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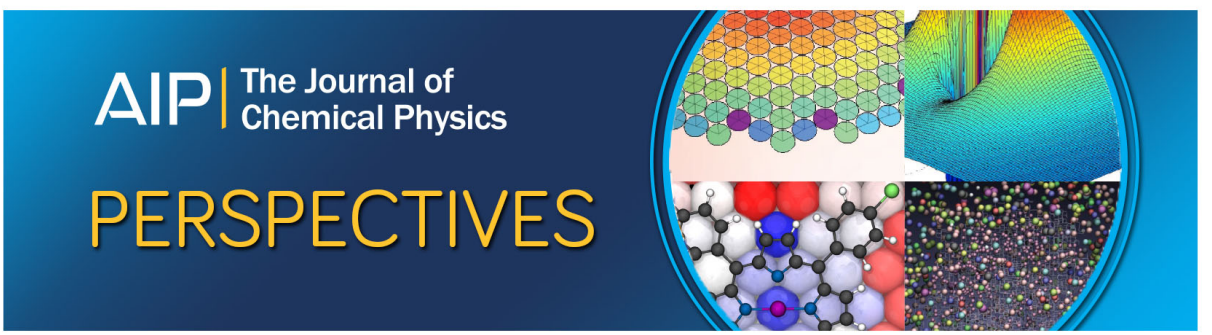

Electronic Energy Levels of Molecular Oxygen*†

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A configuration interaction study of the lower-lying electronic energy levels of molecular oxygen is made. With the 1*s* and 2*s* shells kept filled, the remaining eight electrons are distributed among the twelve spin-orbitals arising from the 2*p* levels on each atom. The atomic functions are represented as Gaussians, which are poor atomic functions but facile integrands in many-center integrals. The molecular orbitals are formed as symmetrical linear combinations of the atomic orbitals, simply for convenience. Inclusion of all configurations implies complete equivalence of all possible constructions of linear combinations.

Out of the 495 configurations (many-electron determinants) a group of nine states of $^3\Sigma_g^-$ character is set up and twelve of $^1\Sigma_g^+$ character. The interaction matrix of each block is computed and diagonalized (by electronic computer). The results for the ground state, which is a triplet, are very good. The binding energy is off by 2 percent, the internuclear distance is off by 1 percent, the fundamental nuclear vibration frequency is off by 4 percent. The lowest singlet state is not given as accurately.

The energies and wave functions for the lowest triplet and singlet are calculated and compared for various values of internuclear separation. Discussion is made of the validity of single configuration theory, from both the Heitler-London and Hund-Mulliken points of view.

I. INTRODUCTION

THE modern theory of molecules, as that of atoms and solids, is based on the one-electron approximation developed along lines characterized as orbital theory. The theory recognizes the electron-nucleus interaction as the dominant potential energy term in the Hamiltonian, for without it there could be no bonded structure, and it assumes a degree of dominance sufficient to justify an independent particle description of the many-electron system. In this way models are developed wherein each electron is assigned to an individual orbital and the wave function of the entire system is constructed as a product of the individual one-electron functions. There are two ways to use this concept of orbitals; one procedure cannot be more than a one-electron approximation, the other has the theoretical possibility of converging to the true solution of the many-electron Schrödinger equation. The first procedure, which can be typified by the name of Hartree-Fock, attempts to arrive at the best possible orbitals to be used in a single product-function. The other procedure, a configuration interaction study, looks for an optimum decomposition of the molecular wave function into a set of manageable and physically understandable product-functions. This paper covers an investigation of the lower-lying electronic energy levels of molecular oxygen expressed in terms of configuration interaction. The electron orbitals are fixed functions but there are enough so that the state of the molecule can be represented as a linear combination of certain configurations.

II. CONFIGURATION THEORY

This is the general program. We begin with a set of N single-particle functions $u_i(\bar{x})$. The symbol $\bar{x}$ stands for the spatial coordinates and a spin coordinate. With a spin-free Hamiltonian, a u_i can be taken as a product of a spatial function and a spin function

$$u_i(\bar{x})=\varphi_i(x)\begin{cases}\alpha\\ \beta\end{cases},$$

where x denotes the three spatial coordinates, α indicates that the z component of spin is $+\frac{1}{2}$, and β indicates that the z component of spin is $-\frac{1}{2}$. It will be shown later that there is no loss of generality in assuming the φ's form an orthonormal set.

The next step is the selection of $n(n\leqslant N)u_i$'s and the assignment of n electrons to this subset. There are $N!/n!(N-n)!$ possible selections. Each selection defines a product wave function which is to be antisymmetrized in accordance with the exclusion principle and which can be concisely written as

$$\psi=(n!)^{-\frac{1}{2}}\det\{u_1(1)u_2(2)\cdots u_n(n)\}.$$

The n tuple in the brackets is the diagonal row of the determinant; it specifies the particular configuration.

The final step is to diagonalize the Hamiltonian in the finite dimensional space spanned by the $N!/n!(N-n)!$ configurations. If N were infinite and the u_i's formed a complete set, this procedure would yield a rigorous solution to the wave equation. With a finite N, we must hope that the configurations used are the most influential ones of a complete set. This is the practical problem. Towards its solution the criterion for best one-electron orbitals should be established. This criterion will not be derived in this paper. However, it is possible to do oxygen to an extent whose complete correspondence in other molecules would be untractable. Examination of the oxygen wave functions may allow some judgment as to what types of configurations are the most important ones.

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III. THE ATOMIC CORRESPONDENCE

A measure of the extent of configuration interaction considered can be seen in the atomic level system at infinite separation. A classification of molecular states must become a classification of atomic states at infinite internuclear separation or, going in the other direction, a molecular state is seen to arise from a superposition and consequent interaction of atomic configurations. In orbital theory we effect this atomic correspondence by constructing molecular orbitals as linear combinations of atomic orbitals.[1] At this point, it is well to review a basic theorem.

If $u_i(\bar{x})$ $(1 \leqslant i \leqslant N)$ is a set of N independent functions and $v_j(\bar{x})$ $(1 \leqslant j \leqslant N)$ is a set whose members are linear combinations of the first set,

$$v_j = \sum_i c_{ij} u_i$$

then the entire set of $N!/n!(N-n)!$ configurations formed with the u_i's as elements is equivalent to the entire set of $N!/n!(N-n)!$ configurations formed with the v_j's as elements. The same energy levels will be derived with either representation. Neither representation can describe the system more completely than the other.[2]

With the freedom guaranteed by the equivalence theorem, the uncombined atomic orbitals themselves may be chosen as molecular orbitals, to form what might be called the primitive set. The calculations can be simplified, usually, by orthogonalizing and symmetrizing the primitive set according to the geometry of the molecule, but it must be understood that although the new representation may be more diagonal, it cannot be more complete.

The primitive set will asymptotically describe atomic states of varying degrees of excitation and ionicity. In general one would have to neglect many high-lying atomic states in order to carry out the calculation. For oxygen we are fortunate in that the obvious selection of atomic orbitals, and all the configurations thereby implied, does not lead to an insurmountable number of configurations. By the obvious selection we mean that set indicated by the normal atomic configuration, $1s^2 2s^2 2p^4$. These twenty functions can be taken as the primitive set for the oxygen molecule,

$$1s\begin{cases}\alpha \\ \beta\end{cases} \quad 2s\begin{cases}\alpha \\ \beta\end{cases} \quad 2p_0\begin{cases}\alpha \\ \beta\end{cases} \quad 2p_+\begin{cases}\alpha \\ \beta\end{cases} \quad 2p_-\begin{cases}\alpha \\ \beta\end{cases}.$$

A set of ten for each atom.[3] At infinite separation we will recognize normal, excited, singly ionized, and doubly ionized oxygen atoms. Actually, only those configurations in which the $1s$ and $2s$ shells are filled will be considered. It is perhaps more honest to say that the primitive set consists of the twelve $2p$ orbitals into which we will assign eight electrons in 495 possible ways.

IV. THE HEITLER-LONDON AND HUND-MULLIKEN APPROXIMATIONS

Expectation of the Present Calculation

Before setting up the full configuration interaction, we would like to review the two standard single configuration approximations, mainly to establish a background for our results. The well-known Heitler-London and Hund-Mulliken schemes are attempts to represent a molecular state as a single configuration. Each is outfitted with an ordered set of wave functions and, starting at the bottom level, electrons are assigned until all the electrons are accounted for. The Heitler-London, sometimes expanded into the valence-bond, configuration describes each electron fixed in its aboriginal atomic state, an approximation accurate only at large separations. The Hund-Mulliken[4] method has an electron distributed equally about each nucleus in a simple type of molecular orbital patterned after the rigorous solution to the hydrogen molecule ion. A Hund-Mulliken configuration is valid for small internuclear distances. It describes strong overlapping of the atoms, and it does not separate into unmixed atomic states at infinite separation.

According to the Heitler-London picture, electrons are paired off with opposite spins. The combination of two normal oxygen atoms should yield a singlet ground state for the molecule (zero-resultant spin). This is just not so. The ground state of the oxygen molecule is a triplet state (one unit of total spin angular momentum). The Hund-Mulliken assignment takes better advantage of p orbital degeneracy. There are two standard molecular orbital levels for each of the atomic p levels. The lowest level is p_0 like and it is filled with two electrons of opposite spin. The other p_0 like level is not next in line; it lies above the $+$ and $-$ levels. Therefore, the next two electrons go into a p_+ level, the next two go into the equivalent p_- level, and the remaining two have a choice of four space-spin positions on the $+$ and $-$ level. Hund's rule, used as in atomic structure, decrees that the state of highest spin should be lowest.

This is a rather sketchy outline of what happens with the two approximations. Nevertheless, disagreement exists and is stimulus for the study of the complete system of configurations. We shall extract, in significant detail, the lowest triplet state and its competing singlet state. Projection of the proper combination of configurations upon the frameworks of the two simple approximations should reveal the domain of

[1] W. Moffitt [Proc. Roy. Soc. (London) **210**, 224 (1951)] maintains that this is too drastic a step and an unnecessary one at this stage. We will return to his criticism at the conclusion of this paper.

[2] Appendix I contains a proof of this theorem.

[3] The functions will be given analytically later on. The notation of 0, $+$, $-$ signifies the component of orbital angular momentum about the internuclear axis as either 0, $+1$, or -1.

[4] The Hund-Mulliken method is often referred to simply as "the molecular orbital method." In this article a molecular orbital is a wave function used in a molecular problem, not necessarily a symmetry orbital. Perhaps we should call the Hund-Mulliken type "standard molecular orbitals."

validity of each and the mode of accommodation of the inappropriate technique to the region belonging to the other. Such an analysis of the wave functions of paramagnetic oxygen should be useful in the study of ferromagnetic solids, for the degeneracies inherent in the oxygen problem approach those involved in the bonding of d-shell electrons.

We will now go on to the computation, returning to the choice of atomic functions.

V. THE ATOMIC FUNCTIONS

A computational detail which presents a major hurdle in this type of problem is the evaluation of many-center integrals. Overlap, kinetic energy, electronic interaction integrals between numerical or simple exponential types of atomic orbitals are very difficult to carry out. At the time this work was begun very few had been explicitly calculated, although much recent work has been done.[5] A suggestion of Boys definitely relieved the situation of any element of impracticability with respect to getting integrals done.[6] Boys demonstrated the simple evaluation of many-center integrals between atomic functions which are Gaussian exponentials

$$x^l y^m z^n \exp(-ar^2).$$

In fact, denoting the various origins of the problem (i.e., positions of the nuclei) by

$$A_x A_y A_z$$
$$B_x B_y B_z, \text{ etc.}$$

and letting

$$x_A = x - A_x \qquad K = -\nabla^2$$
$$aA = \exp(-ar^2) \qquad V_c = 2/r_c$$
$$M = 2/r_{12},$$

then these integrals are given in the paper

$(aA\|bB)$	overlap
$(aA\|K\|bB)$	kinetic energy
$(aA\|V_c\|bB)$	nuclear framework
$(aA^{(1)}bB^{(1)}\|M\|cC^{(2)}dD^{(2)})$	electronic interaction.

The advantage of the method is that integrals involving non-s like functions ($z_A \exp(-ar^2)A$ is a p function) can be obtained from those given in the paper by differentiation. To bring down a z_A into the integrand of an integral here, differentiate with respect to A_z and divide by $2a$.

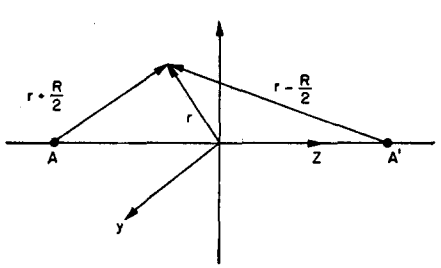


FIG. 1. Coordinate system.

The Gaussians are not the best representations of atomic functions, but that is the point. The proper adjustment of molecular levels will come about not so much from a choice of really good atomic orbitals, but rather from a full perturbation procedure applied to the great number of degenerate molecular functions.

Specifically then, the atomic functions used are

$$1s \rightarrow \exp(-ar^2)$$
$$2s \rightarrow \exp(-br^2) - \gamma \exp(-ar^2)$$
(made orthogonal to the $1s$)
$$2p \rightarrow \begin{Bmatrix} x+iy \\ z \\ x-iy \end{Bmatrix} \exp(-br^2).$$

The energy of an atomic $1s^2$ ($Z=8$) configuration was minimized to get the half-width or a factor for the $1s$ function. As a check, the overlap integral between the two $1s$ functions was evaluated and compared with the corresponding integral in which the standard simple exponential was used. It was demanded that the integrals drop to half their zero separation values at the same point of internuclear separation. The a factor fitted the check nicely.

The b factor of the $2p$ function was determined by a correspondence between overlap integrals. The (p_0, p_0) overlap integral using Gaussians was made to go through zero at the same point that the integral using the simple exponential function does. The final choices are

$$a = 20$$
$$b = 0.8.$$

VI. THE MOLECULAR ORBITALS AS LINEAR COMBINATIONS OF ATOMIC ORBITALS

There are an infinite number of ways to orthonormalize a set of independent functions. Because of the equivalence theorem, we know that in the long run it will make no difference how we do it. The run will be all the more pleasant, however, if we design the molecular orbitals so that the symmetry properties of the determinantal functions will be either obvious or easily discernible.

The Hamiltonian and the coordinate system follow:[7]

$$H = \sum_{i=1}^{16} -\nabla_i^2 - \sum_i \frac{2Z}{|\mathbf{r}_i - \frac{1}{2}R|} - \sum_i \frac{2Z}{|\mathbf{r}_i + \frac{1}{2}R|} + \sum_{i<j} \frac{2}{r_{ij}} + \frac{2Z^2}{R}.$$

Figure 1 is meant to show that the origin is located midway between the two identical nuclei, the z axis lies along the internuclear axis, the internuclear distance is R. Hereafter, we shall distinguish atomic orbitals located on the different nuclei by means of the prime symbol. The following is the notation for the normalized

[5] For a bibliography see C. C. J. Roothaan, J. Chem. Phys. **19**, 1445 (1951).

[6] S. F. Boys, Proc. Roy. Soc. (London) **200**, 542 (1950).

[7] The unit of distance is the Bohr radius $a_0 = 0.5293$A. The unit of energy is the hydrogen atom ionization energy $e^2/2a_0 = 13.602$ ev.

atomic functions:

$$s=(\pi/2a)^{-\frac{3}{4}}\exp[-a(r+\tfrac{1}{2}R)^2]$$
$$s'=(\pi/2a)^{-\frac{3}{4}}\exp[-a(r-\tfrac{1}{2}R)^2]$$
$$\sigma=(\pi/2b)^{-\frac{3}{4}}\exp[-b(r+\tfrac{1}{2}R)^2]$$
$$\sigma'=(\pi/2b)^{-\frac{3}{4}}\exp[-b(r-\tfrac{1}{2}R)^2]$$
$$p_0=2(b)^{\frac{1}{2}}(\pi/2b)^{-\frac{3}{4}}(z+\tfrac{1}{2}R)\exp[-b(r+\tfrac{1}{2}R)^2]$$
$$p_0'=2(b)^{\frac{1}{2}}(\pi/2b)^{-\frac{3}{4}}(z-\tfrac{1}{2}R)\exp[-b(r-\tfrac{1}{2}R)^2]$$
$$p_\pm=(2b)^{\frac{1}{2}}(\pi/2b)^{-\frac{3}{4}}(x\pm iy)\exp[-b(r+\tfrac{1}{2}R)^2]$$
$$p_\pm'=(2b)^{\frac{1}{2}}(\pi/2b)^{-\frac{3}{4}}(x\pm iy)\exp[-b(r-\tfrac{1}{2}R)^2].$$

Now there are certain dynamic and symmetry operators which commute with the Hamiltonian. Configurations can be grouped into sets which are eigenfunctions of these operators and between sets of different character there will be no matrix component of the Hamiltonian. The operators are total spin, z component of total spin, z component of total orbital angular momentum, inversion of all electronic coordinates through the origin, and reflection of all the electronic coordinates through a plane containing the molecular axis. We have combined the atomic orbitals into molecular orbitals of definite axial angular momentum and definite parity (inversion character). They are

$$\varphi_s=\frac{1}{\sqrt{2}}(s+s')\qquad \chi_s=\frac{1}{\sqrt{2}}(s-s')$$
$$\varphi_\sigma=\frac{N}{\sqrt{2}}\{(\sigma+\sigma')+A(s+s')\}$$
$$\chi_\sigma=\frac{P}{\sqrt{2}}\{(\sigma-\sigma')+D(s-s')\}$$
$$\varphi_0=\frac{M}{\sqrt{2}}\{(p_0-p_0')+B(\sigma+\sigma')+C(s+s')\}$$
$$\chi_0=\frac{J}{\sqrt{2}}\{(p_0+p_0')+E(\sigma-\sigma')+F(s-s')\}$$
$$\varphi_\pm=\frac{L}{\sqrt{2}}(p_\pm+p_\pm')$$
$$\chi_\pm=\frac{K}{\sqrt{2}}(p_\pm-p_\pm').$$

They can easily be shown to satisfy the following behavior tablulation:

Under inversion	Axial reflection (yz plane)
$\varphi_s\leftrightarrow\varphi_s$	$\varphi_s\leftrightarrow\varphi_s$
$\varphi_\sigma\leftrightarrow\varphi_\sigma$	$\chi_\sigma\leftrightarrow\chi_s$
$\varphi_0\leftrightarrow\varphi_0$	$\varphi_\sigma\leftrightarrow\varphi_\sigma$
$\chi_s\leftrightarrow-\chi_s$	$\chi_\sigma\leftrightarrow\chi_\sigma$
$\chi_\sigma\leftrightarrow-\chi_\sigma$	$\varphi_0\leftrightarrow\varphi_0$
$\chi_0\leftrightarrow-\chi_0$	$\chi_0\leftrightarrow\chi_0$
$\varphi_\pm\leftrightarrow-\varphi_\pm$	$\varphi_+\leftrightarrow-\varphi_-$
$\chi_\pm\leftrightarrow\chi_\pm$	$\chi_+\leftrightarrow-\chi_-$. (1)

TABLE I. Molecular orbital coefficients.

R	N^2	A	P^2	D
1.5	0.75316	−0.28078	1.80210	−0.19627
2.0	0.87747	−0.24952	1.33989	−0.22753
2.5	0.97632	−0.24048	1.16017	−0.23658
4.0	1.05846	−0.23853	1.06220	−0.23853
6.0	1.06033	−0.23853	1.06033	−0.23853
9.0	1.06033	−0.23853	1.06033	−0.23853
	1.06033	−0.23853	1.06033	−0.23853

R	M^2	B	C	J^2	E	F
1.5	0.89789	−0.38777	−0.00014	5.95571	0.94443	−0.07635
2.0	0.74952	−0.30863	0.03918	2.57830	0.47239	−0.06965
2.5	0.77155	−0.17724	0.03424	1.57892	0.21065	−0.04146
4.0	0.98082	−0.00932	0.00222	1.02004	0.00631	−0.00150
6.0	0.99998	0.00000	0.00000	1.00002	0.00000	0.00000
9.0	1.00000	0.00000	0.00000	1.00000	0.00000	0.00000
	1.00000	0.00000	0.00000	1.00000	0.00000	0.00000

R	L^2	K^2
1.5	0.71095	1.68512
2.0	0.83202	1.25297
2.5	0.92414	1.08942
4.0	0.99834	1.00166
6.0	1.00000	1.00000
9.0	1.00000	1.00000
	1.00000	1.00000

The φ's are already orthogonal to the χ's because of the symmetries. The coefficients are determined by the stipulation that the φ group and the χ group each form an orthonormalized set. Because of the large value of a, the $1s$ functions overlap to an absolutely negligible extent $[\sim\exp(-\frac{1}{2}aR^2)]$ and so the normalization of φ_s and χ_s is independent of R. Things are arranged so that the atomic correspondence is evident. In fact, at infinite separation

$$\varphi_\sigma\to\frac{1}{\sqrt{2}}\{(2s)+(2s)'\}\qquad \chi_\sigma\to\frac{1}{\sqrt{2}}\{(2s)-(2s)'\}$$
$$\varphi_\pm\to\frac{1}{\sqrt{2}}\{(2p)+(2p)'\}\qquad \chi_\pm\to\frac{1}{\sqrt{2}}\{(2p)-(2p)'\}.$$

Table I lists the values of the coefficients at various internuclear distances.

VII. THE MOLECULAR CONFIGURATIONS

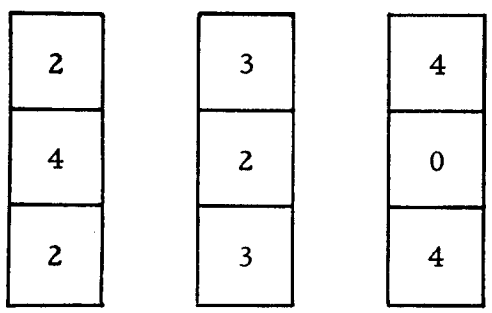
Our orbitals are now fixed and we can begin the assignment of electrons. As stated, the $1s$ and $2s$ shells will be kept filled with eight electrons. The closed shells contribute no spin angular momentum to the molecule, they have even parity, zero axial angular momentum, and are invariant under a reflection operation. We can, therefore, go on to assign the remaining eight electrons to the $2p$ orbitals and classify the molecular configurations without worrying about the inner shells.

Table II begins the cataloguing of states. Each $2p$ level can be filled with a maximum of four electrons; a spin pair can go into the φ orbital and another spin pair can go into the χ orbital. The table exhausts all the possibilities of assignment of eight electrons to the twelve positions.

TABLE II. Possible values of M_L. One-electron angular momentum is denoted by m_l and total axial angular momentum is denoted by M_L. The first three rows of the table indicate the occupation numbers for each level of m_l. The fourth row indicates $M_L=\Sigma_l m_l$.

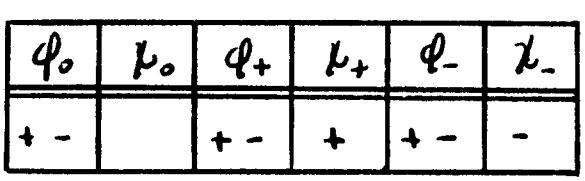
m_l	Number of electrons													
+1	4	4	4	4	4	3	3	3	3	2	2	2	1	1	0
0	4	3	2	1	0	4	3	2	1	4	3	2	4	3	4
−1	0	1	2	3	4	1	2	3	4	2	3	4	3	4	4
M_L	+4	+3	+2	+1	0	+2	+1	0	−1	0	−1	−2	−2	−3	−4

We shall investigate only states of zero total axial angular momentum. The next step is to take the three columns



and expand their possibilities with the details of spin assignment. This has been done in Table III.

Actually, we have only listed states of even total parity, states which transform into themselves under inversion. The parity character of the determinantal function is the product of the individual parity characters. The notational pattern is this: the tabulated electron assignment



stands for the determinant

$$\frac{1}{\sqrt{16!}}\det\{\varphi_s\alpha(1)\varphi_s\beta(2)\chi_s\alpha(3)\chi_s\beta(4)\times\varphi_\sigma\alpha(5)\varphi_\sigma\beta(6)\chi_\sigma\alpha(7)\chi_\sigma\beta(8)\varphi_0\alpha(9)\varphi_0\beta(10)\times\varphi_+\alpha(11)\varphi_+\beta(12)\chi_+\alpha(13)\varphi_-\alpha(14)\times\varphi_-\beta(15)\chi_-\beta(16)\}.$$

Since the closed shells contribute nothing pertinent for classification, we may use the form as a working notation for

$$\sum_P(-1)^p P\cdot\{\varphi_0\alpha(1)\varphi_0\beta(2)\varphi_+\alpha(3)\varphi_+\beta(4)\times\chi_+\alpha(5)\varphi_-\alpha(6)\varphi_-\beta(7)\chi_-\beta(8)\},$$

where P runs over the 8! permutations of the 8 variables and p is the number of interchanges that must be made to obtain the permutation from the standard arrangement.

The interconnections of the various configurations by reflection in an axial plane are shown in the eighth column. The molecular orbital behavior table (Eqs. 1) serves as guide; we have only to account for a possible change in the standard arrangement by the proper sign.

The last column indicates the transformation of each configuration under application of the total spin operator.[8] We have recorded the behavior of only one configuration of a connected group. It is sufficient to include only states of total z component of spin equal to zero.

We shall investigate the ${}^3\Sigma_g^-$ and ${}^1\Sigma_g^+$ states. The symbol ${}^3\Sigma_g^-$ denotes a wave function associated with one unit of total spin angular momentum, zero units of total axial angular momentum, an even parity (g) under inversion, and a change of sign (−) under a reflection through an axial plane. It turns out that the ground state of the oxygen molecule will come about from the interaction of nine ${}^3\Sigma_g^-$ states, while the interesting singlet state will be evolved out of twelve ${}^1\Sigma_g^+$ states. These states are set up from an inspection of Table III and are presented in Eqs. 2. At this point we have our set of initial molecular states, states of definite multiplicity and of definite symmetry. The matrix of the Hamiltonian must now be computed and diagonalized,

$$\begin{aligned}
&\psi_a=2^{-\frac{1}{2}}(I^*-I_s^*)\\
&\psi_b=2^{-\frac{1}{2}}(III^*-III_s^*)\\
&\psi_c=2^{-\frac{1}{2}}(I+I_s)\\
&\psi_d=2^{-\frac{1}{2}}(II+II_s)\\
&\psi_e=2^{-\frac{1}{2}}(IX+IX_s) && {}^3\Sigma_g^-\\
&\psi_f=2^{-\frac{1}{2}}(X+X_s)\\
&\psi_g=\tfrac{1}{2}(III-III_s+VII-VII_s)\\
&\psi_h=\tfrac{1}{2}(IV-IV_s+VI-VI_s)\\
&\psi_i=\tfrac{1}{2}(V-V_s+VIII-VIII_s)\\
&\\
&\psi_a=12^{-\frac{1}{2}}(2I^*+2I_s^*-II^*-II_s^*-III^*-III_s^*)\\
&\psi_b=\tfrac{1}{2}(III^*+III_s^*-II^*-II_s^*)\\
&\psi_c=IV^*\\
&\psi_d=VII^*\\
&\psi_e=2^{-\frac{1}{2}}(V^*+VI^*)\\
&\psi_f=2^{-\frac{1}{2}}(I-I_s)\\
&\psi_g=2^{-\frac{1}{2}}(II-II_s) && {}^1\Sigma_g^+\\
&\psi_h=24^{-\frac{1}{2}}(2III+2III_s-2VII-2VII_s-IV\\
&\qquad -IV_s+VI+VI_s-V-V_s+VIII+VIII_s)\\
&\psi_i=8^{-\frac{1}{2}}(V+V_s-VIII-VIII_s-IV-IV_s+VI+VI_s)\\
&\psi_j=2^{-\frac{1}{2}}(IX-IX_s)\\
&\psi_k=2^{-\frac{1}{2}}(X-X_s)\\
&\psi_l=XI. && (2)
\end{aligned}$$

[8] The spin algebra is standard and is reviewed in Appendix II.

TABLE III. Configuration tabulation.

ψ	φ_0	χ_0	φ_+	χ_+	φ_-	χ_-	Refl.	$S^2\psi$
I^*	+ −	+ −	+	+	−	−	I_s^*	$=2I^*+II^*+II_s^*+III^*+III_s^*$
I_s^*	+ −	+ −	−	−	+	+	I^*	
II^*	+ −	+ −	+	−	+	−	II_s^*	
II_s^*	+ −	+ −	−	+	−	+	II^*	
III^*	+ −	+ −	+	−	−	+	III_s^*	
III_s^*	+ −	+ −	−	+	+	−	III^*	
IV^*	+ −	+ −	+ −		+ −		IV^*	$=0$
V^*	+ −	+ −	+ −			+ −	V^*	$=0$
VI^*	+ −	+ −		+ −	+ −		VI^*	$=0$
VII^*	+ −	+ −		+ −		+ −	VII^*	$=0$
I	+ −		+ −	+	+ −	−	$-I_s$	$=I+I_s$
I_s	+ −		+ −	−	+ −	+	$-I$	
II	+ −		+	+ −	−	+ −	$-II_s$	$=II+II_s$
II_s	+ −		−	+ −	+	+ −	$-II$	
III	+	−	+ −	+	−	+ −	$-VII$	$=2III+IV+IV_s+V+V_s$
III_s	−	+	+ −	−	+	+ −	$-VII_s$	
IV	+	−	+ −	−	+	+ −	$-VI$	
IV_s	−	+	+ −	+	−	+ −	$-VI_s$	
V	+	+	+ −	−	−	+ −	$-VIII$	
V_s	−	−	+ −	+	+	+ −	$-VIII_s$	
VI	+	−	+	+ −	+ −	−	$-IV$	$=2VI+VII+VII_s+VIII+VIII_s$
VI_s	−	+	−	+ −	+ −	+	$-IV_s$	
VII	+	−	−	+ −	+ −	+	$-III$	
VII_s	−	+	+	+ −	+ −	−	$-III_s$	
$VIII$	+	+	−	+ −	+ −	−	$-V$	
$VIII_s$	−	−	+	+ −	+ −	+	$-V_s$	
IX		+ −	+ −	+	+ −	−	$-IX_s$	$=IX+IX_s$
IX_s		+ −	+ −	−	+ −	+	$-IX$	
X		+ −	−	+ −	+	+ −	$-X_s$	$=X+X_s$
X_s		+ −	+	+ −	−	+ −	$-X$	
XI			+ −	+ −	+ −	+ −	XI	$=0$

VIII. SETTING UP AND DIAGONALIZING THE MATRIX

To review the formation of the secular equation. For either of the two noninteracting blocks, ${}^3\sum_g^-$ or ${}^1\sum_g^+$, we approximate an eigenfunction by the form

$$\Psi_\mu=\sum_j a_j{}^\mu\psi_j,$$

where ψ_j is one of the orthonormalized states in the set (Eqs. 2). For a given μ, the numbers $a_j{}^\mu$ may be considered a vector with components along the basic set of axes ψ_j. We shall be asking for eigenvectors and eigenvalues by beginning with

$$H\Psi_\mu=E_\mu\Psi_\mu$$

or

$$H\sum_j a_j{}^\mu\psi_j=E_\mu\sum_j a_j{}^\mu\psi_j.$$

A necessary condition for this to hold is that

$$\sum_j a_j{}^\mu H_{ij}=E_\mu\sum_j a_j{}^\mu\delta_{ij}$$

this being the result of multiplying on both sides by $\psi_i{}^*$ and integrating over all the electronic coordinates, including spin. Interpreting our symbols as matrices and vectors, we may rewrite the last equation as

$$\mathbf{H}\mathbf{a}^\mu=E_\mu\mathbf{a}^\mu.$$

We are to form the matrix of our Hamiltonian between the initial set of configurations. Its eigenvalues are the electronic energy levels; the corresponding eigenvectors are the representations of the electronic wave functions in terms of the initial set of configurations.

The integrals over determinantal functions were reduced to sums of one- and two-electron integrals in the usual way.[9] In this process, one must keep track of the relations between standard arrangements. The all important question of signs depends upon the definitions of standard arrangements. A standard arrangement is a flexible thing, more or less a question of taste, but we have tempered this flexibility by connecting the configurations through symmetry operations. In arranging two configurations in an integral, correlation must be maintained with the "fundamental" standard arrangements listed in Table III.

The inner shell electrons contribute to the diagonal energies in a nontrivial way. First, there is the interaction of the $1s$ and $2s$ electrons among themselves and with the nuclear framework; this energy being the same for each diagonal element, although varying with internuclear distance. The second contribution comes from the interaction of the $2p$ electrons with the inner shell and differs from one state to the other. The φ_0 and χ_0 orbitals are distinguished from the others by the core at finite separation.

Finally, as a computational aid, we mention certain inequalities useful in checking integrals. Roothaan[10] has derived some which are important from both a theoretical and a computational point of view and these are presented in Appendix III along with a new one which brings in the so-called "hybrid" integrals.

[9] J. C. Slater, *Quantum Theory of Matter* (McGraw-Hill Book Company, Inc., New York, 1951) first edition, p. 192.
[10] C. C. J. Roothaan, Revs. Modern Phys. **23**, 69 (1951).

TABLE IV. Tabulation by space orbital.

	$^3\Sigma_g^-$				$^1\Sigma_g^+$			
a	σ_g^2	π_u^2	π_g^2	σ_u^2	σ_g^2	π_u^2	π_g^2	σ_u^2
b	σ_g^2	π_u^2	π_g^2	σ_u^2	σ_g^2	π_u^2	π_g^2	σ_u^2
c	σ_g^2	π_u^4	π_g^2	$\cdots$	σ_g^2	π_u^4	$\cdots$	σ_u^2
d	σ_g^2	π_u^2	π_g^4	$\cdots$	σ_g^2	$\cdots$	π_g^4	σ_u^2
e	$\cdots$	π_u^4	π_g^2	σ_u^2	σ_g^2	π_u^2	π_g^2	σ_u^2
f	$\cdots$	π_u^2	π_g^4	σ_u^2	σ_g^2	π_u^4	π_g^2	$\cdots$
g	σ_g	π_u^3	π_g^3	σ_u	σ_g^2	π_u^2	π_g^4	$\cdots$
h	σ_g	π_u^3	π_g^3	σ_u	σ_g	π_u^3	π_g^3	σ_u
i	σ_g	π_u^3	π_g^3	σ_u	σ_g	π_u^3	π_g^3	σ_u
j	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	π_u^4	π_u^2	σ_u^2
k	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	π_u^2	π_u^4	σ_u^2
l	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	π_u^4	π_u^4	$\cdots$

Diagonalization of high accuracy was performed by Whirlwind, the M.I.T. high-speed electronic digital computer. Using an 8-decimal digit capacity, the machine guaranteed 7 digits in the eigenvalues and about 4 in the eigenvectors. Actually, it is unfair to talk so of the accuracy in the eigenvectors. One might interpret the variation theorem as the statement that an eigenvector need, possibly can, only be determined to about half the digital accuracy of the corresponding eigenvalue. In any case, we can now proceed to the presentation and discussion of results.

IX. RESULTS

Eigenvalues

Table III is a rather too detailed specification of the configurations. It is sufficient and perhaps less confusing to tabulate the states as in Table IV. Here, all that is specified is the space orbital assignment. In fact, only the absolute value of the orbital angular momentum is indicated. (A molecular orbital is symbolized by a Greek small script letter (σ, π, δ, $\cdots$) to indicate the absolute value of the axial angular momentum (0, 1, 2, $\cdots$) and a subscript (g or u) to indicate even or odd parity.) The specified character of the states dictates how spin and orbital motion directions are to be assigned and the determinants grouped.

The triplet state labeled c is the one that would be used in single configuration theory. It represents the Hund-Mulliken approximation described above. Similarly, the singlet state labeled f would be taken as the first approximation to the higher-state of the molecule. Hund's rule finds expression in the matrix where the diagonal energy of the triplet is indicated to be less than that of the singlet by twice the value of an exchange integral.[11] The exchange integral is positive and does not vanish at infinite separation. This persistent energy difference between the singlet and triplet states is one aspect of the incompleteness of single configuration theory. The problem is to maintain the order of states at molecular distances while allowing both states to decompose into two normal oxygen atoms at infinite separation.

Though single configuration theory is wrong at large distances, it is often used for calculations of the dissociation energy. Table V lists the diagonal matrix elements of state c and state f as functions of internuclear distance. The equilibrium separation of oxygen is 2.28 atomic units, and the dissociation energy is 0.3735 atomic units.[12] State c is a miserable representation of actuality. It might very well be argued that the use of Gaussians distorts the theory considerably. Accepting this, it is really quite heartening to see what configuration interaction will do. Table VI lists the energy levels which are the eigenvalues of the matrices which describe the configuration interaction. Before discussing the improvement in dissociation energy, let us first point out the continuity from defined atomic states of various degrees of excitation, ionicity, and degeneracy to the set of noninteracting molecular states. The lowest singlet state still lies above the lowest triplet state at large distances. Both rise coincidentally until about 4 atomic units. From here on in, the molecule takes shape; the triplet energy takes a sharp bonding fall and the singlet state lags above it.

To get a better judgment of the predicted binding energies by other than graphical means, Morse curves can be introduced. This has been done for the lowest triplet and the lowest singlet. The energy is expressed as

$$E=A+D[1-e^{-a(R-R_0)}]^2.$$

The four parameters were determined by forcing agreement with the calculated energy values at $R=1.5$, 2.0, 2.5, and 4.0.[13] For the triplet state

$$A=-0.3728$$
$$D=0.5079$$
$$a=1.649$$
$$R_0=2.255$$

and for the singlet state

$$A=-0.2109$$
$$D=0.3205$$
$$a=1.760$$
$$R_0=2.30.$$

A is, of course, the depth of the energy curve which has its minimum at $R=R_0$. The binding, or dissociation,

TABLE V. Single configuration approximation energies.

R	1.5	2.0	2.5	4.0	6.0	9.0	∞
$^3\Sigma_g^-$	2.78263	−0.11554	−0.11205	0.99287	1.26201	1.37476	1.59798
$^1\Sigma_g^+$	3.03784	0.12248	0.11047	1.19632	1.46401	1.57663	1.79983

[11] The formulas for the matrix elements and the numerical material not included in this paper will be available in a technical report of the Solid State and Molecular Theory Group of M.I.T.

[12] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, New York, 1950).

[13] The a in the formula is not related to the a of the atomic orbitals.

TABLE VI. Final energy values.

R	1.5	2.0	2.5	4.0	6.0	9.0	∞	Atomic multiplet
	2.72829	−0.23468	−0.31694	0.08042	0.00149	−0.00007	0.00000	$O\ O\ {}^3P{}^3P$
	6.40877	1.54484	0.83050	0.27940	0.20262	0.20169	0.20185	$O\ O\ {}^3P{}^1D$
	7.76336	2.38823	1.22172	0.30399	0.20344	0.20179	0.20185	$O\ O\ {}^3P{}^1D$
	8.29122	3.01394	1.87352	0.65839	0.50607	0.50456	0.50463	$O\ O\ {}^3P{}^1S$
$^3\Sigma_g^-$	8.78366	3.46764	1.94880	0.97060	1.0196	1.12510	1.34567	$O^+\ O^-\ {}^4S^2P$
	10.4106	4.00478	2.27794	1.2630	1.3133	1.42527	1.64844	$O^+\ O^-\ {}^2D^2P$
	10.5320	4.46958	2.53580	1.2724	1.3224	1.42787	1.64844	$O^+\ O^-\ {}^2D^2P$
	10.9300	4.70011	3.11485	1.5104	1.5160	1.62718	1.85030	$O^+\ O^-\ {}^2P^2P$
	14.4078	6.54955	4.62401	3.9510	4.5439	4.99493	5.88731	$O^{++}O^{--}\ {}^3P{}^1S$
	2.79791	−0.05417	−0.18362	0.07800	0.00147	−0.00004	0.00000	$O\ O\ {}^3P{}^3P$
	2.99230	1.62544	0.96468	0.18686	0.00234	0.00000	0.00000	$O\ O\ {}^3P{}^3P$
	5.73553	1.92591	1.04601	0.45875	0.40500	0.40369	0.40370	$O\ O\ {}^1D{}^1D$
	6.73148	2.46215	1.39478	0.48964	0.40564	0.40370	0.40370	$O\ O\ {}^1D{}^1D$
	6.84833	2.67301	1.52243	0.59051	0.40635	0.40371	0.40370	$O\ O\ {}^1D{}^1D$
$^1\Sigma_g^+$	8.07864	3.79130	1.73972	0.79866	0.70916	0.70657	0.70648	$O\ O\ {}^1S{}^1D$
	9.17578	3.85523	2.21663	1.1319	1.0107	1.00919	1.0093	$O\ O\ {}^1S{}^1S$
	10.5099	4.37816	2.62522	1.2745	1.3133	1.42526	1.64844	$O^+\ O^-\ {}^2D^2P$
	10.6910	4.82006	3.03125	1.4799	1.5159	1.62718	1.85030	$O^+\ O^-\ {}^2P^2P$
	10.7902	5.36583	3.28579	1.5122	1.5243	1.62972	1.85030	$O^+\ O^-\ {}^2P^2P$
	11.8867	6.75097	4.82246	4.2524	4.7679	5.20356	6.08917	$O^{++}O^{--}\ {}^1D{}^1S$
	14.7282	7.01370	5.09405	4.5536	5.0610	5.50306	6.39193	$O^{++}O^{--}\ {}^1S{}^1S$

energy is calculated from A by correcting for the zero-point vibrational energy of the nuclei. The use of a Morse potential leads to the formula for the dissociation energy D_0 as

$$D_0 = A + a(D/\mu)^{\frac{1}{2}} - (a^2/4\mu),$$

where μ is the mass of an oxygen atom, all quantities given in atomic units.[12]

Another interesting quantity that can be calculated from a Morse curve is the fundamental vibrational frequency ω_e, the frequency with which the nuclei would vibrate if the vibration were a simple harmonic one

$$\omega_e = 2a(D/\mu)^{\frac{1}{2}}.$$

Table VII compares the results of this calculation with the experimental values. Figure 2 is a graph of the Morse curves.[14] The triplet state evolved out of the interaction of nine states which take account of the spin and orbital degeneracies is energetically close to the truth, the limit of truth being set by the variation theorem. Going from the single-configuration to many-configuration theory not only netted us an exceedingly good ground-state energy with correct behavior at infinity, but it also yielded a very good curvature to the energy curve. This point is revealed in the agreement in ω_e. In calculations on a solid, single-configuration theory can be made to give excellent energies, but estimates of compressibility are bound to suffer the effects of the rise of the energy curve to a wrong value at large distances.[15] This is illustrated in Fig. 3 which is a plot of the diagonal energy of state c alongside the true energy curve.

The singlet state does not come out so well. The error in binding energy is about 19 percent, the harmonic frequency is very bad. Moffitt's main criticism is directed at calculations on the higher states of a molecule and this investigation perhaps bears him out. The point he makes is that even the comparatively large number of configurations used in a calculation such as this is not a large enough number to yield a decent picture of the energy levels of the separated atoms. In fact, in so far as the atomic levels are concerned, there is no configuration interaction being considered. The single configuration theory, which we have seen to be very poor for the molecule, is also poor for the atom. We have an inaccurate energy scale of the separated atoms and Moffitt maintains that the excitation energies of the higher molecular states with respect to the ground state are badly in error because of this. The results of this investigation indicate that the ground

[14] The author has been warned that some confusion might arise at this point. It is to be remembered that the Morse curve is supposed to represent the results of this calculation only from about $R=4.0$ inward. From $R=4.0$ to $R=\infty$ a continuous curve is drawn which drops down to the axis as demanded by the calculated values at $R=6.0$, 9.0, and ∞. The quantity D_0 is, except for the zero-point correction, the energy difference of the stable molecule and the dissociated atoms. It is this quantity which is experimentally determined by analysis of band spectra. (See Herzberg, reference 12.) The energy of the dissociated atoms is zero on our energy scale. The dotted asymptotic limits of the Morse curves appear in Fig. 2 for purposes of later discussion; they do not represent the molecular dissociation. The full curve does.

TABLE VII. Molecular parameters.

Param.	Exper.	Calc.	Percent error	
R^0	2.28	2.255	1.1	
D_0	−0.3735	−0.3660	2	$^3\Sigma_g^-$
$\omega_e(\text{cm}^{-1})$	1580.4	1503	4.2	
R^0	2.32	2.30	0.9	
D_0	−0.2527	−0.2051	19	$^1\Sigma_g^+$
$\omega_e(\text{cm}^{-1})$	1432.7	1273	11	

[15] P. O. Löwdin, J. Chem. Phys. 19, 1579 (1951).

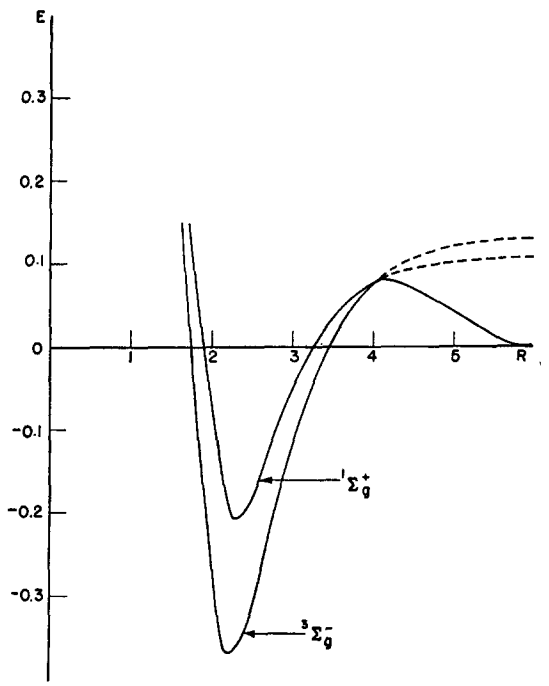


FIG. 2. Morse curve fit to electronic energy.

state itself can be very closely approached even with this inherent fault of the method. As for the higher states, a correction more in the spirit of the calculation than Moffitt's empirical adjustment might be the in-

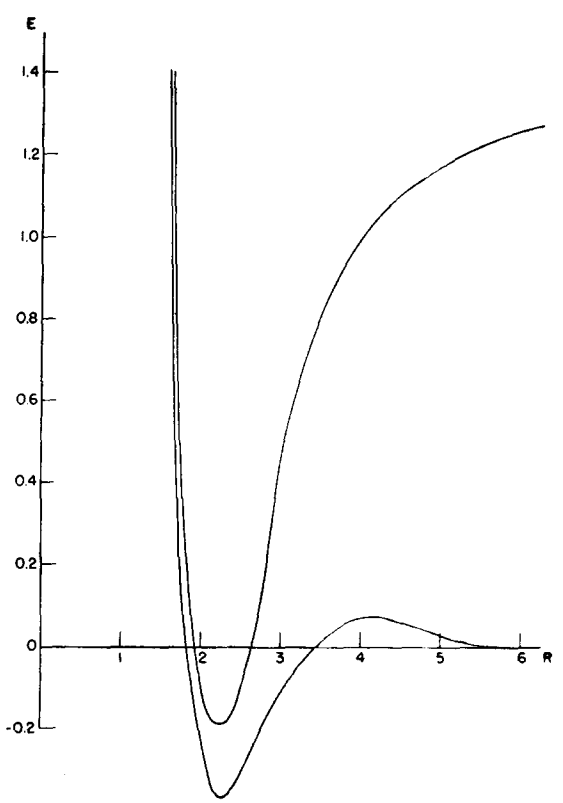


FIG. 3. Single-configuration energy *vs* true energy.

clusion of configurations where the $2s$ electrons, say, were promoted into $2p$ levels. These new configurations need not be treated on equal footing with the other existing ones. That is, perturbation methods might be used to add the little more that is needed.

It is worth while to plot the difference in energy between the singlet and triplet states, as in Fig. 4. This curve is typical of a magnetic competition. The magnetic and nonmagnetic states start out indistinguishable from one another until the magnetic state steeply becomes preferential only to rapidly approach the other state again—perhaps to rise to the unpreferred position—as the internuclear distance decreases.

Eigenvectors

The eigenvectors of the lowest triplet and the lowest singlet states are displayed in Table VIII. (An erratic behavior of the singlet vector at large distances is illusory. The singlet state is doubly degenerate at infinite separation; the computer was somewhat capricious

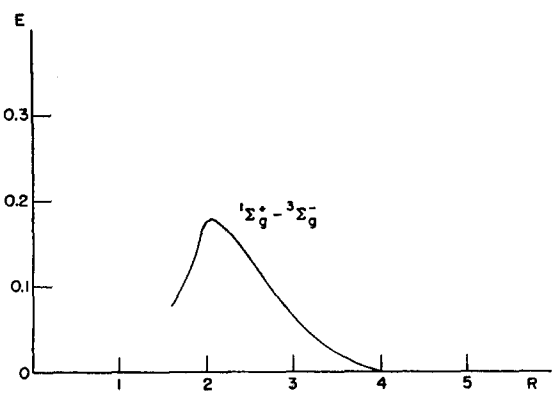


FIG. 4. Triplet-energy difference.

in its choice of ground-state eigenvector at large distances.) From the eigenvectors also, one can see a slow change at large internuclear distance and then the very rapid component readjustment in the molecular region. From $R=4.0$ inward, state c becomes the dominant axis for the triplet and state f predominates for the singlet.

The lack of difference between the triplet and singlet states at large internuclear distances can be shown by transforming to an atomic rather than a molecular representation. At infinite separation we have the eigenvectors which represent the various atomic states. We can express an eigenvector at any other value of internuclear separation as a linear combination of those orthonormal vectors which asymptotically describe the atomic constituents. This has been done in Table IX for the lowest triplet and singlet states. This table would have been the initial table of eigenvectors if orthogonalized atomic functions of the Wannier type had been used instead of the symmetrical molecular orbitals.[16]

[16] For the same type of base transformation applied to the hydrogen molecule and analyzed in detail, see J. C. Slater, J. Chem. Phys. 19, 220 (1951).

TABLE VIII. Ground-state eigenvectors.

R	1.5	2.0	2.5	4.0	6.0	9.0	∞
			$^3\Sigma_g^-$				
a	0.0058	0.0117	0.0240	0.0044	0.0000	0.0000	0.0000
b	0.0055	0.0104	0.0179	0.0077	0.0000	0.0000	0.0000
c	−0.9957	−0.9849	−0.9668	−0.4361	−0.3538	−0.3536	−0.3536
d	0.0475	0.1041	0.1548	0.4005	0.3537	0.3536	0.3536
e	0.0387	0.0646	0.0956	0.3263	0.3534	0.3536	0.3536
f	−0.0047	−0.0182	−0.0455	−0.3161	−0.3534	−0.3536	−0.3536
g	−0.0517	−0.0946	−0.1424	−0.4785	−0.5000	−0.5000	−0.5000
h	−0.0449	−0.0728	−0.0924	0.4626	0.5000	0.5000	0.5000
i	−0.0047	−0.0124	−0.0218	−0.0026	0.0000	0.0000	0.0000
			$^1\Sigma_g^+$				
a	0.0166	−0.0108	−0.0164	0.0148	0.3093	0.4723	0.4269
b	−0.0446	0.0010	−0.0031	−0.0004	0.0003	−0.0001	0.0000
c	−0.9025	−0.0284	−0.0515	−0.0218	−0.2677	−0.4092	−0.3697
d	−0.0070	0.0018	0.0022	−0.0078	−0.2678	−0.4092	0.3697
e	−0.0846	0.0046	0.0130	0.0201	0.3790	0.5784	0.5229
f	0.4167	0.9718	0.9390	0.5035	0.3403	0.1418	0.2254
g	−0.0369	−0.1941	−0.2848	−0.4805	−0.3403	−0.1419	−0.2254
h	0.0262	0.1018	0.1402	0.2423	0.1965	0.0819	0.1301
i	0.0104	0.0264	0.0049	−0.4114	−0.3402	−0.1419	−0.2254
j	−0.0060	−0.0653	−0.1017	−0.3844	−0.3401	−0.1419	−0.2254
k	−0.0022	−0.0240	−0.0569	−0.3724	−0.3401	−0.1419	−0.2254
l	0.0123	0.0331	0.0297	0.0021	0.0000	0.0000	0.0000

With orthogonal orbitals, it is the closest we can get to the projection on the Heitler-London framework promised earlier.

Table IX clearly shows that a single-configuration theory based on orthogonalized atomic functions would have been quite good for large distances. The singlet cannot be distinguished from the triplet. The picture is that of two normal oxygen atoms approaching one another, repelling one another until about 4 atomic units of separation. Excited and ionized states are now to be considered in the formation of the molecular states. At equilibrium separation, the atomic correspondence is completely smeared; any attempt at a perturbation calculation would have to start from the molecular orbital setup. Incidentally, second-order perturbation does not work here. One does not converge to anything like the right value by considering state c as the zeroth-order wave function and computing the energy by a formula such as

$$E=H_{cc}+\sum_k \frac{|H_{ck}|^2}{E-H_{kk}}.$$

There are many other large off-diagonal elements, indirect chains between state c and other states. However, it should be noted that states c, d, e, f, g, and h, which

TABLE IX. Ground-state eigenvectors atomic correspondence.

R	1.5	2.0	2.5	4.0	6.0	9.0	∞
			$^3\Sigma_g^-$				
$O\ O\ ^3P^3P$	0.3875	0.4252	0.4714	0.9934	1.0000	1.0000	1.0000
$O\ O\ ^3P^1D$	0.2539	0.2719	0.2843	0.0437	0.0000	0.0000	0.0000
$O\ O\ ^3P^1D$	0.4179	0.4343	0.4533	0.0333	0.0000	0.0000	0.0000
$O\ O\ ^3P^1S$	0.2098	0.2091	0.2037	0.0062	0.0000	0.0000	0.0000
$O^+\ O^-\ ^4S^2P$	−0.4037	−0.3857	−0.3645	−0.0202	0.0000	0.0000	0.0000
$O^+\ O^-\ ^2D^2P$	−0.0633	−0.0411	−0.0201	0.0276	0.0000	0.0000	0.0000
$O^+\ O^-\ ^2D^2P$	−0.4492	−0.4430	−0.4265	−0.0698	0.0000	0.0000	0.0000
$O^+\ O^-\ ^2P^2P$	−0.3496	−0.3483	−0.3340	−0.0632	0.0000	0.0000	0.0000
$O^{++}O^{--}\ ^3P^1S$	0.2749	0.2112	0.1520	0.0011	0.0000	0.0000	0.0000
			$^1\Sigma_g^+$				
$O\ O\ ^3P^3P$	0.4043	0.2982	0.3467	0.5443	0.9371	0.9772	1.0000
$O\ O\ ^3P^3P$	−0.0098	0.4720	0.5282	0.8305	0.3488	−0.2120	0.0000
$O\ O\ ^1D^1D$	0.2342	−0.1169	−0.1019	−0.0018	−0.0005	0.0002	0.0000
$O\ O\ ^1D^1D$	0.3305	0.1275	0.1181	−0.0020	−0.0003	0.0002	0.0000
$O\ O\ ^1D^1D$	−0.1844	−0.3394	−0.3363	−0.0227	0.0001	0.0000	0.0000
$O\ O\ ^1S^1D$	−0.1647	−0.1001	−0.1019	−0.0019	0.0000	0.0000	0.0000
$O\ O\ ^1S^1S$	0.0244	−0.1981	−0.1715	−0.0026	0.0000	0.0001	0.0000
$O^+\ O^-\ ^2D^2P$	−0.6052	−0.3958	−0.4035	−0.0873	0.0000	0.0000	0.0000
$O^+\ O^-\ ^2P^2P$	0.3333	−0.2315	−0.2338	−0.0651	0.0000	0.0000	0.0000
$O^+\ O^-\ ^2P^2P$	0.0997	0.4977	0.4357	0.0380	0.0000	0.0000	0.0000
$O^{++}O^{--}\ ^1D^1S$	−0.3367	−0.1156	−0.0810	−0.0008	0.0000	−0.0001	0.0000
$O^{++}O^{--}\ ^1S^1S$	0.0994	−0.1500	−0.0993	−0.0008	0.0001	0.0001	0.0000

are the important ones at molecular separations, are the only ones necessary (and all are necessary) to represent two normal oxygen atoms at infinite separation. Is there some good rule of thumb here? Choose the molecular orbitals to be definitely non-atomic, clearly of a "molecular" type. Then consider the configurations necessary to represent the ground state atoms and allow only those configurations to interact. The procedure may be of help for bigger systems.

One last point: the energy curve has a hump. The usual Morse curve representation of a molecular energy curve has the axis as its asymptote; ours, in order to fit four calculated points, must approach a definitely positive value at infinity. We have tried to find some experimental evidence of this hump but there does not seem to be any clear-cut way of exhibiting it or denying it. The vibrational levels come in the right places, but they have not been observed high enough so that the hump would have any unique effect. However, it seems that other people have considered an energy curve which extrapolates to a positive height at infinite separation.

Pauling[17] has been led to the concept of the valence state of an atom, a hypothetical state which is not "one of the stationary spectroscopic states of the isolated atoms, but . . . is defined as that state in which it (the atom) has the same electronic structure as it has in the molecule." In the paper referred to, Pauling deduces the value of the energy of this state by four different methods all of which agree reasonably well with one another. One of the methods is an extrapolation of the vibrational levels, the introduction of a Morse curve which goes to 6.69 ev at infinite separation. (Ours goes to 6.91 ev.) We have not been able to do more with this concept of the valence state, but the fact that it has been introduced lends credence to the hump, or vice versa.

In conclusion, may we again emphasize the fortunate situation with oxygen, that a fairly complete treatment of configuration interaction did not exceed human endurance and machine storage capacity. Except for oxygen and a few other very simple molecules, it is ridiculous to tabulate all the configurations arising from the atomic primitive set of orbitals, as has been done here. It is necessary to have an *a priori* measure by weight of the secular determinant, to be able to say that this configuration is important, this is not. Configuration interaction is imperative if orbital theory is to be used but it must be handled in a manner that does not surge to impracticability.

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APPENDIX I. ORBITAL EQUIVALENCE THEOREM[18]

Let u_i be a set of N independent one-electron functions. If there are $n(\leqslant N)$ electrons, form n independent combinations of the u_i's,

$$\varphi_i=\sum_j c_{ij}u_j \qquad \begin{matrix}1\leq i\leq n\\ 1\leq j\leq N,\end{matrix}$$

where the c_{ij}'s are as yet undetermined. Putting in the symbol for the electronic coordinates (space and spin) we get a matrix relation

$$\varphi_i(x_k)=\sum_j c_{ij}u_j(x_k),$$

or

$$\mathbf{\Phi}\quad \mathbf{CU}.$$

That is, the square matrix $\mathbf{\Phi}$ is the product of two rectangular matrices: $\mathbf{C}$ which is an $n\times N$, and $\mathbf{U}$ which is an NXn. The many-electron wave function is essentially the determinant of $\mathbf{\Phi}$. A determinant is definable only for a square matrix, but it is possible to express the determinant of the product of two rectangular matrices in a significant way.[19] It turns out that the determinant of the product is the sum of products of minors taken from the two rectangular matrices. Begin with the first n columns of $\mathbf{C}$. Multiply the determinant of this $n\times n$ submatrix by the minor formed from the corresponding first n rows of $\mathbf{U}$. The other products in the expansion are formed in the same way. A minor consisting of a selection of n columns of $\mathbf{C}$ is the coefficient of the minor formed from the selection of the corresponding rows of $\mathbf{U}$. But this expansion is the starting point of configuration interaction. The many-electron wave function is a linear combination of the $N!/n!(N-n)!$ determinants formed from the N u_i's. The minors of $\mathbf{C}$ are the coefficients which are to be varied until the Hamiltonian is made diagonal.

This is a somewhat stilted way of getting at configuration interaction, but the equivalence theorem becomes trivial in this formalism. Let

$$v_j=\sum_i R_{ji}u_i$$

be a determined linear combination of the original set.

[17] L. Pauling, Proc. Natl. Acad. Sci. **35**, 229 (1949).

[18] A proof along similar lines was given by P. O. Löwdin in the Quart. Prog. Report of the M.I.T. Solid-State and Molecular Theory Group (January, 1952).

[19] A. G. Aitken, *Determinants and Matrices* (Oliver and Boyd, London, 1939).

Proceeding in the same way as before, we set up

$$\varphi_i(x_k)=\sum_j d_{ij}v_j(x_k)=\sum_{jl} d_{ij}R_{jl}u_l(x_k).$$

Again, there is a rectangular $n\times N$ matrix multiplied by the rectangular $N\times n$ **U** matrix. Since the minors of the former are to be varied anyway, set

$$\mathbf{C}=\mathbf{DR} \quad c_{il}=\sum_j d_{ij}R_{jl}$$

and equivalence is established. Because of the determinantal form of the many-electron wave function, the arbitrariness in the base system of one-electron space carries right through to an arbitrariness in the base system of many-electron space.

APPENDIX II. SPIN ALGEBRA

Let **s** represent the vector operator of one-electron spin. It can be decomposed into three Cartesian components obeying the following commutation rules:

$$s^2s_x-s_xs^2=0$$
$$s_xs_y-s_ys_x=is_z$$
$$s_xs_y+s_ys_x=0$$
$$s_x^2=\tfrac{1}{4}$$
$$s^2=s_x^2+s_y^2+s_z^2=\tfrac{3}{4}.$$

The above formulas are to be completed, of course, by the cyclic substitution of x, y, and z.

Spin eigenfunction and spin eigenvalue are codefined by

$$s_z\alpha=\tfrac{1}{2}\alpha$$
$$s_z\beta=-\tfrac{1}{2}\beta.$$

We will also use the well-known "step-up" and "step-down" operators defined by

$$s_+\alpha=0 \quad s_-\alpha=\beta$$
$$s_+\beta=\alpha \quad s_-\beta=0,$$

or explicitly

$$s_+=s_x+is_y$$
$$s_-=s_z-is_y.$$

The combinatorial rules of a many-electron spin system are simple,

$$\mathbf{S}=\sum_i \mathbf{s}_i$$
$$S_z=\sum_i s_{iz}.$$

These lead to

$$S^2=\sum_i s_i^2+\sum_{i\neq j}\mathbf{s}_i\cdot\mathbf{s}_j$$

and

$$\mathbf{s}_i\cdot\mathbf{s}_j=s_{ix}s_{jx}+s_{iy}s_{jy}+s_{iz}s_{jz}=\tfrac{1}{2}s_{i+}s_{j-}+\tfrac{1}{2}s_{i-}s_{j+}+s_{iz}s_{jz},$$

so that

$$S^2=\sum_i s_i^2+\sum_{i\neq j}s_{i+}s_{j-}+\sum_{i\neq j}s_{iz}s_{jz}.$$

This operator is to be applied to a determinantal wave function, whose antisymmetrical nature narrows things down. The first term

$$\sum_i s_i^2$$

transforms a configuration into itself multiplied by $\frac{3}{4}n$, where n is the number of electrons. The last term

$$\sum_{i\neq j}s_{iz}s_{jz}$$

also does not change the configuration. The multiplication factor is the same for all states having $S_z=0$, for

$$\sum_{i\neq j}s_{iz}s_{jz}=\sum_i{}' s_{iz}\sum_j{}' s_{jz},$$

where the prime denotes summation over all electrons except the i'th. If $S_z=0$, then this inner summation is effectively

$$-s_{iz},$$

and the whole double-summation effectively acts like

$$\sum_i -s_{iz}^2$$

which is equal to $-n/4$.

It is only the step-up step-down term which transforms one configuration into another. The term

$$\sum_{i\neq j}s_{i+}s_{j-}$$

says that we are to take each + and − couple and flip the signs. The flipping of a pair located in one spatial orbital column (Table III) can be interpreted as an interchange of two electrons in the standard arrangement; the configuration is transformed into its negative. We cannot flip only one of the spin functions of a spatial orbital pair because we would then have two electrons occupying the same space-spin orbital and subsequent antisymmetrization would yield a null determinant. The flipping of a spin pair taken from singly occupied space orbitals produces another configuration. The interconnections of the various configurations are simple and the proper combinations can be immediately ascertained.

APPENDIX III. INEQUALITIES

The symbol $(uv|wz)$ stands for

$$\int u^*(1)v(1)\frac{2}{r_{12}}w^*(2)z(2)dx_1dx_2.$$

Roothaan's inequalities are

$$0\leq(uv|vu)\leq(uu|vv)\leq\frac{(uu|uu)+(vv|vv)}{2}.$$

The first integral is commonly called the "exchange" integral and it is positive definite. The other integrals are called "Coulomb" integrals. We have derived another inequality, a geometric mean inequality, and one that brings in the so-called "hybrid" integrals. We begin with the positive definiteness of any exchange integral.

In particular

$$[(Au+v)w|w(Au+v)]\geq 0.$$

In expanded form

$$A^2(uw|wu)+2A(uw|wv)+(vw|wv)\geq 0.$$

That is, this second-degree polynomial in A can have either no real roots or one doubly degenerate real root. The following inequality among the coefficients is nesessary and sufficient:

$$(uw|wv)^2\leq(uw|wu)(vw|wv).$$

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The Photochemical Separation of Isotopes

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A method of successfully separating mercury isotopes by a photochemical process is described. The method involves the use of a monoisotopic resonance lamp as the source of light for the photochemical reaction. In this particular case a Hg^{198} lamp was used to excite only the Hg^{198} atoms. The excited Hg atoms react with water vapor to produce enriched mercuric oxide. In the first experiments an enrichment factor of 1.5 was obtained.

The analysis of the isotopes was undertaken by the use of multilayer dielectric Fabry-Perot interferometers.

I. INTRODUCTION

IN almost all the existing practical methods of separating isotopes, the separation factor of a single stage of the equipment is some function of the mass ratio. This factor is the ratio of the relative abundance of the desired isotopes in the output to the relative abundance in the input material. For typical substances with typical separation methods,[1] it runs from 1.1 to 1.006. There are a few methods which are able to achieve single-stage factors greater than unity. One such method is the mass spectrograph. This paper is concerned with another method which has the possibility of yielding a large separation factor.

Photochemical Separation of Isotopes

This technique involves the separation of isotopes by a photochemical reaction. There have been several attempts in the literature to obtain such photochemical isotope separation, some of which seem to have had a small amount of success.[2,3]

There are three fundamental principles and conditions which must be fulfilled before an isotopic separation can be made. These are:

(1) The absorption spectra of either the isotope itself or some compound containing the isotope should be different for the two isotopes at some wavelength. For example, if the element is a gas, then the absorption spectrum of the vapor will, in general, be different for different isotopes because of the various kinds of isotope shifts. If the material is a compound, then perhaps the dissociation limit will be different for different isotopes. If the material is in a liquid or solid and sharp absorption lines occur, then these lines may be separated or in some particular cases actually absent for different isotopes.

(2) A light source must be found which is of sufficiently narrow spectral band width that it will excite only one particular isotopic species, whether it is an atom or a compound. This particular light source can, in principle, be obtained by many methods. The method which is used here, which has been extremely successful, is the use of a light source made up of only one isotope. The excited radiation emitted from this isotope is absorbed only by one isotope if the lines are sufficiently narrow.

It is also possible to use broad band sources if filters are used which will filter out the light absorbed by only one isotope. If the isotope involved is not very abundant in the naturally occurring element, it is possible to use this naturally occurring element as an absorption filter, since the isotopic constituents in high concentration will preferentially absorb the light. Other filters can be narrow band transmission or reflection filters which admit the light desired.

Occasionally, there may be certain atomic lines which will occur at just the right place to excite a molecular species containing only one isotope. Under these fortuitous circumstances a partial separation is also possible.

(3) A reaction of the excited atom or molecule must

[1] W. Walcher, Ergeb. Exakt. Naturw. p. 155 (1939).
[2] Merton, Ponder, Bowen, and Hartley, Phil. Mag. 43, 430 (1922).
[3] K. Zuber, Helv. Phys. Acta 9, 285 (1936).