

Configuration interaction studies on low-lying states of O₂*

Barry J. Moss and William A. Goddard III

Arthur Amos Noyes Laboratory of Chemical Physics,† California Institute of Technology, Pasadena, California 91125

(Received 17 April 1975)

We report configuration interaction calculations as a function of internuclear distance for the nine states of O₂ corresponding to the (3σ_g)²(1π_u)⁴(1π_g)² and (3σ_g)²(1π_u)³(1π_g)³ configurations, that is, X³Σ_g⁻, a¹Δ_g, b¹Σ_g⁺, c¹Σ_g⁺, C³Δ_u, A³Σ_u⁺, B³Σ_u⁻, ¹Δ_u, ¹Σ_u⁺. By using the generalized valence bond (GVB) orbitals of the X³Σ_g⁻ state, we obtain good quality GVB-CI wavefunctions with only a moderate number of configurations (72 to 98 spatial configurations) despite the use of a large basis set (double-zeta plus *d* polarization functions). The calculated *D_e* for the X³Σ_g⁻ state is 4.88 eV, 93% of the experimental value. The calculated adiabatic excitation energies are on the average about 0.1 eV from the experimental values.

I. INTRODUCTION

The first great success of MO theory was the rationalization of the paramagnetic behavior of the ground state and the prediction of the low-lying excited states.¹ However, full Hartree-Fock (HF) wavefunctions^{2c} of O₂ account for only 1.43 eV out of 5.21 eV of the bond energy and in addition provide a potential curve going to the wrong limits as the internuclear distance *R* → ∞. On the other hand, with a basis adequate for describing dissociation (double zeta plus *d* polarization functions), a full configuration interaction (CI) calculation for the triple states would involve 3 × 10¹¹ determinants, and just including all single and double excitations from the dominant triplet configuration would lead to 28 000 determinants, without excitation from the 1σ_g and 1σ_u orbitals. Thus, studying a number of states of O₂ would lead to considerable expense.

In this paper we use the generalized valence bond (GVB) orbitals^{3,4} for the carrying out of the CI calculations. Since the GVB wavefunction leads to the correct description of the wavefunction as *R* → ∞, the CI wavefunctions are expected to be adequate even for large *R*. The excitation energies for small *R* are accurate to about 0.1 eV, while the bond lengths are generally about 0.02 Å too long.

The calculational details are presented in Sec. II. A qualitative description of the wavefunctions in terms of GVB diagrams is given in Sec. III, followed in Sec. IV by an analysis of the corresponding configurations for the CI calculations. The results and discussions are presented in Sec. V.

II. CALCULATIONAL DETAILS

The basis set used in these studies is the double zeta basis of contracted Gaussians from Dunning⁵ and Huzinaga, supplemented by a set of *d* basis functions on each oxygen (orbital exponent α = 0.9). Such a basis is expected to yield a good description of the potential curves for valence states.

As shown previously,³ the orbital permutational coupling (also called spin coupling) must be allowed to vary with *R* in order to obtain the proper description of dissociation. Thus, the perfect pairing restrictions^{4b} are unsuitable here, and they are not imposed. These GVB

wavefunctions for O₂ are described elsewhere.³

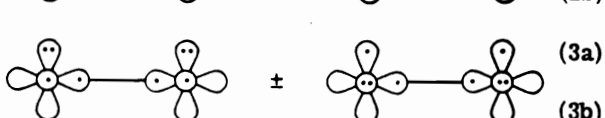
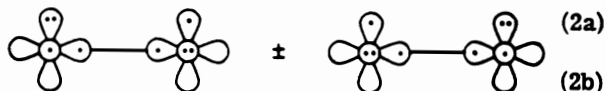
The CI calculations were carried out with the Caltech CI program.⁶

III. QUALITATIVE DESCRIPTION

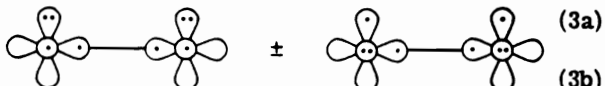
Ignoring the O 1s and O 2s orbitals for the moment, the oxygen atom may be pictured as



where and represent *p* orbitals parallel and perpendicular to the plane of the paper and the dots indicate the occupation.⁴ Combining such configurations on the two atoms so as to describe a sigma bond between them leads to



and



where the line indicates singlet pairing of the connected orbitals. Each configuration in (2) and (3) leads to both a singlet and a triplet state depending on the coupling of the singly-occupied π orbitals. The over-all symmetries obtained with (2) and (3) are:

$$\begin{aligned}
 (2a): & \quad {}^3\Sigma_g^-, \quad {}^1\Delta_g^- \\
 (2b): & \quad {}^1\Sigma_u^-, \quad {}^3\Delta_u^- \\
 (3a): & \quad {}^1\Sigma_g^+, \quad {}^3\Sigma_u^+ \\
 (3b): & \quad {}^1\Delta_g^+, \quad {}^3\Delta_u^+
 \end{aligned} \tag{4}$$

(the two components of each Δ state appear separately). As would be expected from (2) and (3), the states in (4) all go to the limit of two ground state (³P) oxygen atoms as *R* → ∞. However, for small *R* they partition into two groups:

$${}^3\Sigma_g^-, \quad {}^1\Delta_g^-, \quad \text{and} \quad {}^1\Sigma_g^+ \tag{5}$$

with large bond energies (3.5–5.2 eV), and

$${}^1\Sigma_u^-, \quad {}^3\Delta_u^-, \quad \text{and} \quad {}^3\Sigma_u^+ \tag{6}$$

with small bond energies (0.8–1.1 eV). In this VB de-

TABLE I. Configurations for the CI calculations (the $1\sigma_g$ and $1\sigma_u$ orbitals are doubly occupied).

	$2\sigma_g$	$2\sigma_u$	$3\sigma_g$	$3\sigma_u$	$1\pi_{gx}$	$1\pi_{gy}$	$1\pi_{uz}$	$1\pi_{vz}$	Symmetry
(a)	2	2	2	0	2	1	2	1	g
	2	2	2	0	2	1	1	2	u
	2	2	2	0	1	2	2	1	u
	2	2	2	0	1	2	1	2	g
	2	2	1	1	2	1	2	1	u
	2	2	1	1	2	1	1	2	g
	2	2	1	1	1	2	2	1	g
	2	2	1	1	1	2	1	2	u
	2	2	0	2	2	1	2	1	g
	2	2	0	2	2	1	1	2	u
	2	2	0	2	1	2	2	1	u
	2	2	0	2	1	2	1	2	g
(b)	2	2	2	0	2	2	2	0	g
	2	2	2	0	2	2	1	1	u
	2	2	2	0	2	2	0	2	g
	2	2	2	0	2	0	2	2	g
	2	2	2	0	1	1	2	2	u
	2	2	2	0	0	2	2	2	g
	2	2	1	1	All six cases				
	2	2	0	2	All six cases				

scription these states [(5) and (6)] just correspond to the resonant and antiresonant combinations, respectively, of four component configurations.



etc.

In the MO description⁷ the lowest configuration is

$$(1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^2 (2\sigma_u)^2 (3\sigma_g)^2 (1\pi_u)^4 (1\pi_g)^2, \quad (8)$$

leading to the states in (5). The first excited configuration is

$$(1\pi_u)^3 (1\pi_g)^3 \quad (9)$$

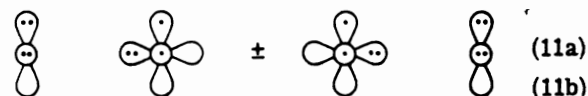
(the σ occupations are unchanged), leading to

$${}^3\Sigma_u^-, {}^1\Delta_u, {}^1\Sigma_u^+ \quad (10)$$

in addition to the states in (6). Thus, the resonant valence bond states (5) correspond to the ground MO con-

figuration, while its antiresonant valence bond states (6) correspond to half of the states of the first excited MO configuration.

Higher valence bond states are obtained with configurations such as



involving an excited state at $R = \infty$. Configuration (11b) gives rise to the ${}^3\Sigma_u^-$ and ${}^1\Delta_u$ states of (10) leading at $R = \infty$ to $O({}^1D) + O({}^3D)$ for ${}^3\Sigma_u^-$ and $O({}^1D) + O({}^1D)$ for ${}^1\Delta_u$. The other configuration (11a) leads to states ($2{}^3\Sigma_g^-, 2{}^1\Delta_g$) that at small R correspond to the

$$(1\pi_u)^2 (1\pi_g)^4 \quad (12)$$

MO configurations (that is, doubly-excited states).

IV. THE CI CALCULATIONS

The GVB calculations were carried out for the triplet and singlet states corresponding to the configurations in (7). This led to doubly-occupied $1\sigma_g$ and $1\sigma_u$ orbitals corresponding closely to combinations of the O 1s orbitals and $2\sigma_g$ and $2\sigma_u$ orbitals corresponding closely to combinations of the O 2s orbitals. The sigma bond pair of (7) can be written in terms of natural orbitals as

$$(\phi_{\sigma_1} \phi_{\sigma_r} + \phi_{\sigma_r} \phi_{\sigma_1}) = (\phi_{3\sigma_g} \phi_{3\sigma_g} - \lambda \phi_{3\sigma_u} \phi_{3\sigma_u}) \quad (13)$$

(ignoring normalization), where it is understood that in each term electron 1 is in the first orbital, electron 2 is in the second, etc. The pi orbitals of (7) are localized but are combined into symmetry functions for the CI, leading to two sets of π_u orbitals. These combinations were taken so that $1\pi_u$ corresponds to a symmetry-projected doubly-occupied orbital while $1\pi_g$ corresponds to a symmetry-projected singly-occupied orbital. The $2\pi_g$ and $2\pi_u$ orbitals each correspond to the other possible projection, but Schmidt-orthogonalized to $1\pi_g$ and $1\pi_u$.

In terms of symmetry functions, (2) leads to the 12

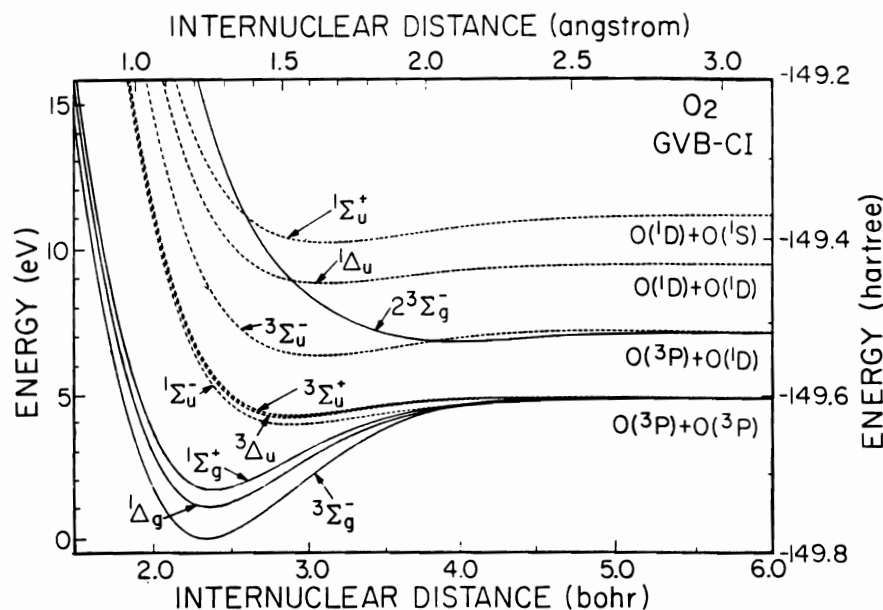


FIG. 1. The calculated potential curves for O_2 . (The points in Table III were interpolated with cubic splines.)

TABLE II. Equilibrium parameters for various states of O₂.

State	Excitation energies (eV)										
	Adiabatic		Vertical Calculated		Exptl	D _e (eV)		R _e (Å)		ω _e (cm ⁻¹)	
	Calc	Exptl ^a	R _e ^{exptl} (1.2075 Å)	R _e ^{calc} (1.2375 Å)		Calc ^b	Exptl ^a	Calc	Exptl ^a	Calc	Exptl ^a
¹ Σ _g ⁺	10.187	(10.3) ^c	13.659	13.066		0.920	(1.12)	1.655		652.8	
¹ Δ _g	8.794	(8.4) ^c	12.084	11.511		0.556	(0.76)	1.648		627.2	
² Σ _g ⁺	6.798		15.956	14.904		0.314		2.101		482.6	
^B Σ _g ⁻	6.308	6.174	9.483	8.917	~8.6 ^e	0.805	1.007	1.625	1.604	667.8	709.1
^A Σ _g ⁺	4.249	4.389	6.583	6.086	~6. ^g	0.626	0.824	1.528	1.522	836.6	799.1
^C Σ _g ⁻	4.173	4.307	6.443	5.953		0.703	0.907	1.522	~1.5	858.6	~750.
^c Σ _g ⁻	3.937	4.099	6.182	5.699		0.939	1.115	1.525	1.517	832.6	794.3
^b Σ _g ⁺	1.691	1.636	1.756	1.710	1.650 ^f	3.185	3.577	1.260	1.227	1505.1	1432.7
^a Δ _g	1.089	0.982	1.118	1.094	0.984 ^f	3.787	4.232	1.249	1.216	1595.0	~1509.3
^X Σ _g ⁺	0	0	0	0	0	4.876	5.213	1.238	1.208	1692.7	1580.2

^aReference 7, including corrections for zero point energies. For values in parentheses, see text.

^bMeasured from the calculated separated-atom limit.

^cEstimated from our theoretical results.

^dReference 13.

^eReference 14.

^fCalculated using the RKR results in Ref. 7.

configurations of Table Ia and (3) leads to the 18 configurations of Table Ib. Carrying out the CI over these configurations leads to a close approximation to the GVB wavefunction (as discussed in more detail below), except that the orbitals are obtained from calculations on the ³Σ_g⁻ state and hence need not be optimum for the other states. In addition, the procedure of symmetrizing the GVB orbitals leads also to 2π_g and 2π_u orbitals omitted in Table I. To remedy these two effects, we have included all single excitations from the valence orbitals of the 30 configurations in Table I, allowing the 2π_g and 2π_u orbitals to also be occupied. In addition, we have included all configurations involving various occupations of the eight valence orbitals of Table I. This leads, for

example, to 98 configurations or 360 determinants for the ¹Σ_g⁺ state and 72 configurations or 224 determinants for the ³Σ_g⁻ state. In contrast, a full CI among these 14 orbitals would involve about 10⁶ determinants. This approach (exciting from all configurations required for describing the various states at R = ∞) is necessary to obtain a consistent treatment of the various states for all R.

V. RESULTS

The calculated potential curves are shown in Fig. 1, and a summary of relevant quantities is given in Table II. The calculated energies are tabulated in Table III.

TABLE III. Calculated (GVB-CI) energies for the states of O₂ (subtract the quoted value from -149.0 to obtain the total energy in hartree).

	R=2.0	2.285616	2.5	3.0	3.5	4.0	4.5	5.0	6.0
^X Σ _g ⁺	0.71401	0.78030	0.77278	0.70471	0.64204	0.61167	0.60480	0.60362	0.60313
^a Δ _g	0.66951	0.73923	0.73559	0.67998	0.63387	0.61346	0.60665	0.60433	0.60313
^b Σ _g ⁺	0.64210	0.71577	0.71562	0.66828	0.62888	0.61165	0.60588	0.60393	0.60298
^c Σ _g ⁻	0.36996	0.55310	0.61054	0.63578	0.62261	0.61173	0.60667	0.60455	0.60325
^C Σ _g ⁻	0.35857	0.54353	0.60173	0.62691	0.61317	0.60483	0.60318	0.60301	0.60295
^A Σ _g ⁺	0.35171	0.53838	0.59761	0.62440	0.61153	0.60377	0.60256	0.60264	0.60280
^B Σ _g ⁻	0.23510	0.43179	0.50188	0.54945	0.54120	0.52673	0.51942	0.51834	0.51979
¹ Δ _g	0.13894	0.33621	0.40739	0.45759	0.45245	0.44168	0.43664	0.43489	0.43364
¹ Σ _g ⁺	0.07784	0.27836	0.35228	0.40610	0.40087	0.38719	0.37849	0.37440	0.37164
² Σ _g ⁺	-0.12144	0.19394	0.32905	0.47208	0.52105	0.53175	0.52621	0.52216	0.52025

TABLE IV. Dipole transition moments^a for O₂. All quantities are in atomic units.

R	³ Σ _g ⁻ - ³ Σ _u ⁻		¹ Δ _g - ¹ Δ _u		¹ Σ _g ⁺ - ¹ Σ _u ⁺	
	M(R)	f(R)	M(R)	f(R)	M(R)	f(R)
2.0	1.0291	0.338	0.9652	0.330	0.9396	0.332
2.285616	0.9748	0.221	0.8670	0.202	0.8078	0.190
2.5	0.8695	0.137	0.7182	0.112	0.6287	0.096
3.0	0.6243	0.040	0.3632	0.020	0.2364	0.010
3.5	0.3900	0.010	0.1227	0.002	0.0257	0.000
4.0	0.1476	0.001	0.0245	0.000	-0.0188	0.000
4.5	0.0381	0.000	0.0033	0.000	-0.0127	0.000
5.0	0.0055	0.000	0.0000	0.000	0.0058	0.000
6.0	0.0001	0.000	-0.0003	0.000	-0.0012	0.000

^aGiven electronic wavefunctions ψ_j and ψ_k ,

$$M_{jk}(R) \equiv \langle \psi_j | \sum_{i=1}^{16} z_i | \psi_k \rangle$$

and

$$f_{jk}(R) \equiv \frac{2}{3} \Delta E_{jk} [M_{jk}(R)]^2.$$

The oscillator strength indicates the total strength of the transition assuming that $M(R)$ is independent of R . Clearly, such an approximation must be used with caution here.

A. Small R

The calculated dissociation energy for the ground state is $D_e = 4.88$ eV, which is 93% of the experimental value,⁷⁻⁹ 5.21 eV. The calculated adiabatic excitation energies to the six experimentally known excited states of Table I are off by 0.11, 0.06, -0.16, -0.13, -0.14, and 0.13 eV, respectively, an average error of 0.12 eV.¹⁰

The calculated bond lengths for the lowest seven states are calculated to be 0.030, 0.033, 0.033, 0.008, 0.022, 0.007, and 0.021 Å longer than the experimental values. Using a cubic spline fit to obtain the force constant k_e leads to $\omega_e = \sqrt{k_e/\mu}$, about 5 to 7% higher than the experimental ω_e for the first six states and about 6% too low

TABLE V. Calculated oscillator strengths at the calculated R_e . All quantities are in atomic units.

Transition	Absorption		Emission	
	R_e	f_e	R_e	f_e
$B^3\Sigma_u^- \leftrightarrow X^3\Sigma_g^-$	2.339	0.200	3.070	0.0335
$^1\Delta_u \leftrightarrow a^1\Delta_g$	2.360	0.169	3.115	0.0123
$^1\Sigma_u^+ \leftrightarrow b^1\Sigma_g^+$	2.382	0.145	3.127	0.0045

for $B^3\Sigma_u^-$.

The error in the calculated dissociation energies is 0.4 eV for the states in (5), 0.2 eV for the states in (6), and 0.2 eV for $B^3\Sigma_u^-$. Thus, the error is 0.4 eV for states with $R_e \approx 1.2$ Å and 0.2 eV for states with $R_e \approx 1.6$ Å, a reasonable result, since the correlation errors should decrease exponentially as R increases. Assuming a similar 0.2 eV error in the calculated D_e for $^1\Delta_u$ and $^1\Sigma_u^+$ (both with $R_e \sim 1.65$ Å) leads to a predicted T_e of 8.4 eV for $^1\Delta_u$ and 10.3 eV for $^1\Sigma_u^+$.

There has been some difficulty^{7,11,12} in establishing the T_e for the transitions to the $c^1\Sigma_u^-$, $C^3\Delta_u$, and $A^3\Sigma_u^+$ states owing to difficulty in establishing the vibrational numbering in the observed transitions. The numbering in the $A^3\Sigma_u^+$ state seems, however, to finally be established,¹¹ although the $c^1\Sigma_u^-$ and especially the $C^3\Delta_u$ states are uncertain.¹² Using the present numbering schemes yields energy separations⁷ of 0.21 and 0.08 eV for $c-C$ and $C-A$, in good agreement with our calculated values of 0.24 and 0.08 eV (vibrational spacings are ~ 0.1 eV). Thus, our results indicate that the vibrational numbering of the $c^1\Sigma_u^-$ and $C^3\Delta_u$ states has been correctly assigned (assuming $A^3\Sigma_u^+$ to be correct).

The experimental absorption spectrum (the Schumann-Runge band systems) exhibits a broad peak around 8.6

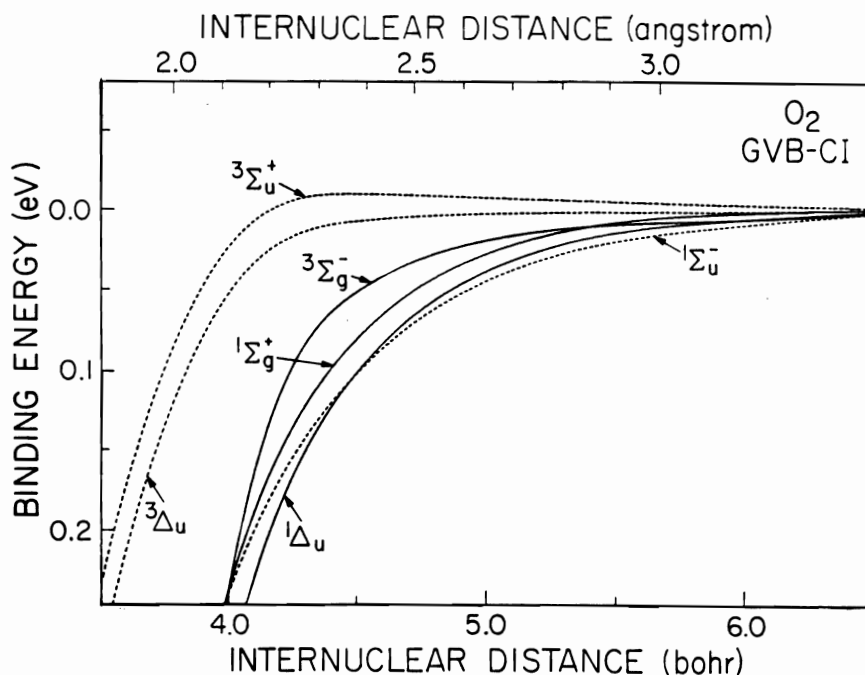


FIG. 2. The calculated potential energy curves for the states dissociating to O(³P) plus O(³P).

TABLE VI. Energy contributions of dominant configurations of the GVB-CI wavefunction for the X³Σ_g⁻ state of O₂.

No.	Character ^a	Configuration								Energy contribution (mhartree)							
		2σ _g	2σ _u	3σ _g	3σ _u	π _{ux}	π _{fx}	π _{uy}	π _{fy}	R _e ^b	3a ₀	4a ₀	6a ₀				
1	HF	2	2	2	0	2	1	2	1	2167.2	1295.4	312.7	98.0				
2	C(3σ _g)	2	2	0	2	2	1	2	1	12.4	25.2	89.3	94.9				
3	I(π _{ux} , π _{uy})	2	2	2	0	1	2	1	2	14.2	24.4	65.0	86.9				
4	...	2	2	0	2	1	2	1	2	1.6	13.1	65.6	85.7				
5	I(3σ _g , π _u)	2	2	1	1	2	1	1	2	31.6	51.0	89.0	200.4				
						1	2	2	1								
6	R(π _u , #1)	{2	2	2	0	2	0	1	0	1	1	1	0	13.8	10.9	3.7	0.9
		{2	2	2	0	1	1	1	0	2	0	1	0				
7	R(π _u , #2)	{2	2	0	2	2	0	1	0	1	1	1	0	1.1	2.6	1.5	0.8
		{2	2	0	2	1	1	1	0	2	0	1	0				
8	R(π _u , #5)	{2	2	1	1	1	0	2	0	1	1	1	0	3.0	6.9	3.7	1.1
		{2	2	1	1	1	1	1	0	1	0	2	0				
9	R(π _u , #5)	{2	2	1	1	2	0	1	0	1	0	1	1	5.9	3.9	1.8	1.3
		{2	2	1	1	1	0	1	1	2	0	1	0				
10	I(3σ _g , π _g)	{2	2	1	1	2	1	0	0	2	0	1	0	7.2	6.0	2.5	1.1
		{2	2	1	1	2	0	1	0	2	1	0	0				
11	I(π _u , π _g)	{2	2	2	0	1	0	2	0	2	1	0	0	3.6	1.8	0.0	0.2
		{2	2	2	0	2	1	0	0	1	0	2	0				
12	C(π _u)	{2	2	2	0	0	0	2	1	2	0	1	0	2.4	1.9	0.8	0.3
		{2	2	2	0	2	0	1	0	0	0	2	1				
13	R(2σ _u , #1)	2	1	2	1	2	0	1	0	2	0	1	0	1.7	1.1	0.3	0.0
14	C(2σ _u)	2	0	2	2	2	0	1	0	2	0	1	0	1.1	2.3	0.7	0.0

^aConfigurations above the line are the GVB configurations. R indicates an orbital readjustment effect (single excitation); C indicates correlation of a particular doubly-occupied orbital; I indicates an interpair correlation effect. #n indicates a correlation of dominant configuration n.

^bR_e=2.285616 a₀.

eV (recent values being 8.58,^{13a} 8.82,^{13c} 8.76,^{13d} and 8.67^{13e}), leading to an oscillator strength of about 0.16 (recent values being 0.156,^{13a} 0.162,^{13b} 0.142,^{13c} and 0.161^{13e}); the older higher values of 0.193 and 0.215 were apparently due to experimental difficulties^{13a}).

These results are in reasonable agreement with our results for the B³Σ_g⁻-X³Σ_g⁻ transition—a vertical excitation energy of 8.9 eV for f=0.20.

The maximum in the A³Σ_g⁺-X³Σ_g⁻ transition is difficult to establish since the threshold for B³Σ_g⁻-X³Σ_g⁻ is at 6.05 eV. However, the maximum for the Herzberg continuum (presumably dominated by A-X) does appear to be above 5.9 eV,¹⁴ consistent with the value 6.08 eV, we calculate for the A-X vertical transition.

These results indicate that our potential curves are reliable approximations to the exact potential curves for these states.

Previous accurate calculations on the X³Σ_g⁻ and B³Σ_g⁻ states have been reported by Schaefer² using "first-order" CI wavefunctions. For the B state he finds a D_e of 0.76 eV and an R_e of 1.64 Å and for the X state he finds a D_e of 4.72 eV and an R_e of 1.22 Å. Both are in good agreement with our results.

The only previous comprehensive study is that of Schaefer and Harris^{2d} carrying out full CI as a function of R for a minimum basis. Their results are in good qualitative agreement with ours, leading to correct trends in D_e, r_e, and ω_e.

Ohno and co-workers^{15a} suggested that the B³Σ_g⁻ state is diffuse, but a later study of Morokuma¹⁶ showed that it is not—a result in agreement with our studies and that of Schaefer² and with recent studies by Ohno *et al.*^{15b}

B. Transition moments

There are only three dipole-allowed transitions among the nine states considered in this paper,

$$X^3\Sigma_g^- - B^3\Sigma_u^-, \quad (14)$$

$$a^1\Delta_g - ^1\Delta_u, \quad (15)$$

$$b^1\Sigma_g^+ - ^1\Sigma_u^+. \quad (16)$$

The dipole transition moments $M_{jk}(R)$ for these transitions are given as a function of R in Table IV. In each case $M(R)$ goes to zero for large R, but for the transitions involving the singlet states, $M(R)$ is not monotonic.

In the case that $M_{jk}(R)$ is independent of R, the total transition probability from any vibrational level of j to all vibrational levels of k is proportional to

$$f_{jk} = \frac{2}{3} (E_k - E_j) [M_{jk}(R)]^2, \quad (17)$$

the oscillator strength. As shown in Table V, this is not a good approximation for transitions (14)–(16); however, using the f corresponding to R_e for a state gives a reasonable measure of the transition strength from the v=0 level. For the X³Σ_g⁻ state, this leads to f=0.200 (see Table V) for the absorption to the B³Σ_g⁻ state, in

TABLE VII. Energy contributions of dominant configurations of the GVB-CI wavefunctions for the ¹Δ_g⁺ and ¹Σ_g⁺ states of O₂ (at R=2.285616 a₀).

No.	Character	Configuration								Energy contribution (mhartree)					
		2σ _g	2σ _u	3σ _g	3σ _u	π _{ux}		π _{gx}		π _{uy}		π _{gy}		¹ Δ _g ⁺	¹ Σ _g ⁺
1	HF	2	2	2	0	2	0	2	2	2	0	2	2	303.6	253.3
2	C(π _u)	2	2	2	0	0	2	2	2	2	0	2	2	30.8	42.9
3	C(3σ _g)	2	2	0	2	2	0	2	2	2	0	2	0	14.6	14.1
4	...	2	2	0	2	0	2	2	2	2	0	2	2	2.5	3.1
5	I(3σ _g , π _u)	2	2	1	1	1	1	2	2	1	1	2	2	29.7	26.9
6	I(π _g , π _u)	2	2	2	0	1	0	1	0	2	1	1	0	10.3	4.4
7	I(3σ _g , π _g)	2	2	1	1	2	0	0	0	2	1	1	0	8.5	9.1
8	I(π _{ux} , π _{uy})	2	2	2	0	1	0	1	0	1	0	2	1	2.2	2.4
9	I(3σ _g , π _u)	2	2	1	1	2	0	0	0	1	0	2	1	3.4	3.5
10	I(3σ _g , π _g , #2)	2	2	1	1	0	0	2	0	2	1	1	0	2.3	2.2
11	R(π _u , #5)	2	2	1	1	2	0	2	0	1	0	0	1	3.4	3.5
12	C(π _g)	2	2	2	2	2	0	0	0	2	0	0	0	0.0	1.3
13	C(2σ _g)	0	2	2	0	2	0	2	0	2	0	2	0	0.0	1.9
14	C(2σ _u)	2	0	2	0	2	0	2	0	2	0	2	0	0.0	6.4

reasonable agreement with the best experimental estimates⁷ of $f=0.16$ (*vide supra*). On the other hand, using the R_e for the $B^3\Sigma_u^-$ state, the f for emission to $X^3\Sigma_g^-$ is calculated to be $f=0.0335$.

The singlet transitions (15) and (16) correspond also to $\pi \rightarrow \pi^*$ transitions (in the MO language) and are nearly as strong as the $B-X$ transition leading to $f=0.169$ and $f=0.145$, respectively, for absorption at the corresponding R_e . Just as in the triplet case, the f for emission from the ¹Δ_u and ¹Σ_u⁺ states is small: $f=0.0123$ and $f=0.0045$, respectively.

C. Large R

Except for $B^3\Sigma_u^-$ and $A^3\Sigma_u^+$, there currently is no reliable experimental information on the potential curves for these states for $R > 2 \text{ \AA}$. There are interesting crossings among the first six states in the region of $3\frac{1}{2}$ to $6 a_0$ as shown in Fig. 2, and we will examine here some of the reasons for this behavior.

Of these six states, only ³Σ_u⁺ is found to have a hump in the potential curve (the calculated energy barrier is 0.32 mhartree = 0.0087 eV.¹⁷ For $R > 4.5 a_0$, the ¹Σ_u⁻ state is found to be the lowest state. Given these varia-

tions, we would expect significant differences in the cross sections for formation of O₂ in the various states



It should be possible to use our results to calculate¹⁸ approximate rate constants for these processes, and it should be possible to design experimental methods¹⁹ of distinguishing between the various processes. With such studies one may get a better understanding of the mechanisms of forming molecules in excited states, processes involved in gas discharges, flames, chemical lasers, and in the upper atmosphere.

For $R \sim 6 a_0$, we find that the three triplet states are equally spaced, as are the singlet states (both with spacings of about 0.15 mhartree) but that the singlet states are about one step below the triplet states, leading to four groups, ¹Σ_u⁻ lowest, ³Σ_g⁻ and ¹Δ_g next, ³Δ_u and ¹Σ_g⁺ next, and ³Σ_u⁺ highest.

This pattern of evenly spaced levels can be understood as follows: Assuming that the overlap of orbitals on different centers is zero, we coupled the orbitals as in (2) and (3), *except* that the singly-occupied orbitals on each center are taken as triplet paired as in the free atom

TABLE VIII. Energy contribution of dominant configurations of the GVB-CI wavefunction for the ${}^1\Sigma_u^-$, ${}^3\Delta_u^-$, ${}^3\Sigma_u^-$, and ${}^1\Delta_u^-$ state of O₂ (at $R 2.285616 a_0$).

No.	Character	Configuration				π_{ux}				π_{ux}				Energy contribution (mhartree)				
		$2\sigma_g$	$2\sigma_u$	$3\sigma_g$	$3\sigma_u$	1	2	1	2	1	2	1	2	1	2	${}^1\Sigma_u^-$	${}^3\Delta_u^-$	${}^3\Sigma_u^-$
1	HF	2	2	2	0	1	2	2	1	1	1	2	1	2	506.8	422.2	166.2	81.7
2	$C(3\sigma_g)$	2	2	0	2	1	2	2	1	1	2	1	2	2	21.5	20.8	46.6	3.9
3	$I(3\sigma_g, \pi_g)$	2	2	1	1	2	1	2	1	2	1	2	1	2	3.7	1.4	66.5	67.1
4	$I(3\sigma_g, \pi_u)$	2	2	1	1	1	2	1	2	1	2	1	2	2	1.3	5.6	34.1	31.8
5	$R(\pi_u)$	2	2	2	0	1	0	2	0	1	1	1	0	2	2.8	2.0	21.4	19.5
6	$R(\pi_g)$	2	2	2	0	1	0	1	1	2	0	1	0	2	0.6	1.6	9.4	8.2
7	$R(2\sigma_u)$	2	1	2	1	1	0	2	0	2	0	1	0	2	0.6	2.1	4.1	3.1
8	$I(3\sigma_g, \pi_g)$	2	2	1	1	1	1	1	0	2	0	1	0	2	13.8	15.0	3.1	2.9
9	$I(3\sigma_g, \pi_g)$	2	2	1	1	1	0	2	0	2	1	0	0	2	7.5	7.0	0.6	0.5
10	$I(3\sigma_g, \pi_u)$	2	2	1	1	1	0	2	0	1	0	1	1	2	5.9	5.8	0.5	0.6
11	$I(3\sigma_g, \pi_u)$	2	2	1	1	0	0	2	1	2	0	1	0	2	2.8	2.7	0.4	0.3
12	$I(\pi_{ux}, \pi_{gy})$	2	2	2	0	2	0	1	0	2	1	0	0	2	2.9	0.6	22.3	15.6
13	$I(\pi_{ux}, \pi_{uy})$	2	2	2	0	0	0	2	1	1	0	2	0	2	0.6	0.1	3.5	2.7
14	...	2	2	0	2	2	1	0	0	2	0	1	0	2	0.1	0.0	3.1	2.9
15	...	2	2	0	2	1	0	2	0	1	1	1	0	2	0.1	0.1	2.0	2.0
16	$R(2\sigma_g, \#3)$	1	2	2	1	2	0	1	0	2	0	1	0	2	0.8	0.2	7.3	7.7
17	$R(2\sigma_g, \#4)$	1	2	2	1	1	0	2	0	1	0	2	0	2	0.4	0.1	1.3	1.0

(as a result, the p_x orbitals on opposite centers are no longer singlet paired). This leads to equally spaced triplet levels with a spacing of

$$\epsilon_1 \equiv 2[y_i x_i | y_r x_r]; \quad (19)$$

where the bracketed quantity is the two-electron integral involving electron 1 in y_i and x_i and electron 2 in y_r and x_r . Using atomic orbitals at $6a_0$, (19) leads to $\epsilon_1 = 0.1174$ mh. The corresponding calculation for the singlet states leads to

$$E({}^1\Delta_g) - E({}^1\Sigma_g) = \epsilon_1 + [y_r x_i | x_r y_i] + [y_r y_i | x_r x_i], \quad (20a)$$

$$E({}^1\Sigma_g^*) - E({}^1\Delta_g) = \epsilon_1 + [y_r x_i | x_r y_i], \quad (20b)$$

which with atomic orbitals (at $6a_0$) leads to spacings of 0.1208 mhartree and 0.1176 mhartree, respectively.

Although this simple approximation accounts for these spacings correctly, it does *not* lead to the proper spacing between singlet and triplet states; the average of the singlet states should be 0.18 mhartree below the triplet states rather than 0.15 mhartree above them, as cal-

culated assuming zero overlap²⁰ (at $6a_0$ the overlap of atomic $p\pi$ orbitals is 0.003, while the overlap of atom $p\sigma$ is 0.023).

In Fig. 1 we see that the $2^3\Sigma_g^-$ state is calculated to cross the $B^3\Sigma_u^-$ state at 2 \AA , with the $2^2\Sigma_g^-$ state possessing a broad minimum at slightly larger R . It is possible that a coupling between the levels of the $2^3\Sigma_g^-$ and $B^3\Sigma_u^-$ states²¹ is responsible for the rotational line broadening long observed²² in the $B-X$ absorption spectra.^{2b,22-24} From (11) we see that one must combine the states as $\Psi(B^3\Sigma_u^-) \pm \Psi(2^3\Sigma_g^-)$ in order to describe, say, a $O({}^1D)$ state on the left and a $O({}^3P)$ state on the right. Thus, for larger R , where the splitting between the Born-Oppenheimer states is larger, these coupling terms could be quite important.

D. Analysis of the CI wavefunctions

In order to indicate the relative importance of configurations for the various states, we have calculated

TABLE IX. Energy contribution of dominant configurations of the GVB-CI wavefunctions for the ³Δ_g⁺, ³Σ_g⁺, ¹Δ_g⁺ and ¹Σ_g⁺ states of O₂ (at R=2, 285616 a₀).

No.	Character	Configuration				π _{xx}				π _{yy}				Energy contribution (mhartree) ^a				
		2σ _g	2σ _u	3σ _g	3σ _u	1	2	1	2	1	2	1	2	1	2	³ Δ _g ⁺	³ Σ _g ⁺	¹ Δ _g ⁺
1	HF	2	2	2	0	1	2	1	2	2	2	2	2	2	133.7	124.0	443.8	345.1
2	C(3σ _g)	2	2	0	2	1	2	1	2	2	2	2	2	2	19.5	19.5	4.4	3.8
3	I(3σ _g , π _g)	2	2	1	1	2	2	0	2	2	2	2	0	2	1.4	1.4	66.5	68.8
4	I(3σ _g , π _u)	2	2	1	1	0	2	2	2	2	2	2	2	0.6	0.6	31.9	29.0	
5	R(π _g)	2	2	2	0	1	2	0	1	2	0	2	0			3.9	3.5	
6	R(π _u)	2	2	2	0	0	2	1	0	2	0	2	0			10.5	9.3	
7	R(2σ _u)	2	1	2	1	1	2	0	1	0	2	0	2	2.0	2.0	3.7	4.6	
8	I(3σ _g , π _g)	2	2	1	1	1	2	1	0	2	1	1	0	13.3	13.2			
9	I(3σ _g , π _g)	2	2	1	1	1	2	0	0	2	0	2	0	6.3	6.3			
10	I(3σ _g , π _u)	2	2	1	1	1	2	0	1	0	2	1	0	5.6	5.7			
11	I(3σ _g , π _u)	2	2	1	1	0	2	0	1	1	2	0	2	2.5	2.5			
12	I(π _{gx} , π _{gy})	2	2	2	0	2	2	0	0	2	1	1	0			17.9	10.9	
13	I(π _{ux} , π _{uy})	2	2	2	0	0	2	0	2	1	0	2	1			2.8	2.2	
14	...	2	2	0	2	2	2	0	0	2	1	1	0			3.0	2.7	
15	I(π _u , π _g)	2	2	2	0	2	2	0	0	1	0	2	1			4.0	2.3	
16	I(π _u , π _g)	2	2	2	0	0	2	0	2	1	1	0	0			8.3	7.6	
17	R(2σ _g , #3)	1	2	2	1	2	2	0	0	2	0	2	0			7.8	8.3	
18	C(2s)	1	1	2	0	2	2	0	2	0	2	0	2	0			0.0	30.5
		2	0	1	1	2	2	0	2	0	2	0	2	0			0.0	3.0
		0	2	1	1	2	2	0	2	0	2	0	2	0			0.0	2.2

^aA blank space indicates a contribution less than 1.0 mhartree.

the energy contribution of each configuration using the formula

$$\Delta E_{\mu} = C_{\mu}^2 (E - H_{\mu\mu}) / (1 - C_{\mu}^2). \quad (21)$$

This corresponds to the energy increase that would occur if configuration μ is deleted while keeping all other CI coefficients fixed. In the case of several spin eigenfunctions corresponding to one spatial configuration, we have merely added the separate contributions. Although the ΔE_{μ} serve to indicate the important configurations, the total energy is not the sum of ΔE_{μ} ; the

resulting ΔE_{μ} for the dominant configuration(s) is of little significance.

Table VI shows the important configurations for the $X^3\Sigma_g^-$ state for various R . All configurations with $\Delta E_{\mu} > 1$ mhartree at R_e are included. The configurations occurring in an expansion of the GVB wavefunction are listed above the line in Table VI. At large R , the GVB configurations are all important and are clearly dominant. For small R , the HF configuration is the major configuration, and some significant non-GVB configurations

are found. In characterizing these configurations we use the notation described in footnote b of Table V.

Tables VI, VII, VIII, and IX contain similar analyses for the various states of O₂, all for R_g.

VI. SUMMARY

The approach we used here to obtain accurate wavefunctions of O₂ was to first solve self-consistently for the GVB wavefunction of the ground state, X³Σ_g⁻. We then converted the GVB orbitals to symmetry functions, leading to 14 orbitals in terms of which the CI calculations were carried out. This is a very simple, inexpensive way to obtain wavefunctions. The close agreement between the calculated results and experiment indicates that the GVB-CI method leads to accurate wavefunctions. The limitation is that since the wavefunctions are based upon the orbitals from a particular state, this simple GVB-CI approach is expected to be adequate only for other states of similar character. Thus, for O₂ we considered only nine of the electronic states. To describe Rydberg and other valence excited states, we would have to either (a) include many more virtual functions in the CI, or (b) solve self-consistently for the GVB wavefunction of other appropriate states.

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

†Contribution No. 5095.

R. S. Mulliken, Phys. Rev. 32, 880 (1928).

²(a) H. F. Schaefer III, J. Chem. Phys. 54, 2207 (1971); (b) H. F. Schaefer III and W. H. Miller, J. Chem. Phys. 55, 4107 (1971); (c) P. E. Cade (unpublished), see Ref. 2a; (d) H. F. Schaefer III and F. E. Harris, J. Chem. Phys. 48, 4946 (1968).

³B. J. Moss, F. W. Bobrowicz, and W. A. Goddard III, J. Chem. Phys. (in press).

⁴(a) W. A. Goddard III, T. H. Dunning, Jr., W. J. Hunt, and P. J. Hay, Acc. Chem. Res. 6, 368 (1973); (b) W. J. Hunt, P. J. Hay, and W. A. Goddard III, J. Chem. Phys. 57, 738 (1972).

⁵T. H. Dunning, Jr., J. Chem. Phys. 53, 2823 (1970).

⁶Written by F. W. Bobrowicz, Ph.D. thesis, California Institute of Technology, 1974, and N. W. Winter, using the spin eigenfunction routines of R. C. Ladner, Ph.D. thesis, California Institute of Technology, 1971. Modifications were made by B. J. Moss, L. B. Harding, S. P. Walch, and W. A. Goddard III.

⁷P. Krupenie, J. Phys. Chem. Ref. Data 1, 423 (1972). This

reference is more complete than Ref. 9.

⁸G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules* (Van Nostrand, New York, 1950).

⁹B. Rosen, *Spectroscopic Data Relative to Diatomic Molecules* (Pergamon, Oxford, 1970).

¹⁰Using the same basis set and a similar CI for the oxygen atoms leads to excitation energies from O(³P) to O(¹D) and O(¹S) of 2.237 and 3.993 eV as compared to experimental values of 1.97 and 4.19 eV. This is one source of error in the calculations.

¹¹H. P. Broida and A. G. Gaydon, Proc. R. Soc. A 222, 181 (1954); V. Degen and R. W. Nicholls, J. Phys. B 2, 1240 (1969).

¹²V. Degen, Can. J. Phys. 46, 783 (1968); G. Herzberg, Can. J. Phys. 31, 657 (1953).

¹³(a) R. Goldstein and F. N. Mastrup, J. Opt. Soc. Am. 56, 765 (1966); (b) G. N. Haddad, thesis, 1967, quoted in A. J. D. Farmer, W. Fabian, B. R. Lewis, K. H. Lokan, and G. N. Haddad, J. Quant. Spectrosc. Radiat. Transfer 8, 1739 (1968); (c) P. H. Metzger and G. R. Cook, *ibid.* 4, 107 (1964); R. E. Huffman, Y. Tanaka, and J. C. Larabee, Discuss. Faraday Soc. 37, 159 (1964); (e) K. Watanabe, E. C. Y. Inn, and M. Zelikoff, J. Chem. Phys. 21, 1026 (1953); (f) K. Watanabe and F. F. Marmo, J. Chem. Phys. 25, 965 (1956).

¹⁴(a) V. Hasson and R. W. Nicholls, J. Phys. B 4, 1789 (1971); (b) M. Ackerman, F. Biaueme, and G. Kockarts, Planet. Space Sci. 18, 1639 (1970).

¹⁵(a) H. Taketa, H. Tatewaki, O. Nomura, and K. Ohno, Theor. Chim. Acta 11, 369 (1968); (b) K. Ohno (private communication).

¹⁶K. Morokuma and H. Konishi, J. Chem. Phys. 55, 402 (1971).

¹⁷We use mhartree to indicate 0.001 hartree. 1 mhartree = 0.02721 eV = 0.6275 kcal.

¹⁸R. T. Pack, R. L. Snow, and W. T. Smith, J. Chem. Phys. 56, 926 (1972); D. O. Ham, D. W. Trainor, and F. Kaufman, J. Chem. Phys. 53, 4395 (1970); R. E. Roberts, R. B. Bernstein, and C. F. Curtiss, J. Chem. Phys. 50, 5163 (1969); S. W. Benson and T. Fueno, J. Chem. Phys. 36, 1597 (1962).

¹⁹P. Harteck and R. R. Reeves, Jr., Discuss. Faraday Soc. 37, 82 (1964).

²⁰With zero overlap, $E_{1\Delta_g} - E_{3\Delta_u} = K_{x_r, x_r} + (K_{x_r, x_r} + K_{x_r, x_r} - [y_r, x_r | x_r, y_r]) = 0.1509$ mhartree at 6 a_0 .

²¹It is often assumed that states of different inversion symmetry are not coupled by the Born-Oppenheimer breakdown terms. Such couplings arise, however, since the center of mass of the electrons does not coincide with the center of mass of the nuclei.

²²P. G. Wilkinson and R. S. Mulliken, Astrophys. J. 125, 594 (1957).

²³See the brief review on p. 443 of Ref. 7.

²⁴J. N. Murrell and J. M. Taylor, Mol. Phys. 16, 609 (1969).

