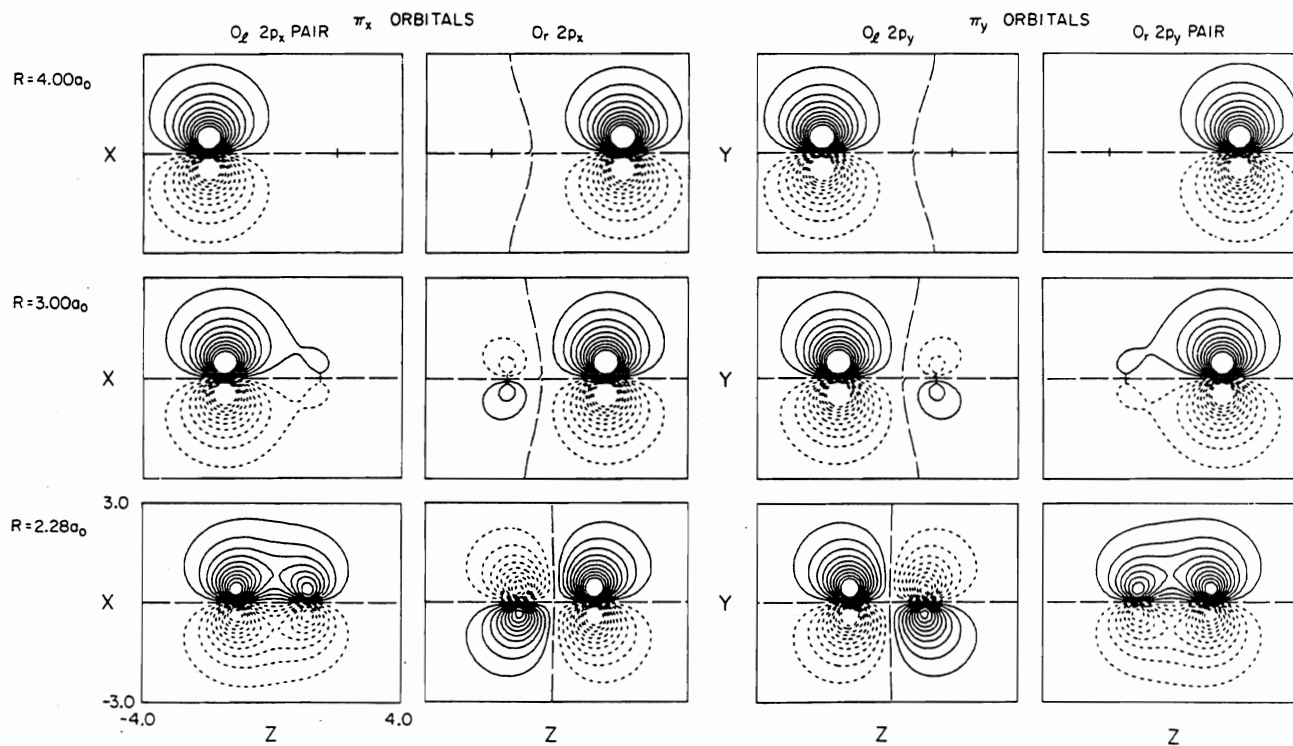
(a)  $O_2$  SIGMA ORBITALS (GVB)(b)  $O_2$  PI ORBITALS (GVB)

FIG. 2. GVB orbitals for  $O_2$  as a function of internuclear distance. Long dashed lines indicate zero amplitude. Solid and short dashed lines indicate positive and negative amplitude. Spacing between successive contours is 0.05 a.u.

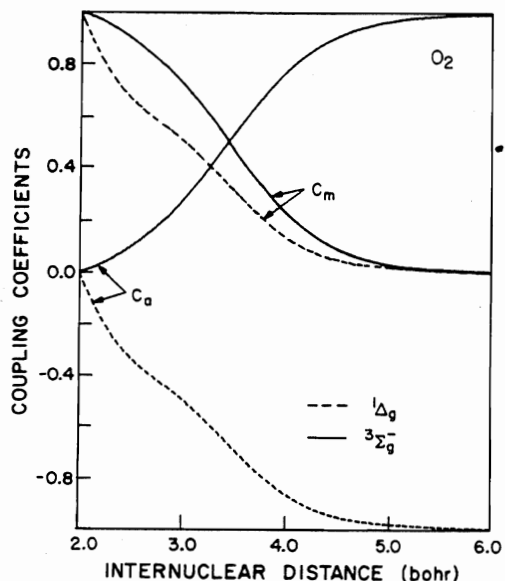


FIG. 3. GVB orbital coupling coefficients for O<sub>2</sub> as a function of internuclear distance. These coefficients are defined in Eq. (8) and have been normalized so that  $|C_m| + |C_a| = 1$  and  $C_m \geq 0$ .

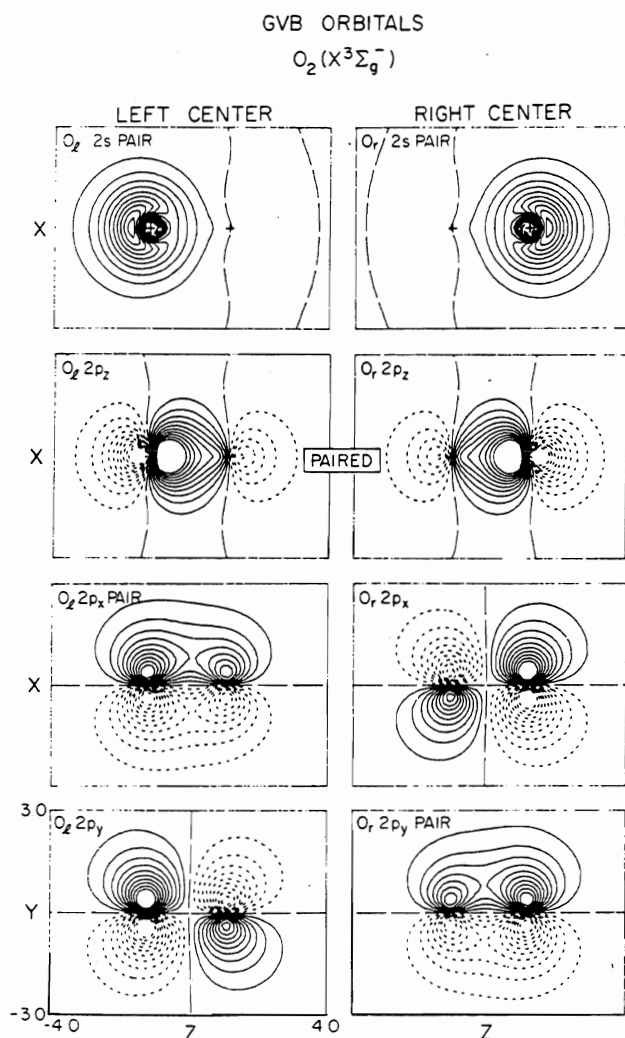


FIG. 4. The GVB orbitals for the  ${}^3\Sigma_g^-$  state at  $R_e$ .

TABLE II. Basic configurations for GVB-CI (the  $1\sigma_g$  and  $1\sigma_u$  orbitals are doubly occupied).

$2\sigma_g$	$2\sigma_u$	$3\sigma_g$	$3\sigma_u$	$1\pi_{ux}$	$1\pi_{gx}$	$1\pi_{uy}$	$1\pi_{gy}$	Inversion symmetry
2	2	2	0	2	1	2	1	<i>g</i>
2	2	2	0	2	1	1	2	<i>u</i>
2	2	2	0	1	2	2	1	<i>u</i>
2	2	2	0	1	2	1	2	<i>g</i>
2	2	1	1	2	1	2	1	<i>u</i>
2	2	1	1	2	1	1	2	<i>g</i>
2	2	1	1	1	2	2	1	<i>g</i>
2	2	1	1	1	2	1	2	<i>u</i>
2	2	0	2	2	1	2	1	<i>g</i>
2	2	0	2	2	1	1	2	<i>u</i>
2	2	0	2	1	2	2	1	<i>u</i>
2	2	0	2	1	2	1	2	<i>g</i>
2	2	2	0	2	2	2	0	<i>g</i>
2	2	2	0	2	2	1	1	<i>u</i>
2	2	2	0	2	2	0	2	<i>g</i>
2	2	2	0	2	0	2	2	<i>g</i>
2	2	2	0	1	1	2	2	<i>u</i>
2	2	2	0	0	2	2	2	<i>g</i>
2	2	1	1	all six cases				
2	2	0	2	all six cases				

leading to  ${}^1\Delta_g$  and  ${}^3\Sigma_g^-$  states [use of a minus sign in (12) leads to  ${}^1\Sigma_u^-$  and  ${}^3\Delta_u$  states]. The GVB method has been extended<sup>15</sup> to allow for such spatial projection techniques (denoted as GVB-SP; however, the calculations are expensive and the programs are not suitable for  $D_{\infty h}$  symmetry). However, from previous experience the GVB-SP orbitals for O<sub>2</sub> are expected to be similar to the GVB orbitals and in this study we have obtained wavefunctions of the proper total symmetry by carrying out small configuration interaction (CI) calculations using the GVB orbitals.

These CI calculations were carried out as follows: The GVB orbitals corresponding to combinations of O1s and O2s orbitals on the atoms are denoted as  $1\sigma_g$ ,  $1\sigma_u$ ,  $2\sigma_g$ , and  $2\sigma_u$ ; the GVB orbitals corresponding to the  $\sigma$  bond are combined into symmetry orbitals denoted as  $3\sigma_g$  and  $3\sigma_u$ . The doubly occupied  $\pi$  orbitals (both  $x$  and  $y$ ) are combined into symmetry functions denoted as  $1\pi_u$  and  $2\pi_g$ , and the singly occupied  $\pi$  orbitals (both  $x$  and  $y$ ) are converted into symmetry functions denoted as  $2\pi_u$  and  $1\pi_g$ . The  $2\pi_u$  and  $2\pi_g$  orbitals obtained by this process are very similar to  $1\pi_u$  and  $1\pi_g$ . For the CI calculations we obtained  $2\bar{\pi}_u$  and  $2\bar{\pi}_g$  orbitals by orthogonalizing to the  $1\pi_u$  and  $1\pi_g$  orbitals.

In terms of symmetry functions the GVB wavefunction has the form

$$\alpha [\phi_{1\sigma_g}^2 \phi_{1\sigma_u}^2 \phi_{2\sigma_g}^2 \phi_{2\sigma_u}^2 (\phi_{3\sigma_g}^2 - \lambda_1 \phi_{3\sigma_u}^2) \times (\phi_{1\pi_{ux}}^2 \phi_{1\pi_{gx}} - \lambda_2 \phi_{1\pi_{gx}}^2 \phi_{1\pi_{ux}}) \times (\phi_{1\pi_{uy}}^2 \phi_{1\pi_{gy}} - \lambda_2 \phi_{1\pi_{gy}}^2 \phi_{1\pi_{uy}}) \chi] \quad (13)$$

(if we assume that  $2\pi_u = 1\pi_u$  and  $2\pi_g = 1\pi_g$ ). Expanding out (13) leads to the 12 terms above the line in Table II. [In (13) we assumed the molecular orbital coupling (6)



and did not include the  $(3\sigma_g)^1(3\sigma_u)^1$  term; for more general couplings these terms are required as noted in Table II.] Half the configurations in Table II have  $u$  symmetry and could be omitted for the  $g$  states. The remaining six spatial configurations would lead to a wavefunction quite close to the spatially projected GVB wavefunction, except for the slight restrictions we have made in the  $\pi$  orbitals ( $2\pi_u = 1\pi_u$ ,  $2\pi_g = 1\pi_g$ ). In order to allow for readjustments in these  $\pi$  orbitals, we allowed single excitations from the 12 configurations of Table II (above the line) into the  $2\pi_u$  and  $2\pi_g$  orbitals. In order to allow for readjustments in the orbitals due to the presence of spatial projection terms, we allowed a full CI among the eight valence orbitals.

The GVB wavefunction for the states corresponding to (2a) and (2b) leads to the 18 configurations below the line (12 of  $g$  symmetry). In order to describe all the low-lying states of O<sub>2</sub> with a CI compatible with a spatially projected GVB wavefunction, we added these 18 to the above 12 and carried out similar types of excitations. The result was 72 configurations for  $^3\Sigma_g^-$  and 98 configurations for  $^1\Delta_g$  or  $^1\Sigma_g^+$ . Later we will report a study of a number of additional excited states of O<sub>2</sub> using this set of configurations.

Our GVB-CI calculation for O<sub>2</sub> is similar to Schaefer's first-order wavefunction.<sup>17</sup> The difference is that we used GVB calculations to determine 14 optimum (valence) O<sub>2</sub> orbitals as a function of  $R$ , whereas in the first-order procedure one uses the iterative natural orbital procedure to determine ten optimum valence O<sub>2</sub> orbitals. Then in the GVB-CI wavefunction we include high-order excitations (up to fourth-order among ten of the GVB orbitals plus single excitations from all of these configurations into the four remaining GVB orbitals. In the first-order wavefunction one includes double excitations from the dominant configuration (a quadruple excitation was also included in Ref. 17) but allows up to single excitations to the 20 virtual orbitals.

### C. Energies

The energies from the GVB calculations are tabulated in Table I and plotted in Fig. 5, where we see that the GVB wavefunctions do behave properly, leading to ground state O atoms as the bond is stretched to infinity. This is

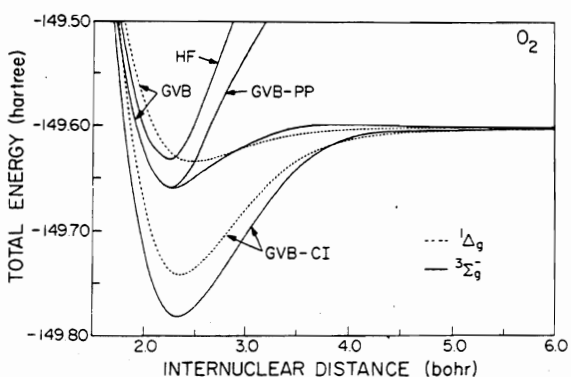


FIG. 5. Potential energy curves for the  $^3\Sigma_g^-$  and  $^1\Delta_g$  states of O<sub>2</sub> from HF, GVB-PP, GVB, and GVB-CI calculations.

TABLE III. Parameters of the potential curves of O<sub>2</sub> from the GVB-CI calculations.

	$^3\Sigma_g^-$		$^1\Delta_g$	
	Calc.	Expt. <sup>a</sup>	Calc.	Expt. <sup>a</sup>
$R_e$ (Å)	1.238	1.208	1.249	1.216
$D_e$ (eV)	4.88	5.21	3.79	4.23
$\omega_e$ (cm <sup>-1</sup> )	1693	1580	1595	1509
$\Delta E$ (eV)	...	...	1.089	0.982

<sup>a</sup>Experimental values are from Ref. 16.

in clear contrast to the HF and GVB-PP curves which do not exhibit this correct behavior at large  $R$ . At  $R_e$ , the  $^1\Delta_g$ - $^3\Sigma_g^-$  separation is 0.87 eV, in good agreement with experiment (0.98 eV).<sup>16</sup> However, there is little point in dwelling upon these curves since they do not include the spatial projection effects. It is, rather, the potential curves obtained from the CI calculations using the GVB orbitals that are of importance.

The CI results are reported in Table I and plotted in Fig. 5. The calculated values for the bond distance  $R_e$ , bond energy  $D_e$ , and vibrational frequency  $\omega_e$  are listed in Table III and compared with experimental results. Thus these calculations account for 92.9% of the bond energy and lead to an  $R_e$  too large by 1.7%. For comparison, Schaefer<sup>17</sup> carried out "first-order" CI calculations on the  $^3\Sigma_g^-$  state obtaining 90.6% of the bond energy and an  $R_e$  1.1% too large.

The excellence of these CI results suggests to us that the GVB orbitals contain the essential features of these states of O<sub>2</sub> and hence that the concepts developed here and based on these orbitals are valid.

\*Partially supported by a grant (GP-40783X) from the National Science Foundation.

<sup>†</sup>National Science Foundation Trainee, 1970-71; ARCS Foundation Fellow, 1971-73; Woodrow Wilson Fellow, 1972; National Science Foundation Fellow, 1972-73. Present address: Battelle Memorial Institute, 505 King Avenue, Columbus, OH 43201.

<sup>‡</sup>Contribution No. 5046.

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