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LONG-RANGE INTERACTION POTENTIALS FOR OXYGEN

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SUMMARY

Electron configurations and valence bond interaction energies are derived for the 18 molecular combinations of two ground-state oxygen atoms. The method differs from previous valence bond calculations in three important respects: (1) correlations between molecular and atomic states are included, (2) proper relations between the various multielectron bonds and antibonds are employed, and (3) configuration interactions between molecular states of the same symmetry are determined. Many of the long-range interaction potentials are affected substantially by these modifications.

INTRODUCTION

Long-range interaction forces between atoms are significant input data for calculations of the nonequilibrium (transport) properties of collision-dominated gases. Often used for this purpose is the approximation of perfect pairing (ref. 1), in which molecular energies are expressed as linear combinations of bond and antibond energies based upon symmetry and spin pairing considerations. Although the absolute results for individual collisions may be inaccurate, the method is thought to establish fairly reliable and useful relations between the various potentials operating in a gas. (See ref. 2 for a further discussion.) Hence, if a small number of such potentials are available from ab initio quantum mechanical calculations or experimental data, the others will follow from the simple perfect pairing expressions.

A principal objective of the present research is to improve the existing relations (ref. 3) between the 18 long-range interaction potentials experienced by colliding ground-state oxygen atoms. The present paper is thus a continuation of reference 4, which reviewed and analyzed the conventional perfect pairing theory and applied it, with modifications, to the relatively simple example of molecular nitrogen. Also found in reference 4 is the assertion that previous treatments (ref. 3) of grazing oxygen collisions are questionable for three reasons: (1) the electron configurations of molecules and atoms were not correlated to prevent dissociation products from being mixtures of several atomic states, (2) the strengths of the various multielectron bonds and antibonds were not properly related according to overlap and other considerations, and (3) configuration interactions between molecular states of the same symmetry were not included. These deficiencies are corrected in the current research.

The procedure is outlined as follows: the determination of the nine wave functions pertinent to oxygen ^3P atoms, the deduction of molecular electron configurations from correlation studies of the atomic states, and the calculation of interaction potentials by valence bond methods applied to the electron configurations. Interactions between molecular states of the same symmetry are imposed automatically by the correlation analysis, as are the magnitudes and directions of the corresponding energy shifts. All 18 interatomic potentials are found to differ from the expressions in reference 3, the trend definitely being toward simpler representations, more convenient relations between potentials, and increased symmetry with respect to each other and the dissociation asymptote.

Perhaps the most pronounced effect of the correlation analysis is the flattening of nine of the 18 potential curves in their outer regions. Hence, the contributions of these states to the collision integrals and cross sections of kinetic theory are somewhat diminished from previous calculations, which, therefore, appear to underestimate the transport coefficients of atomic oxygen at high temperatures. Some confirmation of this flatness is obtained for the ground state of molecular oxygen by extrapolating the corresponding Rydberg-Klein-Rees semiempirical potential curve to large internuclear separations. The present results for this particular example are more easily connected to the extrapolated semiempirical curve than are the results of reference 3.

Finally, extrapolations of selected long-range electron structures and potential energies to intermediate internuclear separations successfully predict the ordering of the six most stable molecular states and suggest a number of potential humps and curve crossings in the process.

SYMBOLS

a,b	atoms or molecular states
E	equilibrium energy
$g^{\pm}$	molecular orbital eigenstates of electron angular momenta
H_{ab}	interaction matrix element between molecular states a and b
J_{σ}, J_{π}	two-electron exchange energies of σ- or π-type symmetry; sometimes denoted $J_{2\sigma}$ and $J_{2\pi}$, or simply J when speaking figuratively

$J_{1\sigma}, J_{1\pi}$	one-electron exchange energies of σ- or π-type symmetry
M_L	magnetic quantum number for total electronic orbital angular momentum (atom)
M_S	magnetic quantum number for total electron spin (atom)
p_x, p_y, p_z	atomic p functions or orbitals
Q	collision cross section
Q_1	one-electron Coulomb energy
$u^{\pm}$	molecular orbital eigenstates of electron angular momenta
x, y, z	Cartesian coordinates, also abbreviated notation for atomic orbitals p_x, p_y, p_z
α, β	electron spin functions
Λ	magnetic quantum number for total electronic orbital angular momentum (molecule)
ϕ	atom-atom interaction potential
ϕ'	eigenvalue solution of secular energy equation
$\left.\begin{matrix}\phi_1, \phi_2, \\ \phi_3, \phi_4\end{matrix}\right\}$	potentials for one-, two-, three-, and four-electron bonds and antibonds
ϕ_a, ϕ_b	interaction potentials for molecular states a and b of same symmetry (no configuration interaction)
ϕ'_a, ϕ'_b	same as ϕ_a and ϕ_b but with configuration interaction

Subscripts:

g	"gerade" or even symmetry with respect to geometric center of oxygen molecule

u	"ungerade" or odd symmetry with respect to geometric center of oxygen molecule

Special notations:

$^3P, ^1D$	states of atomic oxygen
$^5\Delta_g$, A $^3\Sigma_u^+$, $^1\Pi_g$, . . .	standard molecular states
$\sigma_g, \sigma_u, \pi_g^+,$ $\pi_u^+, \pi_g^-, \pi_u^-$	standard molecular orbital notations; π-orbitals sometimes appear without superscripts
1, $\bar{1}$, 0	atomic orbital combinations $x + iy$, $x - iy$, z, respectively
$\left(1\,\bar{1}\,0\middle|1\right)$	typical atomic state function defined by equation (1)
$\left(M_L, M_S\right)$	angular momentum-spin state for atom
1,2,3,4	sets of coordinates for elections 1, 2, 3, 4
+,-	superscripts meaning even or odd symmetry with respect to plane containing internuclear axis (z)

ATOMIC ^{3}P FUNCTIONS

The p-electron configurations of the nine angular momentum-spin states $\left(M_L, M_S\right)$ for oxygen ^3P atoms are fundamental to the construction, by correlation analyses, of the long-range electron configurations of the 18 molecular states dissociating into normal products. A typical example is the (1,1) state corresponding to the atomic wave function

$$\left(1\,\bar{1}\,0\middle|1\right) = (4!)^{-1/2} \begin{vmatrix} 1(1)\alpha(1) & \bar{1}(1)\alpha(1) & 0(1)\alpha(1) & 1(1)\beta(1) \\ 1(2)\alpha(2) & \bar{1}(2)\alpha(2) & 0(2)\alpha(2) & 1(2)\beta(2) \\ 1(3)\alpha(3) & \bar{1}(3)\alpha(3) & 0(3)\alpha(3) & 1(3)\beta(3) \\ 1(4)\alpha(4) & \bar{1}(4)\alpha(4) & 0(4)\alpha(4) & 1(4)\beta(4) \end{vmatrix} \qquad (1)$$

where 1, $\bar{1}$, and 0 are one-electron functions pertaining to the individual magnetic quantum numbers 1, -1, and 0, respectively, α and β are spin functions, and the arguments 1, 2, 3, and 4 refer to electrons. Equation (1) defines the notation $\left(1\,\bar{1}\,0\middle|1\right)$.

Two of the remaining eight $\left(M_L,M_S\right)$ states are obtained immediately from equation (1) by the application of the familiar ladder or step-down operator in angular momentum space. They are

$$(0,1)\ :\ \left(1\ \bar{1}\ 0 \,|\, 0\right) \tag{2}$$

and

$$(-1,1)\ :\ \left(1\ \bar{1}\ 0 \,|\, \bar{1}\right) \tag{3}$$

However, configurations (1), (2), and (3) are not directly subject to the simple geometric interpretation required for correlation studies and the application of the approximation of perfect pairing. A better representation for such purposes is obtained by writing $1 = x + iy$, $\bar{1} = x - iy$, and $0 = z$, where x, y, and z stand for p_x, p_y, and p_z atomic orbitals, respectively, and by expanding the wave functions in these terms. For example,

$$\begin{aligned}\frac{i}{2}\left(1\ \bar{1}\ 0 \,|\, 1\right) &= \frac{i}{2}\left(x+iy\quad x-iy\quad z \,|\, x+iy\right)\\ &= \left(x\ y\ z \,|\, x+iy\right)\\ &= \left(x\ y\ z \,|\, x\right) + i\left(x\ y\ z \,|\, y\right)\end{aligned} \tag{4}$$

Similar expansions apply to all wave functions to yield the following complete set of oxygen ${}^3P$ electron configurations:

$$(1,1)\ :\ \left(x\ y\ z \,|\, x\right) + i\left(x\ y\ z \,|\, y\right) \tag{5}$$

$$(1,0)\ :\ \left(x\ y \,|\, x\ z\right) - \left(x\ z \,|\, x\ y\right) + i\left(x\ y \,|\, y\ z\right) - i\left(y\ z \,|\, x\ y\right) \tag{6}$$

$$(1,-1)\ :\ \left(x \,|\, x\ y\ z\right) + i\left(y \,|\, x\ y\ z\right) \tag{7}$$

$$(0,1)\ :\ \left(x\ y\ z \,|\, z\right) \tag{8}$$

$$(0,0)\ :\ \left(x\ z \,|\, y\ z\right) - \left(y\ z \,|\, x\ z\right) \tag{9}$$

$$(0,-1)\ :\ \left(z \,|\, x\ y\ z\right) \tag{10}$$

$$(-1,1)\ :\ \left(x\ y\ z \,|\, x\right) - i\left(x\ y\ z \,|\, y\right) \tag{11}$$

$$(-1,0)\ :\ \left(x\ y\,|\,x\ z\right) - \left(x\ z\,|\,x\ y\right) - i\left(x\ y\,|\,y\ z\right) + i\left(y\ z\,|\,x\ y\right) \tag{12}$$

and

$$(-1,-1)\ :\ \left(x\,|\,x\ y\ z\right) - i\left(y\,|\,x\ y\ z\right) \tag{13}$$

Expressions (6), (7), (9), (10), (12), and (13) are deduced from expressions (5), (8), and (11) by using the step-down operator in spin space.

MOLECULAR ELECTRON CONFIGURATIONS

Long-range molecular electron configurations are found by combining atomic states (5) to (13) in every possible way corresponding to two colliding oxygen ^3P atoms a and b. If the z-axis coincides with that of the molecule, a p_z electron on atom a combines with another on atom b to form either a $(\sigma)^2$ configuration for paired spins or a $(\sigma_g)(\sigma_u)$ configuration for parallel spins; similarly, three and four p_z electrons yield $(\sigma_g)^2(\sigma_u)$ and $(\sigma)^4$ configurations, respectively, and π_g^+, π_u^+, π_g^-, and π_u^- orbitals are occupied by p_x and p_y electrons. The g and u subscripts standing for even and odd symmetries with respect to the molecular center are purposely absent in $(\sigma)^2$ and $(\sigma)^4$ to indicate the valence-bond character of these configurations near the dissociation limit (ref. 4). A further discussion is given in appendix A.

A simple example of the complete correlation procedure is the following development for the $O_2\left(^5\Delta_g\right)$ state:

$$\begin{aligned}
{}^5\Delta_g\ &:\ (1,1)_a + (1,1)_b \\
&:\ \left[\left(x\ y\ z\,|\,x\right)_a + \left(x\ y\ z\,|\,x\right)_b\right] + \left[\left(x\ y\ z\,|\,y\right)_a + \left(x\ y\ z\,|\,y\right)_b\right] \\
&\quad + \left[\left(x\ y\ z\,|\,x\right)_a + \left(x\ y\ z\,|\,y\right)_b\right] + \left[\left(x\ y\ z\,|\,y\right)_a + \left(x\ y\ z\,|\,x\right)_b\right] \\
&:\ 2^{-1}\left(\sigma_g\right)\left(\sigma_u\right)\Big[(\pi^+)^4\left(\pi_u^-\right)\left(\pi_g^-\right) + \left(\pi_u^+\right)\left(\pi_g^+\right)(\pi^-)^4 \\
&\qquad + \left(\pi_u^+\right)^2\left(\pi_g^+\right)\left(\pi_u^-\right)\left(\pi_g^-\right)^2 + \left(\pi_u^+\right)\left(\pi_g^+\right)^2\left(\pi_u^-\right)^2\left(\pi_g^-\right)\Big]
\end{aligned} \tag{14}$$

Except for the last part of this expression, in which subconfigurations are defined from the previous part and each has a one-fourth probability of being measured, the positive signs within the various brackets and also in $(1,1)_a + (1,1)_b$ denote schematically the interaction of atoms a and b. Finally, since the first two subconfigurations in the last part of expression (14) establish g-type symmetry for the molecule as a whole, the last two subconfigurations are chosen accordingly from several possibilities.

Although comparisons between expressions (5) and (11) show the atom-atom combinations in the middle part of expression (14) to be equally appropriate for $(1,1)_a + (-1,1)_b$ collisions, the situation is complicated by the fact that Σ molecular states of opposite symmetries with respect to a plane containing the z-axis are usually nondegenerate and must be so distinguished by + or - superscripts (ref. 5). Hence, the following results are obtained by arbitrarily suppressing either the pair $\left[(x\,y\,z|x)_a + (x\,y\,z|x)_b\right]$ and $\left[(x\,y\,z|y)_a + (x\,y\,z|y)_b\right]$ or the pair $\left[(x\,y\,z|x)_a + (x\,y\,z|y)_b\right]$ and $\left[(x\,y\,z|y)_a + (x\,y\,z|x)_b\right]$ in each collision:

$$a\,{}^5\Sigma_g^+ \;:\; 2^{-1/2}(\sigma_g)(\sigma_u)\left[(\pi^+)^4(\pi_u^-)(\pi_g^-) + (\pi_u^+)(\pi_g^+)(\pi^-)^4\right] \tag{15}$$

$${}^5\Sigma_g^- \;:\; 2^{-1/2}(\sigma_g)(\sigma_u)\left[(\pi_u^+)^2(\pi_g^+)(\pi_u^-)(\pi_g^-)^2 + (\pi_u^+)(\pi_g^+)^2(\pi_u^-)^2(\pi_g^-)\right] \tag{16}$$

and

$${}^5\Sigma_u^- \;:\; 2^{-1/2}(\sigma_g)(\sigma_u)\left[(\pi_u^+)^2(\pi_g^+)(\pi_u^-)^2(\pi_g^-) + (\pi_u^+)(\pi_g^+)^2(\pi_u^-)(\pi_g^-)^2\right] \tag{17}$$

The validity of the arbitrary suppression of pairs of interaction terms in the development of expressions (15) to (17) is not obvious and must be investigated thoroughly. Three observations are pertinent to this objective:

(1) Molecular Δ states cannot be written as linear combinations of Σ states. Expressions (14) to (16) contradict this statement unless the $a\,{}^5\Sigma_g^+$ and ${}^5\Sigma_g^-$ states either do not occur or do not have the assigned electron configurations. The second alternative requires configuration interactions with additional states of the same symmetry.

(2) The arbitrary suppression of pairs of interaction terms would not be required for the $a\,{}^5\Sigma_g^+$ and ${}^5\Sigma_u^-$ states if the corresponding long-range energies were identical. Linear combinations of ${}^5\Sigma$ states with different symmetries and equal energies are permitted by quantum theory if the resulting electron configurations are also ${}^5\Sigma$. Such linear combinations would restore each pair of interaction terms to equivalent roles of prominence in the final electron descriptions.

(3) The combination of $(0,1)_a$ with $(0,1)_b$ to yield

$$b\,{}^5\Sigma_g^+ \;:\; (\sigma)^4(\pi_u^+)(\pi_g^+)(\pi_u^-)(\pi_g^-) \tag{18}$$

is the only ${}^5\Sigma$ possibility not yet considered.

Observations (1) and (3) imply that the $^5\Sigma_g^-$ state cannot be formed from ground-state oxygen atoms, nor can the $^5\Sigma_g^-$ oxygen molecule dissociate into normal atoms. This conclusion agrees with the more complex analysis based on group theory (ref. 5, p. 321) and, thus, supports the present correlation procedure. In addition, the a $^5\Sigma_g^+$ state of expression (15) and the b $^5\Sigma_g^+$ state of expression (18) must interact so as to equalize the long-range energies of a $^5\Sigma_g^+$ and $^5\Sigma_u^-$ according to observation (2); hence, simple correlation studies automatically impose configuration interactions and also predict magnitudes and directions of the corresponding energy shifts. Further details are provided in the next section.

Only one other example is needed to illustrate completely the various considerations used in determining the 18 $O(^3P) + O(^3P)$ molecular states and electron configurations. In contrast with expressions (15) to (17), the configurations

$$\begin{aligned}
{}^5\Pi_g \;&:\; (1,1)_a + (0,1)_b \\
&:\; \Big[(x\ y\ z\,|\,x)_a + (x\ y\ z\,|\,z)_b\Big] + \Big[(x\ y\ z\,|\,y)_a + (x\ y\ z\,|\,z)_b\Big] \\
&:\; 2^{-1}\Big\{(\sigma_g)^2(\sigma_u)\Big[(\pi_u^+)^2(\pi_g^+)(\pi_u^-)(\pi_g^-) + (\pi_u^+)(\pi_g^+)(\pi_u^-)^2(\pi_g^-)\Big] \\
&\qquad + (\sigma_g)(\sigma_u)^2\Big[(\pi_u^+)(\pi_g^+)^2(\pi_u^-)(\pi_g^-) + (\pi_u^+)(\pi_g^+)(\pi_u^-)(\pi_g^-)^2\Big]\Big\}
\end{aligned} \tag{19}$$

and

$$\begin{aligned}
{}^5\Pi_u \;&:\; (1,1)_a + (0,1)_b \\
&:\; 2^{-1}\Big\{(\sigma_g)^2(\sigma_u)\Big[(\pi_u^+)(\pi_g^+)^2(\pi_u^-)(\pi_g^-) + (\pi_u^+)(\pi_g^+)(\pi_u^-)(\pi_g^-)^2\Big] \\
&\qquad + (\sigma_g)(\sigma_u)^2\Big[(\pi_u^+)^2(\pi_g^+)(\pi_u^-)(\pi_g^-) + (\pi_u^+)(\pi_g^+)(\pi_u^-)^2(\pi_g^-)\Big]\Big\}
\end{aligned} \tag{20}$$

contain double the number of subconfigurations necessary to involve every constituent atomic determinant. The alternative of two $^5\Pi_g$ and two $^5\Pi_u$ molecular states is not allowed because each would have 50 percent probability of dissociating into normal products and 50 percent probability of dissociating into ionized products, according to whether the electrons in $(\sigma_g)^2(\sigma_u)$ and $(\pi_u^+)^2(\pi_g^+)$, for example, are evenly or unevenly split between the atoms. Configuration interactions analogous to those of reference 4, in which the molecular orbital occupations $(\sigma_g)^2$ and $(\sigma_u)^2$ at short ranges are replaced with the valence bond occupation $(\sigma)^2$ at large separations, insure normal products and result in the doubling displayed here.

Another difference between configurations (19) and (20) and the $^5\Delta_g$ state of expression (14) is that the $(1,1)_a + (0,1)_b$ combination does not select a definite g or u symmetry as does $(1,1)_a + (1,1)_b$; hence, a $^5\Pi$ state of each symmetry must occur. All molecular states with the total magnetic spin quantum number equal to 2 and with dissociation into normal atoms have now been derived in agreement with the results of group theory (ref. 5, p. 321).

The 12 remaining molecular electron configurations are obtained in a similar manner and are listed as follows:

$$\begin{aligned} {}^3\Delta_u \ :\ 8^{-1/2}\Big\{&(\sigma)^2\Big[(\pi^+)^4(\pi_u^-)(\pi_g^-) + (\pi_u^+)(\pi_g^+)(\pi^-)^4 + (\pi_u^+)^2(\pi_g^+)(\pi_u^-)(\pi_g^-)^2 + (\pi_u^+)(\pi_g^+)^2(\pi_u^-)^2(\pi_g^-)\Big] \\ &+ (\sigma_g)(\sigma_u)\Big[(\pi^+)^4(\pi^-)^2 + (\pi^+)^2(\pi^-)^4 + (\pi_u^+)^2(\pi_g^+)(\pi_u^-)^2(\pi_g^-) + (\pi_u^+)(\pi_g^+)^2(\pi_u^-)(\pi_g^-)^2\Big]\Big\} \end{aligned} \tag{21}$$

$$\begin{aligned} {}^3\Pi_g \ :\ 8^{-1/2}\Big\{&(\sigma_g)^2(\sigma_u)\Big[(\pi_u^+)(\pi_g^+)^2(\pi^-)^2 + (\pi^+)^2(\pi_u^-)(\pi_g^-)^2 \\ &\qquad + (\pi_u^+)^2(\pi_g^+)(\pi_u^-)(\pi_g^-) + (\pi_u^+)(\pi_g^+)(\pi_u^-)^2(\pi_g^-)\Big] \\ &+ (\sigma_g)(\sigma_u)^2\Big[(\pi_u^+)^2(\pi_g^+)(\pi^-)^2 + (\pi^+)^2(\pi_u^-)^2(\pi_g^-) \\ &\qquad + (\pi_u^+)(\pi_g^+)^2(\pi_u^-)(\pi_g^-) + (\pi_u^+)(\pi_g^+)(\pi_u^-)(\pi_g^-)^2\Big]\Big\} \end{aligned} \tag{22}$$

$$\begin{aligned} {}^3\Pi_u \ :\ 8^{-1/2}\Big\{&(\sigma_g)^2(\sigma_u)\Big[(\pi_u^+)^2(\pi_g^+)(\pi^-)^2 + (\pi^+)^2(\pi_u^-)^2(\pi_g^-) \\ &\qquad + (\pi_u^+)(\pi_g^+)^2(\pi_u^-)(\pi_g^-) + (\pi_u^+)(\pi_g^+)(\pi_u^-)(\pi_g^-)^2\Big] \\ &+ (\sigma_g)(\sigma_u)^2\Big[(\pi_u^+)(\pi_g^+)^2(\pi^-)^2 + (\pi^+)^2(\pi_u^-)(\pi_g^-)^2 \\ &\qquad + (\pi_u^+)^2(\pi_g^+)(\pi_u^-)(\pi_g^-) + (\pi_u^+)(\pi_g^+)(\pi_u^-)^2(\pi_g^-)\Big]\Big\} \end{aligned} \tag{23}$$

$$A\,{}^3\Sigma_u^+ \ :\ 2^{-1}\Big\{(\sigma)^2\Big[(\pi^+)^4(\pi_u^-)(\pi_g^-) + (\pi_u^+)(\pi_g^+)(\pi^-)^4\Big] + (\sigma_g)(\sigma_u)\Big[(\pi^+)^4(\pi^-)^2 + (\pi^+)^2(\pi^-)^4\Big]\Big\} \tag{24}$$

$$\begin{aligned} X\,{}^3\Sigma_g^- \;:\; 2^{-1}\Big\{&(\sigma)^2\Big[(\pi_u^+)^2(\pi_g^+)(\pi_u^-)^2(\pi_g^-) + (\pi_u^+)(\pi_g^+)^2(\pi_u^-)(\pi_g^-)^2\Big] \\ &+ (\sigma_g)(\sigma_u)\Big[(\pi_u^+)^2(\pi_g^+)(\pi_u^-)(\pi_g^-)^2 + (\pi_u^+)(\pi_g^+)^2(\pi_u^-)^2(\pi_g^-)\Big]\Big\} \end{aligned} \tag{25}$$

$$b\,{}^3\Sigma_u^+ \;:\; 2^{-1/2}(\sigma)^4\Big[(\pi^+)^2(\pi_u^-)(\pi_g^-) + (\pi_u^+)(\pi_g^+)(\pi^-)^2\Big] \tag{26}$$

$${}^1\Delta_g \;:\; 2^{-1}(\sigma)^2\Big[(\pi^+)^4(\pi^-)^2 + (\pi^+)^2(\pi^-)^4 + (\pi_u^+)^2(\pi_g^+)(\pi_u^-)^2(\pi_g^-) + (\pi_u^+)(\pi_g^+)^2(\pi_u^-)(\pi_g^-)^2\Big] \tag{27}$$

$$\begin{aligned} {}^1\Pi_g \;:\; 2^{-1}\Big\{&(\sigma_g)^2(\sigma_u)\Big[(\pi_u^+)(\pi_g^+)^2(\pi^-)^2 + (\pi^+)^2(\pi_u^-)(\pi_g^-)^2\Big] \\ &+ (\sigma_g)(\sigma_u)^2\Big[(\pi_u^+)^2(\pi_g^+)(\pi^-)^2 + (\pi^+)^2(\pi_u^-)^2(\pi_g^-)\Big]\Big\} \end{aligned} \tag{28}$$

$$\begin{aligned} {}^1\Pi_u \;:\; 2^{-1}\Big\{&(\sigma_g)^2(\sigma_u)\Big[(\pi_u^+)^2(\pi_g^+)(\pi^-)^2 + (\pi^+)^2(\pi_u^-)^2(\pi_g^-)\Big] \\ &+ (\sigma_g)(\sigma_u)^2\Big[(\pi_u^+)(\pi_g^+)^2(\pi^-)^2 + (\pi^+)^2(\pi_u^-)(\pi_g^-)^2\Big]\Big\} \end{aligned} \tag{29}$$

$$a\,{}^1\Sigma_g^+ \;:\; 2^{-1/2}(\sigma)^2\Big[(\pi^+)^4(\pi^-)^2 + (\pi^+)^2(\pi^-)^4\Big] \tag{30}$$

$${}^1\Sigma_u^- \;:\; 2^{-1/2}(\sigma)^2\Big[(\pi_u^+)^2(\pi_g^+)(\pi_u^-)(\pi_g^-)^2 + (\pi_u^+)(\pi_g^+)^2(\pi_u^-)^2(\pi_g^-)\Big] \tag{31}$$

and

$$b\,{}^1\Sigma_g^+ \;:\; (\sigma)^4(\pi^+)^2(\pi^-)^2 \tag{32}$$

Absent from this list are combinations of expressions (5) to (13) which correspond to zero magnetic spin quantum numbers on both atoms. Unlike the other spin combinations, such pairings do not represent pure spin states because of the multiplicity of couplings and phase relations between the atomic spin vectors as they precess about the molecular axis. All the pure singlet states are obtained from combinations of atomic states with $M_S = 1$ and $M_S = -1$.

By way of contrast, the molecular electron configurations used by Vanderslice, Mason, and Maisch (ref. 3) are given by

$$ {}^5\Delta_g \;:\; (\sigma_g)(\sigma_u)(\pi^+)^4(\pi_u^-)(\pi_g^-) \tag{33} $$

$$ {}^5\Pi_g \;:\; (\sigma_g)^2(\sigma_u)(\pi_u^+)^2(\pi_g^+)(\pi_u^-)(\pi_g^-) \tag{34} $$

$$ {}^5\Pi_u \;:\; (\sigma_g)(\sigma_u)^2(\pi_u^+)^2(\pi_g^+)(\pi_u^-)(\pi_g^-) \tag{35} $$

$$ a\,{}^5\Sigma_g^+ \;:\; (\sigma_g)(\sigma_u)(\pi_u^+)^2(\pi_g^+)(\pi_u^-)(\pi_g^-)^2 \tag{36} $$

$$ {}^5\Sigma_u^- \;:\; (\sigma_g)(\sigma_u)(\pi_u^+)^2(\pi_g^+)(\pi_u^-)^2(\pi_g^-) \tag{37} $$

$$ b\,{}^5\Sigma_g^+ \;:\; (\sigma)^4(\pi_u^+)(\pi_g^+)(\pi_u^-)(\pi_g^-) \tag{38} $$

$$ {}^3\Delta_u \;:\; (\sigma_g)^2(\pi^+)^4(\pi_u^-)(\pi_g^-) \tag{39} $$

$$ {}^3\Pi_g \;:\; (\sigma_g)^2(\sigma_u)(\pi_u^+)^2(\pi_g^+)(\pi_u^-)(\pi_g^-) \tag{40} $$

$$ {}^3\Pi_u \;:\; (\sigma_g)^2(\sigma_u)(\pi_u^+)^2(\pi_g^+)(\pi_u^-)^2 \tag{41} $$

$$ A\,{}^3\Sigma_u^+ \;:\; (\sigma_g)^2(\pi_u^+)^2(\pi_g^+)(\pi_u^-)(\pi_g^-)^2 \tag{42} $$

$$ X\,{}^3\Sigma_g^- \;:\; (\sigma_g)^2(\pi_u^+)^2(\pi_g^+)(\pi_u^-)^2(\pi_g^-) \tag{43} $$

$$ b\,{}^3\Sigma_u^+ \;:\; (\sigma_g)(\sigma_u)(\pi_u^+)^2(\pi_g^+)(\pi_u^-)^2(\pi_g^-) \tag{44} $$

$$ {}^1\Delta_g \;:\; (\sigma_g)^2(\pi^+)^4(\pi_u^-)^2 \tag{45} $$

$$^{1}\Pi_{g} \ : \ \left(\sigma_{g}\right)^{2}\left(\sigma_{u}\right)\left(\pi_{u}^{+}\right)^{2}\left(\pi_{g}^{+}\right)\left(\pi_{u}^{-}\right)\left(\pi_{g}^{-}\right) \tag{46}$$

$$^{1}\Pi_{u} \ : \ \left(\sigma_{g}\right)^{2}\left(\sigma_{u}\right)\left(\pi_{u}^{+}\right)^{2}\left(\pi_{g}^{+}\right)\left(\pi_{u}^{-}\right)^{2} \tag{47}$$

$$a\ ^{1}\Sigma_{g}^{+} \ : \ \left(\sigma_{g}\right)^{2}\left(\pi_{u}^{+}\right)^{2}\left(\pi_{g}^{+}\right)\left(\pi_{u}^{-}\right)^{2}\left(\pi_{g}^{-}\right) \tag{48}$$

$$^{1}\Sigma_{u}^{-} \ : \ \left(\sigma_{g}\right)^{2}\left(\pi_{u}^{+}\right)^{2}\left(\pi_{g}^{+}\right)\left(\pi_{u}^{-}\right)\left(\pi_{g}^{-}\right)^{2} \tag{49}$$

and

$$b\ ^{1}\Sigma_{g}^{+} \ : \ (\sigma)^{4}\left(\pi_{u}^{+}\right)^{2}\left(\pi_{u}^{-}\right)^{2} \tag{50}$$

Configurations (33) to (50) differ substantially from those of the present research for two reasons: (1) correlations between the oxygen molecule and its dissociation products are not included in reference 3 and (2) Vanderslice, Mason, and Maisch identify two-electron bonds and antibonds more closely with molecular orbital theory than with valence bond theory. Consequently, the two-electron occupation $\left(\sigma_{g}\right)^{2}$ often replaces $(\sigma)^{2}$, for example, and thus fails to note the important configuration interaction with $\left(\sigma_{u}\right)^{2}$ that distinguishes between neutral and ionized products (ref. 4). The simple configurations of expressions (33) to (50) are determined mostly from energy arguments which are seldom reliable (ref. 4); they do not imply simpler or more symmetric interaction potentials compared with those of expressions (14), (15), and (17) to (32). In addition, the configurations for $a\ ^{5}\Sigma_{g}^{+}$, $A\ ^{3}\Sigma_{u}^{+}$, $b\ ^{3}\Sigma_{u}^{+}$, and $a\ ^{1}\Sigma_{g}^{+}$ in expressions (36), (42), (44), and (48) do not yield the correct + or - symmetries. (See appendix A.)

INTERACTION POTENTIALS

As explained in reference 4, the energy of each individual subconfiguration in expressions (14), (15), and (17) to (32) is computed as if that subconfiguration existed alone, the interactions between them serving merely to establish different energy asymptotes for different dissociation products. The subconfiguration energies are weighted by the squares of their coefficients and then added to yield the atom-atom interaction potentials ϕ. All subpotentials ϕ_{i} in each subconfiguration are expressed in terms of the exchange energies J_{i} according to the following relations (ref. 4):

$$\phi_{2} \approx \pm J_{2} \equiv \pm J \tag{51}$$

$$\phi_3 \approx \phi_1 = Q_1 \pm J_1 \approx \pm J_1 \tag{52}$$

and

$$\phi_4 \approx -2J_2 \equiv -2J \tag{53}$$

where the subscripts denote the number of electrons in the bond or antibond being considered and Q_1 is the one-electron Coulomb integral.

The justification for equation (52) follows from screening arguments and the fact that J_1 is proportional to overlap integrals between atomic orbitals on different atoms, whereas J_2 and Q_1 are proportional to squares of overlap integrals (ref. 4). Since the three-electron configuration described by the molecular orbital determinant

$$(a+b \quad a-b \mid a\pm b)$$

is equivalent to the molecular orbital-valence bond arrangement

$$(a \; b \mid a\pm b)$$

and since the two valence bond electrons effectively screen the atomic cores from the molecular orbital electron, ϕ_3 should be closely approximated by ϕ_1 and only slightly perturbed by energies proportional to squares of overlap integrals. At the same time, the molecular orbital electron is much less efficient in screening the atomic cores from the valence bond electrons; hence, the neglect of their J_2 contributions to ϕ_3 is consistent with the retention of J_2 in two- and four-electron bonds pertaining to smaller effective nuclear charges and, therefore, to greater overlap between atomic functions. Finally, Q_1 is neglected in equation (52) because it also relates to overlap integrals which are smaller than normal as the result of incomplete screening.

A typical example of the procedure for finding long-range interaction potentials from molecular electron configurations is provided in the following manner by the $^5\Delta_g$ state of expression (14) and the energies in equations (51) to (53):

$$\begin{aligned}\phi\left(^5\Delta_g\right) &= \frac{1}{4}\left(-J_\sigma - 2J_\pi - J_\pi\right) + \frac{1}{4}\left(-J_\sigma - J_\pi - 2J_\pi\right) \\ &\quad + \frac{1}{4}\left(-J_\sigma + J_{1\pi} - J_{1\pi}\right) + \frac{1}{4}\left(-J_\sigma - J_{1\pi} + J_{1\pi}\right) \\ &= -\left(J_\sigma + \frac{3}{2} J_\pi\right)\end{aligned} \tag{54}$$

Each exchange energy in equation (54) is labeled by the σ or π electron occupation from which it derives, there being no exchanges between electrons occupying orbitals of different geometric orientations because of overlap considerations. Positive signs are chosen for two- and three-electron bonds such as $(\sigma)^2$ and $\left(\pi_u^+\right)^2\left(\pi_g^+\right)$, the first of which does not exist in this particular example, and negative signs for antibonds such as $\left(\sigma_g\right)\left(\sigma_u\right)$ and $\left(\pi_u^+\right)\left(\pi_g^+\right)^2$. Since all exchange energies are negative by definition (ref. 4), the $^5\Delta_g$ state of molecular oxygen is obviously repulsive in its outer regions.

The remaining 17 interaction potentials are deduced in similar fashion and listed in the second column of table I. As required by the discussion following expression (17), the energy of the $a\,^5\Sigma_g^+$ state is shifted downward from the value

$$\phi\left(a\,^5\Sigma_g^+\right) = -\left(J_\sigma + 3J_\pi\right) \tag{55}$$

to coincide with the energy of the $^5\Sigma_u^-$ state given by

$$\phi\left(^5\Sigma_u^-\right) = -J_\sigma \tag{56}$$

For such a shift to be possible, the energy of the configuration interacting $b\,^5\Sigma_g^+$ state must lie above that of the $a\,^5\Sigma_g^+$ state, which it does according to the relation

$$\phi\left(b\,^5\Sigma_g^+\right) = -2\left(J_\sigma + J_\pi\right) \tag{57}$$

and the fact that J_σ has larger magnitudes than J_π because of greater overlap between p_z atomic functions.

Corresponding to the downward shift of the $a\,^5\Sigma_g^+$ energy is an upward shift of the $b\,^5\Sigma_g^+$ energy by an amount determined from the use of equations (55) to (57) in the well-known variational principle of quantum mechanics. This principle relates the low-level (no configuration interaction) approximations ϕ_a and ϕ_b for the molecular states a and b to the final energies (denoted by primes) through the secular equation

$$\begin{vmatrix} \phi_a - \phi' & H_{ab} \\ H_{ab} & \phi_b - \phi' \end{vmatrix} = 0 \tag{58}$$

If ϕ_a, ϕ_b, and one of the ϕ' solutions are known, the off-diagonal interaction energies H_{ab} can be eliminated in the expansion of equation (58) to yield

$$\phi_b' = \phi_a + \phi_b - \phi_a' \tag{59}$$

The substitution into equation (59) of $a\,^5\Sigma_g^+$ for state a, $b\,^5\Sigma_g^+$ for state b, and $\phi\left(^5\Sigma_u^-\right)$ for ϕ_a' finally gives

$$\begin{aligned}\phi'\left(b\,^5\Sigma_g^+\right) &= \phi\left(a\,^5\Sigma_g^+\right) + \phi\left(b\,^5\Sigma_g^+\right) - \phi\left(^5\Sigma_u^-\right)\\ &= -2\left(J_\sigma + \frac{5}{2}J_\pi\right)\end{aligned} \tag{60}$$

Similar treatments are required for the triplet and singlet Σ configurations with the results

$$\begin{aligned}\phi'\left(b\,^3\Sigma_u^+\right) &= \phi\left(A\,^3\Sigma_u^+\right) + \phi\left(b\,^3\Sigma_u^+\right) - \phi\left(X\,^3\Sigma_g^-\right)\\ &= -2J_\pi - 2J_\sigma - 0\\ &= -2\left(J_\sigma + J_\pi\right)\end{aligned} \tag{61}$$

and

$$\begin{aligned}\phi'\left(b\,^1\Sigma_g^+\right) &= \phi\left(a\,^1\Sigma_g^+\right) + \phi\left(b\,^1\Sigma_g^+\right) - \phi\left(^1\Sigma_u^-\right)\\ &= \left(J_\sigma - J_\pi\right) - 2\left(J_\sigma - J_\pi\right) - J_\sigma\\ &= -2\left(J_\sigma - \frac{1}{2}J_\pi\right)\end{aligned} \tag{62}$$

Also shown in table I are the Vanderslice, Mason, and Maisch interaction potentials (ref. 3) computed from the electron configurations of expressions (33) to (50) and the assumption that each electron occupies a molecular orbital. The electron energies are defined arbitrarily to be $J_2/2$ (that is, $J/2$) in attractive orbitals and $-3J_2/2$ (that is, $-3J/2$) in repulsive orbitals, so that the two-electron subpotentials

$$\phi_2\left[\left(\sigma_g\right)^2\right] = 2(J_\sigma/2) = J_\sigma \tag{63}$$

and

$$\phi_2\left[\left(\sigma_g\right)\left(\sigma_u\right)\right] = \frac{J_\sigma}{2} - \frac{3J_\sigma}{2} = -J_\sigma \tag{64}$$

satisfy valence bond requirements. The four-electron subpotential is given correctly by the expression

$$\phi_4\left[(\sigma)^4\right] = 2(J_\sigma/2) - 2(3J_\sigma/2) = -2J_\sigma \tag{65}$$

However, the three-electron subpotentials

$$\phi_3\left[\left(\sigma_g\right)^2\left(\sigma_u\right)\right] = 2(J_\sigma/2) - 3J_\sigma/2 = -J_\sigma/2 \tag{66}$$

and

$$\phi_3\left[\left(\sigma_g\right)\left(\sigma_u\right)^2\right] = J_\sigma/2 - 2(3J_\sigma/2) = -5J_\sigma/2 \tag{67}$$

calculated by the procedure of reference 3 fail to satisfy equation (52) because no distinction is made between exchange energies varying as the first and second powers of the overlap integrals. Equations (66) and (67) are nonsymmetric with respect to the dissociation asymptote, neither equation predicting an attractive force; hence, stable configurations such as the helium molecule-ion would not be possible within this framework. A further discussion is given in appendix B.

DISCUSSION OF RESULTS

Starting with correlations between molecular and atomic states and continuing through configuration interactions and the assignments of individual electron energies, the methods of the present research and reference 3 are so different that the complete lack of correspondence between the long-range interaction potentials listed in columns 2 and 3 of table I is understandable. Just as in the previous calculations for nitrogen (ref. 4), the present modifications greatly enhance the symmetry characteristics of the potential energy curves with respect to both the dissociation asymptote and each other. Among the useful relations between potentials are the following expressions:

$$\phi\left({}^3\Delta_u\right) = \frac{1}{2}\left[\phi\left({}^1\Delta_g\right) + \phi\left({}^5\Delta_g\right)\right] \tag{68}$$

$$\phi\left({}^3\Pi_g\right) = \phi\left({}^3\Pi_u\right) = \frac{1}{2}\left[\phi\left({}^1\Pi_g\right) + \phi\left({}^5\Pi_g\right)\right] = \frac{1}{2}\left[\phi\left({}^1\Pi_u\right) + \phi\left({}^5\Pi_u\right)\right] \tag{69}$$

$$\phi\left(b\,{}^3\Sigma_u^+\right) = \frac{1}{2}\left[\phi\left(b\,{}^1\Sigma_g^+\right) + \phi\left(b\,{}^5\Sigma_g^+\right)\right] \tag{70}$$

$$\phi\left(A\,^3\Sigma_u^+\right) = \frac{1}{2}\left[\phi\left(a\,^1\Sigma_g^+\right) + \phi\left(a\,^5\Sigma_g^+\right)\right] \tag{71}$$

and

$$\phi\left(X\,^3\Sigma_g^-\right) = \frac{1}{2}\left[\phi\left(^1\Sigma_u^-\right) + \phi\left(^5\Sigma_u^-\right)\right] \tag{72}$$

In both sets of calculations in table I the appearance of only two exchange energies, J_σ and J_π, permits all 18 long-range interaction potentials to be expressed as linear combinations of two given ones; however, even this much complexity may not be required for computations of high-temperature transport coefficients. Since overlap considerations imply magnitudes of J_σ far greater than J_π in the range of internuclear separations most important for high-temperature transport properties, a good approximation should be the setting of all potentials equal to zero except those found from the second column of table I to satisfy

$$\begin{aligned}\phi\left(^1\Delta_g\right) &\approx \phi\left(a\,^1\Sigma_g^+\right) \approx \phi\left(^1\Sigma_u^-\right) \approx -\phi\left(a\,^5\Sigma_g^+\right) \approx -\phi\left(^5\Sigma_u^-\right)\\ &\approx -\phi\left(^5\Delta_g\right) \approx -2^{-1}\phi\left(b\,^5\Sigma_g^+\right) \approx -2^{-1}\phi\left(b\,^3\Sigma_u^+\right) \approx -2^{-1}\phi\left(b\,^1\Sigma_g^+\right) \approx J_\sigma\end{aligned} \tag{73}$$

The weighted collision cross sections corresponding to these potentials then combine to give the effective value

$$\begin{aligned}Q_{mean} &\approx \frac{48}{81}\,Q(\phi\approx 0) + \frac{24}{81}\,Q(\phi\approx\pm J_\sigma) + \frac{9}{81}\,Q(\phi\approx -2J_\sigma)\\ &\approx \frac{8}{27}\,Q(\phi\approx\pm J_\sigma) + \frac{1}{9}\,Q(\phi\approx -2J_\sigma)\end{aligned} \tag{74}$$

where Λ-doubling is included in the coefficients.

A similar analysis of the third column in table I yields

$$\begin{aligned}Q_{mean} &\approx \frac{26}{81}\,Q\left(\phi\approx -\frac{J_\sigma}{2}\right) + \frac{13}{27}\,Q(\phi\approx\pm J_\sigma)\\ &+ \frac{10}{81}\,Q\left(\phi\approx -\frac{5J_\sigma}{2}\right) + \frac{2}{27}\,Q(\phi\approx -2J_\sigma)\end{aligned} \tag{75}$$

which is larger than the effective cross section in equation (74) because of nonzero contributions from every molecular state. Only 41 percent of the modified potentials contribute to the effective cross section; hence, transport coefficients based on the results of reference 3 may be somewhat smaller than the true values for a gas of pure atomic oxygen.

Further comparisons between the two sets of long-range interaction potentials and collision cross sections are not very productive at this stage because of the lack of good transport data at high temperatures. Reliable formulas for J_σ also are not available. However, several interesting conclusions and observations can be made by extrapolating and adjusting the molecular electron configurations of expressions (14), (15), and (17) to (32) to cover smaller internuclear separations.

EXTRAPOLATIONS OF SELECTED ELECTRON CONFIGURATIONS TO INTERMEDIATE INTERNUCLEAR SEPARATIONS

Two fundamental difficulties are associated with the preceding analysis: (1) the internuclear separation below which the configuration interactions between similar Σ states cease to be significant is not known and (2) the close-range limit of the region in which combinations of electron subconfigurations are necessary for correlation purposes is uncertain. Whereas the first difficulty is resolved if J_π is negligible in equations (55) to (62), the second requires considerable thought for most interactions. Although some evidence is given in reference 4 that relations between potentials are more consistent with intermediate-range calculations and spectroscopic data when correlation is maintained, other arguments point to the breaking of certain types of correlation at relatively far distances. In principle, of course, the statistical weights of the electron subconfigurations in any molecular state can be obtained as functions of the separation from ab initio quantum calculations, but this approach is beyond the scope of the present research.

One example of the type of correlation which may be broken or altered at fairly large separations is displayed by the $^1\Delta_g$ state of expression (27). A likely evolution of the electron configuration as the internuclear separation decreases is given by

$$\begin{aligned}
{}^1\Delta_g \ : \ & 2^{-1}(\sigma)^2\left[(\pi^+)^4(\pi^-)^2 + (\pi^+)^2(\pi^-)^4 + \left(\pi_u^+\right)^2\left(\pi_g^+\right)\left(\pi_u^-\right)^2\left(\pi_g^-\right) + \left(\pi_u^+\right)\left(\pi_g^+\right)^2\left(\pi_u^-\right)\left(\pi_g^-\right)^2\right] \\
& \rightarrow 2^{-1}(\sigma)^2\left[(\pi^+)^4(\pi^-)^2 + (\pi^+)^2(\pi^-)^4 + 2\left(\pi_u^+\right)^2\left(\pi_g^+\right)\left(\pi_u^-\right)^2\left(\pi_g^-\right)\right] \\
& \rightarrow 2^{-1}\left(\sigma_g\right)^2\left[(\pi^+)^4(\pi^-)^2 + (\pi^+)^2(\pi^-)^4 + 2\left(\pi_u^+\right)^2\left(\pi_g^+\right)\left(\pi_u^-\right)^2\left(\pi_g^-\right)\right] \\
& \rightarrow 2^{-1}\left(\sigma_g\right)^2\left[(\pi^+)^4\left(\pi_u^-\right)^2 + \left(\pi_u^+\right)^2(\pi^-)^4 + 2\left(\pi_u^+\right)^2\left(\pi_g^+\right)\left(\pi_u^-\right)^2\left(\pi_g^-\right)\right]
\end{aligned} \tag{76}$$

where the second step represents an alteration in the π-orbital occupations corresponding to the lowest energy choice. The reason for this change being likely at relatively large distances is the fact that it can occur without suppressing any of the four combinations inherent in collisions between (1,1) and (1,-1) atoms; in addition, the configuration interaction between $\left(\pi_u^+\right)^2\left(\pi_g^+\right)\left(\pi_u^-\right)^2\left(\pi_g^-\right)$ and $\left(\pi_u^+\right)\left(\pi_g^+\right)^2\left(\pi_u^-\right)\left(\pi_g^-\right)^2$, which is required at very large distances to distinguish between normal and ionized products, should dissipate rapidly with decreasing separation.

Steps 3 and 4 of expression (76) correspond first to the substitution of $\left(\sigma_g\right)^2$ for $(\sigma)^2$ and then to the substitution of $\left(\pi_u\right)^2$ for $(\pi)^2$, the priorities relating to overlap influences on the dissipation of the two-electron configuration interactions discussed in reference 4. Although the limits on the internuclear separation for the various stages of expression (76) are not defined by this procedure, the qualitative evolution of the molecular electron configuration to the less specific notation $\left(\sigma_g\right)^2\left(\pi_u\right)^4\left(\pi_g\right)^2$ is confirmed by Herzberg (ref. 5, p. 345). Finally, the energy evolution associated with expression (76) is given by

$$\begin{aligned}\phi\left({}^1\Delta_g\right) &= J_\sigma - \frac{1}{2} J_\pi \rightarrow J_\sigma + J_{1\pi} - \frac{1}{2} J_\pi \\ &\rightarrow 2J_{1\sigma} + J_{1\pi} - \frac{1}{2} J_\pi \rightarrow 2J_{1\sigma} + 2J_{1\pi} - J_\pi \qquad (77)\end{aligned}$$

The two remaining molecular states evolving to $\left(\sigma_g\right)^2\left(\pi_u\right)^4\left(\pi_g\right)^2$ configurations are $a\,{}^1\Sigma_g^+$ and $X\,{}^3\Sigma_g^-$ according to the following expressions:

$$\begin{aligned}a\,{}^1\Sigma_g^+ \ :\ & 2^{-1/2}(\sigma)^2\left[(\pi^+)^4(\pi^-)^2 + (\pi^+)^2(\pi^-)^4\right] \\ &\rightarrow 2^{-1/2}\left(\sigma_g\right)^2\left[(\pi^+)^4(\pi^-)^2 + (\pi^+)^2(\pi^-)^4\right] \\ &\rightarrow 2^{-1/2}\left(\sigma_g\right)^2\left[(\pi^+)^4\left(\pi_u^-\right)^2 + \left(\pi_u^+\right)^2(\pi^-)^4\right] \qquad (78)\end{aligned}$$

and

$$\begin{aligned}X\,{}^3\Sigma_g^- \ :\ 2^{-1}\Big\{&(\sigma)^2\left[\left(\pi_u^+\right)^2\left(\pi_g^+\right)\left(\pi_u^-\right)^2\left(\pi_g^-\right) + \left(\pi_u^+\right)\left(\pi_g^+\right)^2\left(\pi_u^-\right)\left(\pi_g^-\right)^2\right] \\ &+ \left(\sigma_g\right)\left(\sigma_u\right)\left[\left(\pi_u^+\right)^2\left(\pi_g^+\right)\left(\pi_u^-\right)\left(\pi_g^-\right)^2 + \left(\pi_u^+\right)\left(\pi_g^+\right)^2\left(\pi_u^-\right)^2\left(\pi_g^-\right)\right]\Big\}\end{aligned}$$

(Equation continued on next page)

$$
\begin{aligned}
&\rightarrow 2^{-1}\Big\{2(\sigma)^2\left(\pi_u^+\right)^2\left(\pi_g^+\right)\left(\pi_u^-\right)^2\left(\pi_g^-\right)\\
&\qquad + \left(\sigma_g\right)\left(\sigma_u\right)\Big[\left(\pi_u^+\right)^2\left(\pi_g^+\right)\left(\pi_u^-\right)\left(\pi_g^-\right)^2 + \left(\pi_u^+\right)\left(\pi_g^+\right)^2\left(\pi_u^-\right)^2\left(\pi_g^-\right)\Big]\Big\}\\
&\rightarrow (\sigma)^2\left(\pi_u^+\right)^2\left(\pi_g^+\right)\left(\pi_u^-\right)^2\left(\pi_g^-\right)\\
&\rightarrow \left(\sigma_g\right)^2\left(\pi_u^+\right)^2\left(\pi_g^+\right)\left(\pi_u^-\right)^2\left(\pi_g^-\right)
\end{aligned}
\tag{79}
$$

Corresponding to these configurations are the energy evolutions

$$
\begin{aligned}
\phi\left(a\ {}^1\Sigma_g^+\right) &= J_\sigma \rightarrow J_\sigma - J_\pi \rightarrow 2J_{1\sigma} - J_\pi\\
&\rightarrow 2J_{1\sigma} + 2J_{1\pi} - 2J_\pi
\end{aligned}
\tag{80}
$$

and

$$
\begin{aligned}
\phi\left(X\ {}^3\Sigma_g^-\right) &= 0 \rightarrow J_{1\pi} \rightarrow J_\sigma + 2J_{1\pi}\\
&\rightarrow 2J_{1\sigma} + 2J_{1\pi}
\end{aligned}
\tag{81}
$$

where recognition of the interaction with $b\ {}^1\Sigma_g^+$ is taken in the first step of equation (80).

A convenient summary of equations (77), (80), and (81) near the equilibrium separation is contained in the expression

$$
\phi\left({}^1\Delta_g\right) \approx \frac{1}{2}\left[\phi\left(X\ {}^3\Sigma_g^-\right) + \phi\left(a\ {}^1\Sigma_g^+\right)\right]
\tag{82}
$$

whereby the energy of the ${}^1\Delta_g$ state lies midway between that of $X\ {}^3\Sigma_g^-$ and $a\ {}^1\Sigma_g^+$. Also established by the same equations are $X\ {}^3\Sigma_g^-$ as the ground state and $a\ {}^1\Sigma_g^+$ as the highest of the three most stable configurations. These results agree perfectly with the spectroscopic ordering of equilibrium energies and are surprisingly close to the observed ratios (ref. 5, pp. 346, 446, and 560)

$$
E\left(a\ {}^1\Sigma_g^+\right) \ :\ E\left({}^1\Delta_g\right) \ :\ E\left(X\ {}^3\Sigma_g^-\right) = 2.63 \ :\ 1.98 \ :\ 1.00
\tag{83}
$$

Responsible for this success are the correlation analyses of the preceding paragraphs, which trace from the isolated atoms and thus permit a more detailed study of the three molecular states characterized by the Herzberg notation $(\sigma_g)^2(\pi_u)^4(\pi_g)^2$. Without such detail, Herzberg (ref. 5, pp. 358 and 359) concluded that the $X\,{}^3\Sigma_g^-$ energy is shifted downward from the other two because of configuration interaction with a ${}^3\Sigma_g^-$ state dissociating into ${}^3P$ and ${}^1D$ atoms. This assumption no longer seems necessary to explain the basic energy ordering, although it may well contribute to the asymmetric spacing implied by equation (83).

A second group of three stable configurations corresponds to the Herzberg notation $(\sigma_g)^2(\pi_u)^3(\pi_g)^3$ and to the following evolutions as the internuclear separation decreases:

$$\begin{aligned} A\,{}^3\Sigma_u^+ \;:\; & 2^{-1}\Big\{(\sigma)^2\Big[(\pi^+)^4(\pi_u^-)(\pi_g^-) + (\pi_u^+)(\pi_g^+)(\pi^-)^4\Big] + (\sigma_g)(\sigma_u)\Big[(\pi^+)^4(\pi^-)^2 + (\pi^+)^2(\pi^-)^4\Big]\Big\} \\ & \rightarrow 2^{-1/2}(\sigma)^2\Big[(\pi^+)^4(\pi_u^-)(\pi_g^-) + (\pi_u^+)(\pi_g^+)(\pi^-)^4\Big] \\ & \rightarrow 2^{-1/2}(\sigma_g)^2\Big[(\pi^+)^4(\pi_u^-)(\pi_g^-) + (\pi_u^+)(\pi_g^+)(\pi^-)^4\Big] \end{aligned} \tag{84}$$

$$\begin{aligned} {}^3\Delta_u \;:\; & 8^{-1/2}\Big\{(\sigma)^2\Big[(\pi^+)^4(\pi_u^-)(\pi_g^-) + (\pi_u^+)(\pi_g^+)(\pi^-)^4 + (\pi_u^+)^2(\pi_g^+)(\pi_u^-)(\pi_g^-)^2 + (\pi_u^+)(\pi_g^+)^2(\pi_u^-)^2(\pi_g^-)\Big] \\ & \quad + (\sigma_g)(\sigma_u)\Big[(\pi^+)^4(\pi^-)^2 + (\pi^+)^2(\pi^-)^4 + (\pi_u^+)^2(\pi_g^+)(\pi_u^-)^2(\pi_g^-) + (\pi_u^+)(\pi_g^+)^2(\pi_u^-)(\pi_g^-)^2\Big]\Big\} \\ & \rightarrow 2^{-1}(\sigma)^2\Big[(\pi^+)^4(\pi_u^-)(\pi_g^-) + (\pi_u^+)(\pi_g^+)(\pi^-)^4 + (\pi_u^+)^2(\pi_g^+)(\pi_u^-)(\pi_g^-)^2 + (\pi_u^+)(\pi_g^+)^2(\pi_u^-)^2(\pi_g^-)\Big] \\ & \rightarrow 2^{-1}(\sigma_g)^2\Big[(\pi^+)^4(\pi_u^-)(\pi_g^-) + (\pi_u^+)(\pi_g^+)(\pi^-)^4 + (\pi_u^+)^2(\pi_g^+)(\pi_u^-)(\pi_g^-)^2 + (\pi_u^+)(\pi_g^+)^2(\pi_u^-)^2(\pi_g^-)\Big] \end{aligned} \tag{85}$$

and

$$\begin{aligned} {}^1\Sigma_u^- \;:\; & 2^{-1/2}(\sigma)^2\Big[(\pi_u^+)^2(\pi_g^+)(\pi_u^-)(\pi_g^-)^2 + (\pi_u^+)(\pi_g^+)^2(\pi_u^-)^2(\pi_g^-)\Big] \\ & \rightarrow 2^{-1/2}(\sigma_g)^2\Big[(\pi_u^+)^2(\pi_g^+)(\pi_u^-)(\pi_g^-)^2 + (\pi_u^+)(\pi_g^+)^2(\pi_u^-)^2(\pi_g^-)\Big] \end{aligned} \tag{86}$$

Associated with these expressions are the energy evolutions

$$\phi\left(A\,{}^3\Sigma_u^+\right) = 0 \rightarrow -2J_\pi \rightarrow J_\sigma - 3J_\pi \rightarrow 2J_{1\sigma} - 3J_\pi \tag{87}$$

$$\phi\left({}^3\Delta_u\right) = -J_\pi \rightarrow J_\sigma - \frac{3}{2}J_\pi \rightarrow 2J_{1\sigma} - \frac{3}{2}J_\pi \tag{88}$$

and

$$\phi\left({}^1\Sigma_u^-\right) = J_\sigma \rightarrow 2J_{1\sigma} \tag{89}$$

so that

$$\phi\left({}^3\Delta_u\right) = \frac{1}{2}\left[\phi\left({}^1\Sigma_u^-\right) + \phi\left(A\,{}^3\Sigma_u^+\right)\right] \tag{90}$$

The states $A\,{}^3\Sigma_u^+$, ${}^3\Delta_u$, and ${}^1\Sigma_u^-$ are in the order of increasing stability near the equilibrium separation of nuclei.

Since equations (87) to (89) do not involve the $J_{1\pi}$ contributions to equations (77), (80), and (81), the energies of the second group of three molecular states $\left(\text{i.e.,}\ {}^1\Sigma_u^-, {}^3\Delta_u, \text{and}\ A\,{}^3\Sigma_u^+\right)$ lie above those of the first group at equilibrium distances. This observation plus the energy ordering of the second group and the relation displayed in equation (90) are in general agreement with the conclusions of Moffitt (ref. 6) and Fumi and Parr (ref. 7), but not with Herzberg (ref. 5, pp. 446 and 560; also, ref. 8), who lists ${}^3\Delta_u$ as the lowest state in the second group.

An overall survey of the six stable configurations discussed in the present section suggests crossings of the $X\,{}^3\Sigma_g^-$ potential energy curve with those of the ${}^1\Delta_g$, $a\,{}^1\Sigma_g^+$, and ${}^1\Sigma_u^-$ states and the ${}^3\Delta_u$ curve with that of $A\,{}^3\Sigma_u^+$; in addition, potential humps or maxima located somewhere between equilibrium and large internuclear separations are predicted for the ${}^3\Delta_u$ and $A\,{}^3\Sigma_u^+$ states. Potential humps also may occur in the ${}^5\Pi_g$ and ${}^5\Pi_u$ curves, all Π states being at least slightly stable at sufficiently small separations.

Another interesting observation concerns the fact that the ground $X\,{}^3\Sigma_g^-$ state is not the most attractive one at large distances, that distinction falling to $a\,{}^1\Sigma_g^+$ and ${}^1\Sigma_u^-$; meanwhile, the most repulsive configuration belongs to $b\,{}^5\Sigma_g^+$. Few of these conclusions are shared by Vanderslice, Mason, and Maisch (ref. 3), who also fail to distinguish between the individual energies in each triad of strongly stable molecular states. Many important details are either missing or incorrectly described in reference 3 because of the lack of correlation between molecular and atomic configurations and the arbitrary assignments of molecular orbital energies.

Finally, the energy evolutions of equations (77) and (80) forecast a much better success for the extrapolations of Rydberg-Klein-Rees semiempirical $^1\Delta_g$ and a $^1\Sigma_g^+$ potentials to large distances than for the extrapolation of the $X\,^3\Sigma_g^-$ curve in equation (81). As observed in reference 3, the outer extremity of the Rydberg-Klein-Rees $X\,^3\Sigma_g^-$ curve is too steep to be connected smoothly with Vanderslice, Mason, and Maisch's strongly attractive valence bond energy at still larger separations. A rather sharp bending of the Rydberg-Klein-Rees curve leading to a very gentle approach to the dissociation asymptote is implied; hence, a good indirect confirmation of the flatness of the long-range $X\,^3\Sigma_g^-$ tail in the present analysis is obtained.

CONCLUDING REMARKS

Correlations between the electron structures of oxygen molecules and their dissociation products are shown to significantly alter previous determinations of the 18 long-range interatomic forces operating in a pure gas of normal oxygen atoms; in addition, certain correlations predict and specify the energy shifts resulting from configuration interactions with states of the same symmetry. Unlike much of the existing body of research, a consistent mixture of valence bond and molecular orbital energies is assigned to the various bonding and antibonding configurations. Reasonable extrapolations of the electron structures and potential energies to intermediate distances successfully predict the ordering of the six most stable molecular states and suggest a number of potential humps and curve crossings in the process.

Among the conclusions pertaining to large internuclear separations is the prediction that the transport coefficients for atomic oxygen have been underestimated at high temperatures by researchers using the approximation of perfect pairing. Because of the correlation analyses and other considerations in the present paper, nine of the 18 atom-atom interaction potentials are nearly flat in the outer regions and, thus, do not contribute effectively to the collision integrals and cross sections of kinetic theory. Some confirmation of this flatness is obtained for the ground state of molecular oxygen by studying the long-range extrapolation of the corresponding Rydberg-Klein-Rees semiempirical potential energy curve.

Langley Research Center,
National Aeronautics and Space Administration,
Hampton, Va., November 5, 1970.

APPENDIX A

ELECTRON CONFIGURATIONS AND INTERACTIONS

To a large degree, both the present research and that of reference 3 involve the writing of valence bond energies directly from simple molecular orbital descriptions of electron configurations. However, in expressing double σ-orbital occupations by the symbol $(\sigma)^2$ instead of $\left(\sigma_g\right)^2$ or $\left(\sigma_u\right)^2$ for electrons with paired spins, for example, the present paper explicitly recognizes a major difficulty with molecular orbital language that reference 3 does not – namely, that configuration interaction between $\left(\sigma_g\right)^2$ and $\left(\sigma_u\right)^2$ at large internuclear separations makes the atomic orbital or valence bond description more appropriate. The statements in reference 3 that a pair of electrons in a bonding molecular orbital contribute the valence bond energy J and that the aforementioned configuration interaction is a second-order effect are individually incorrect and mutually inconsistent. Molecular orbitals cease to exist when such configuration interactions are important, so that the practice of arbitrarily assigning valence bond energies to these configurations cannot possibly give relations between the two descriptions. Extensions of this procedure to three-electron bonds and antibonds are certain to yield significant errors. (See the text and appendix B.)

Another difficulty with the notation and electronic states of reference 3 is the apparent confusion in some expressions of the meaning of the $+$ and $-$ superscripts on the π-orbitals. Vanderslice, Mason, and Maisch clearly adopt the convention used in the present paper of letting these superscripts represent the reflection symmetries of the orbitals with respect to a plane containing the molecular axis, which is by far the most convenient interpretation for the geometrical and overlap considerations so essential for the subsequent applications of the approximation of perfect pairing. In some states, however, these authors seem to inadvertently change this convention to one in which the same superscripts refer to the two different senses of rotation of a single electron about the molecular axis. For example, their configuration for the a $^1\Sigma_g^+$ state can be expressed (π-electrons only) as

$$\left(u^+ \, u^- \, g^+ \middle| u^+ \, u^- \, g^-\right)$$

which does not produce a Σ^+ state unless the orbitals are defined by the angular momentum eigenfunction relations

$$u^{\pm} = 2^{-1/2}\left(\pi_u^+ \pm i\pi_u^-\right) \tag{A1}$$

and

$$g^{\pm} = 2^{-1/2}\left(\pi_g^+ \pm i\pi_g^-\right) \qquad \text{(A2)}$$

The left-hand and right-hand sides of equations (A1) and (A2) invoke the two different superscript conventions.

According to references 6 and 7, the complete wave function for the a $^1\Sigma_g^+$ state near the equilibrium separation is given by

$$2^{-1/2}\left[\left(u^+ \; u^- \; g^+ \middle| u^+ \; u^- \; g^-\right) + \left(u^+ \; u^- \; g^- \middle| u^+ \; u^- \; g^+\right)\right]$$

so that the electron configuration becomes

$$a\,{}^1\Sigma_g^+ \; : \; 2^{-1/2}\left(\sigma_g\right)^2\left[\left(\pi^+\right)^4\left(\pi_u^-\right)^2 + \left(\pi_u^+\right)^2\left(\pi^-\right)^4\right] \qquad \text{(A3)}$$

with the aid of equations (A1) and (A2). A second $^1\Sigma_g^+$ state considered in these references is

$$^1\Sigma_g^+ \; : \; 2^{-1/2}\left[\left(u^+ \; g^+ \; g^- \middle| u^- \; g^+ \; g^-\right) + \left(u^- \; g^+ \; g^- \middle| u^+ \; g^+ \; g^-\right)\right]$$

$$\rightarrow 2^{-1/2}\left(\sigma_g\right)^2\left[(\pi^+)^4\left(\pi_g^-\right)^2 + \left(\pi_g^+\right)^2(\pi^-)^4\right] \qquad \text{(A4)}$$

the interaction of which with expression (A3) gives

$$a\,{}^1\Sigma_g^+ \; : \; 2^{-1/2}\left(\sigma_g\right)^2\left[(\pi^+)^4(\pi^-)^2 + (\pi^+)^2(\pi^-)^4\right] \qquad \text{(A5)}$$

for the inner regions of the potential tail.

Hence, the configuration interaction which Vanderslice, Mason, and Maisch neglect, at least verbally, is responsible for the destruction of π-molecular orbitals and the introduction of valence bond concepts in a completely systematic way. The arbitrary assignment of valence bond energies to molecular orbitals can only lead to confusion and incorrect extrapolations to more complicated systems; it can never explain the basic process.

Expressions (A3) and (A5) are identical with the third and second steps, respectively, of expression (78), the first step of which corresponds to an additional configuration interaction to replace $\left(\sigma_g\right)^2$ with $(\sigma)^2$ at larger internuclear separations. Molecular orbitals persist at longer ranges for σ-electrons because of greater overlap. The vast differences between the electron configuration of expression (A5) and that given in reference 3 for the a $^1\Sigma_g^+$ state are caused primarily by the aforementioned misinterpretation of + and - superscripts on π-orbitals.

Similar studies of the bound $^1\Delta_g$, X $^3\Sigma_g^-$, A $^3\Sigma_u^+$, $^3\Delta_u$, and $^1\Sigma_u^-$ states yield the same conclusions and show configurations based on references 6 and 7 to be identical with one or more steps of expressions (76), (79), (84), (85), and (86).

APPENDIX B

THREE-ELECTRON ENERGIES

As mentioned in the text and discussed more fully in reference 4, Vanderslice, Mason, and Maisch (ref. 3) have proposed a formal technique for extrapolating two-electron energies to three-electron configurations. The essential feature of the method is the assignment of valence bond energies to single electrons, all reference to electron pairs being eliminated. Although correct energies can be obtained in this manner for two- and four-electron bonds and antibonds, the procedure is artificial because it overlooks in its verbal description, but not in its energy assignments, the important correlation effects that keep electrons apart. Hence, the same energies applied to singly occupied molecular orbitals (as in one- or three-electron σ and π configurations) impose correlation effects which do not exist in such examples.

The mathematical and conceptual consequences of imposing nonexistent correlation effects on the electron energies of singly occupied molecular orbitals are severe. No longer can the helium molecule-ion form a stable state, nor do the long-range attractive and repulsive potential tails of the hydrogen molecule-ion appear as approximate mirror images of each other across the dissociation asymptote if the interaction energies $J/2$ and $-3J/2$ of reference 3 are assigned to individual electrons. Magnitudes of molecular orbital interaction energies are changed from dependencies on overlap integrals between atomic functions to dependencies on squares of overlap integrals by the introduction of nonexistent correlation effects. Theories which ignore such distinctions cannot possibly apply to molecules (for example, oxygen) in which not all σ and π configurations are comprised of even numbers of electrons.

True correlation effects in two-electron bonds are gradually dissipated as the internuclear separation is decreased from the regions of the potential tails considered both in this paper and in reference 3. Simultaneously, the configuration interactions that cause the correlation effects and produce $(\sigma)^2$ from $(\sigma_g)^2$ and $(\sigma_u)^2$, for example, also dissipate and thereby lead to the full recovery of molecular orbital descriptions. Each electron now traverses the molecule more or less independently of the other and, except for the comparatively small Coulomb interactions between them, can be assigned single-electron molecular orbital energies. Only for such intermediate-to-small internuclear separations is the one-electron bond strength approximately half that of the two-electron system. Vanderslice, Mason, and Maisch's extrapolation of this result to larger separations is not valid because the advent of configuration interactions and associated correlation effects makes the two-electron bond energies proportional to squares of overlap integrals instead of the direct proportionalities characteristic of one- and three-electron configurations; hence, the two-electron bond is actually weaker than the one-electron bond in the regions of potential tails. Crossings of one- and two-electron bond energies must occur as the distance increases from equilibrium separations.

Two-electron antibonds, on the other hand, are always best described by valence bond theory because of the equivalence of

$$(a+b \quad a-b)$$

to

$$(a \quad b)$$

Correlation effects persist in this example at all internuclear separations; consequently, the assignments in reference 3 of different energies to the electrons presumably occupying different molecular orbitals is fictitious. Neither electron acts independently of the other and therefore the behavior and properties of neither electron can be compared with the situation prevailing when the other electron is absent.

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TABLE I.- INTERACTION POTENTIALS FOR $O(^3P)$ - $O(^3P)$ COLLISIONS

Molecular state	ϕ (present paper)	ϕ (ref. 3)
$^5\Delta_g$	$-\left(J_\sigma + \frac{3}{2}J_\pi\right)$	$-\left(J_\sigma + 3J_\pi\right)$
$^5\Pi_g$	$-J_\pi$	$-\frac{1}{2}\left(J_\sigma + 3J_\pi\right)$
$^5\Pi_u$	$-J_\pi$	$-\frac{5}{2}\left(J_\sigma + \frac{3}{5}J_\pi\right)$
$b\ ^5\Sigma_g^+$	$-2\left(J_\sigma + \frac{5}{2}J_\pi\right)$	$-2\left(J_\sigma + J_\pi\right)$
$a\ ^5\Sigma_g^+$	$-J_\sigma$	$-\left(J_\sigma + 3J_\pi\right)$
$^5\Sigma_u^-$	$-J_\sigma$	$-\left(J_\sigma + J_\pi\right)$
$^3\Delta_u$	$-J_\pi$	$J_\sigma - 3J_\pi$
$^3\Pi_g$	0	$-\frac{1}{2}\left(J_\sigma + 3J_\pi\right)$
$^3\Pi_u$	0	$-\frac{1}{2}\left(J_\sigma - J_\pi\right)$
$b\ ^3\Sigma_u^+$	$-2\left(J_\sigma + J_\pi\right)$	$-\left(J_\sigma + J_\pi\right)$
$A\ ^3\Sigma_u^+$	0	$J_\sigma - 3J_\pi$
$X\ ^3\Sigma_g^-$	0	$J_\sigma - J_\pi$
$^1\Delta_g$	$J_\sigma - \frac{1}{2}J_\pi$	$J_\sigma - J_\pi$
$^1\Pi_g$	J_π	$-\frac{1}{2}\left(J_\sigma + 3J_\pi\right)$
$^1\Pi_u$	J_π	$-\frac{1}{2}\left(J_\sigma - J_\pi\right)$
$b\ ^1\Sigma_g^+$	$-2\left(J_\sigma - \frac{1}{2}J_\pi\right)$	$-2\left(J_\sigma - J_\pi\right)$
$a\ ^1\Sigma_g^+$	J_σ	$J_\sigma - J_\pi$
$^1\Sigma_u^-$	J_σ	$J_\sigma - 3J_\pi$

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