A Method of Diatomics in Molecules. I. General Theory and Application to H₂O[1]

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An approximate theory is presented in which the electronic structure of a polyatomic molecule is expressed in terms of electronic structures for *all* possible diatomic and monatomic fragments which compose it. The primary purposes of the theory are: (1) to predict stabilities of polyatomic molecules; (2) to provide understanding of deviations from strict additivity of bond energies; and (3) to give semiempirical explanation for nonbonded interactions. The general approach bears a strong resemblance to the well-known Slater–Eyring semiempirical valence-bond method, except that in the new theory there appear no calibration parameters, no exchange integrals, and no coulomb integrals, but only overlap integrals and experimental diatomic and monatomic energies. Problems involving multiple exchanges do not occur in the new treatment. An application to the right-angled conformation of H₂O gives an energy of atomization in essential agreement with experiment. For H₂O, the O–H and H–H bond energies are calculated to be 120.4 and 11.2 kcal., respectively, and the O-atom promotional energy is 21.0 kcal. These may be compared with the calculated O–H bond energy 118 kcal. and O-atom promotional energy 11 kcal. for the OH radical.

Introduction

One main obstacle on the road to predicting quantum mechanically and interpreting molecular atomization energies is the profound effect of electron correlation, especially of the intraatomic kind, on total electronic energy. Really theoretical accounting of this correlation energy requires a very large set of configurational wave functions in the conventional variational calculation. In 1951, Moffitt proposed a possible way to allow for intraatomic correlation in molecular calculations by admitting experimental energies of atomic and ionic states in a particular way; this new approach was called the atoms-in-molecules (AIM) method.[2]

In the AIM method, eigenfunctions for electronic states of the separated atoms are used to construct the molecular basis wave functions. Alternatively, a polyatomic molecule might be visualized as formed by interaction of diatomic molecules (and at least one atom, for the odd-atom case). Since atoms probably are perturbed more than diatomics on polyatomic molecule formation, an immediate and conceivably improved extension of the AIM method would be one which employed electronic states of separated diatomics (and those of one atom, if necessary) for construction of the unperturbed wave functions. This particular approach to polyatomic structure is, however, *not* the one to be developed in this paper.

In the next section we describe a theory in which the electronic structure of a polyatomic molecule is represented conventionally by a resonance of valence-bond structures. The total hamiltonian operator is cast into a form which contains only hamiltonians for *all* possible diatomic and monatomic fragments in the polyatomic, but no interaction operators. If good valence-bond approximations of the diatomic and monatomic ground and excited state eigenfunctions are available, it becomes possible to evaluate the general energy matrix for the polyatomic in terms of the overlap matrix (for the starting canonical set of polyatomic structures) and experimental diatomic and monatomic energies. The general approach bears a strong resemblance to the well-known semiempirical valence-bond method,[3] except that in the new theory there appear no exchange integrals, no coulomb integrals, and no calibration parameters.

In the next section, also, it is shown that diatomics-in-molecules theory leads straightforwardly to a natural expression for the atomization energy of a polyatomic as a sum over *all* bond energies less the total atomic promotional energy.

The theory is applied to right-angled H₂O in the last section.

Theory

General.—We begin by considering valence-bond structure wave functions for a given polyatomic system

$$\Psi_n = \sum_r b_{nr} D_r \tag{1}$$

The D_r represent determinantal wave functions (antisymmetrized products of atomic spin orbitals), and the b_{nr} are coefficients chosen so that (1) Ψ_n is antisymmetric with respect to interchange of spin factors of orbitals forming an electron-pair, (2) Ψ_n is the proper eigenfunction of S^2 (square of total spin angular momentum) and S_z (component of S upon z-axis), and (3) Ψ_n is normalized for infinite separation of the atoms.[4]

We suppose that a polyatomic molecule can be represented by a resonance of two or more valence-bond canonical structures Ψ_n like eq. 1.

$$\Psi = \Sigma a_n \Psi_n \tag{2}$$

In order to determine the optimum coefficients a_n for which the expectation value of the molecular energy W is minimized,[5] one must first solve the secular determinant $|H_{nm} - S_{nm} W| = 0$, in which

$$S_{nm} = \int \Psi_n \Psi_m d\tau, \quad H_{nm} = \int \Psi_n H \Psi_m d\tau \tag{3}$$

We may write $\Psi_m = A\psi_m$, where A is the total antisymmetrization operator and ψ_m is a linear combination of *simple products* of atomic spin orbitals; we shall refer to ψ_m as the *primitive function* for the mth structure.[6] Now, a typical energy matrix element can be written

$$H_{nm} = \int \Psi_n A H \psi_m d\tau \tag{4}$$

since the operators H and A commute.

We next consider a general atoms-in-molecules expression of the total Hamiltonian operator for the polyatomic molecule

$$H = \sum_P H_P + \sum_P \sum_{Q > P} V_{PQ} \tag{5}$$

Each H_P contains all kinetic energy operators and all intraatomic potential energy terms in H which depend

(1) Supported in part by a grant from the National Science Foundation. Paper presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 5, 1963.

(2) W. Moffitt, *Proc. Roy. Soc.* (London), **A210**, 245 (1951).

(3) H. Eyring and M. Polanyi, *Z. physik. Chem.*, **B12**, 279 (1931); J. O. Hirschfelder, H. Eyring, and B. Topley, *J. Chem. Phys.*, **4**, 170 (1936); J. C. Slater, *Phys. Rev.*, **38**, 1109 (1931); J. H. Van Vleck and P. C. Cross, *J. Chem. Phys.*, 1, 357 (1934); H. Voge, *ibid.*, **4**, 581 (1936).

(4) All conditions but the first are optional in valence-bond theory; condition 2 simplifies calculations significantly.

(5) The functions Ψ_n depend parametrically upon the relative positions of the nuclei under the Born–Oppenheimer approximation; W is minimized for fixed positions of the nuclei.

(6) Electrons are assigned to the atomic spin orbitals in a serial manner: electrons 1 to n_A to atomic spin orbitals associated with atom A, the next set of electrons to atom B, etc. Such electron assignments may differ from one primitive function to another because of different ionicities of the associated valence-bond structures.

exclusively upon the coordinates of electrons assigned originally to atom P and not upon the coordinates of any nuclei other than nucleus P; V_{PQ} contains all interatomic interaction potential energy terms in H depending upon electron and nuclear coordinates common to atom P and atom Q only. There are, of course, many different ways to partition H in this way depending upon the original assignment of electron numbers to the various atoms. The atoms-in-molecules form of H will be determined in each particular energy matrix element H_{nm} by the assignment of electrons within the primitive function ψ_m upon which H is set to operate (eq. 4 and footnote 6).

The hamiltonian H_{PQ} for a *diatomic* molecule PQ, again written in its atoms-in-molecules form, is

$$H_{PQ} = H_P + H_Q + V_{PQ} \qquad (6)$$

If this expression is solved for V_{PQ} and then substituted into eq. 5, we obtain

$$H = \Sigma H_P + \sum_P \sum_{Q < P} (H_{PQ} - H_P - H_Q) \qquad (7)$$

$$= \sum_P \sum_{Q > P} H_{PQ} - (N - 2) \sum_P H_P \qquad (8)$$

where N is the total number of atoms in the polyatomic. We shall refer to each of these forms of H as the *diatomics-in-molecules* (DIM) Hamiltonian; they contain explicitly no "interaction" operators but only hamiltonians for the constituent diatomic molecules and atoms. The total energy of a polyatomic is expressed as the sum of energies of all possible diatomic fragments (for each fragment, the energy of "both atoms in the fragment" as well as their interaction energy is implicit) minus the sum of atom energies as many times as necessary to correct for their multiple inclusion in the diatomic fragment energy sum.

If eq. 8 is substituted into eq. 4, we obtain

$$H_{nm} = \sum_P \sum_{Q > P} H_{nm}^{PQ} - (N - 2) \sum_P H_{nm}^P \qquad (9)$$

where

$$H_{nm}^{PQ} = \int \Psi_n A H_{PQ} \psi_m d\tau \qquad (10)$$

$$H_{nm}^P = \int \Psi_n A H_P \psi_m d\tau \qquad (11)$$

For $n = m$, H_{nn}^{PQ}/S_{nn} may be regarded as the valence state energy of the diatomic molecule PQ in the polyatomic molecule as described by the single valence-bond structure Ψ_n; H_{nn}^P/S_{nn} is the valence state energy of the atom P in the polyatomic as described by structure Ψ_n.[7,8]

It must be noted at this point that the matrices[9] $\langle H^{PQ} \rangle$ and $\langle H^P \rangle$ are not separately hermitian, and indeed are not fully independent. Since $\langle H \rangle$ is hermitian, $\langle H \rangle = \langle H \rangle^+$, and thus

$$\sum_P \sum_{Q > P} [(H^{PQ}) - (H^{PQ})^+] - (N - 2) \sum_P (H^P) -$$
$$(H^P)^+] = 0 \quad (12)$$

We may rewrite eq. 9 in the form

$$H_{nm} = \sum_P \sum_{Q > P} \bar{H}_{nm}^{PQ} - (N - 2) \sum_P \bar{H}_{nm}^P \quad (13)$$

where

$$\bar{H}_{nm}^{PQ} = {}^1/{}_2 (H_{nm}^{PQ} + H_{mn}^{PQ}) \qquad (14)$$

$$\bar{H}_{nm}^P = {}^1/{}_2 (H_{nm}^P + H_{mn}^P) \qquad (15)$$

There is now no necessary relation between the elements of what we may call the diatomic valence state energy matrices $\langle \bar{H}^{PQ} \rangle$ and atomic valence state energy matrices $\langle \bar{H}^P \rangle$. Both are hermitian, and both are defined uniquely in any representation which

(7) A. L. Companion and F. O. Ellison, *J. Chem. Phys.*, **28**, 1 (1958).

(8) F. O. Ellison, *ibid.*, **36**, 3107 (1962).

(9) The matrix $\langle H^{PQ} \rangle$, for example, is that matrix the elements of which are H_{nm}^{PQ}.

may be constructed linearly from our set of canonical valence-bond structures Ψ_n.[10]

Equation 13 is fundamental in the method of diatomics in molecules. We have partitioned the general energy matrix element H_{nm} into parts corresponding to independent contributions from each diatomic and monatomic fragment. No approximations have been made thus far in the theory. Any error resulting in applications of this first portion of the method can be attributed to the use of a limited set of canonical structures (eq. 1 and 2); this restriction is common to nearly all theories of electronic structure.

In the next section, we show how the diatomic and monatomic contributions (H_{nm}^{PQ} and H_{nm}^P) to the matrix elements H_{nm} may be evaluated in terms of overlap integrals S_{nm} between polyatomic structures and *experimental* energies of the diatomic and monatomic fragments.

Evaluation of the H_{nm}^{PQ}.—We first consider a partitioning of the total antisymmetrization operator A

$$A = A_{PQ}^{(PQ)} A_{PQ} A_{(PQ)} \qquad (16)$$

The operator $A_{(PQ)}$ antisymmetrizes that set of electrons which are *not* originally assigned to the diatomic fragment PQ, A_{PQ} antisymmetrizes that set of electrons which *are* originally assigned to PQ, and $A_{PQ}^{(PQ)}$ is the partial or "supplementary" antisymmetrizer which complete the identity. The assignment of electrons to the two sets, belonging to and not belonging to the diatomic fragment PQ, is specified by the assignment of electrons[6] within the primitive function ψ_m in front of which A stands in the integrand of eq. 10. If now eq. 16 is substituted into eq. 10, we find that

$$H_{nm}^{PQ} = \int \Psi_n A_{PQ}^{(PQ)} H_{PQ} A_{PQ} A_{(PQ)} \psi_m d\tau \qquad (17)$$

since H_{PQ} commutes with $A_{(PQ)}$ and with A_{PQ}.

It is recalled that the primitive function ψ_m is a linear combination of simple products of atomic spin orbitals

$$\psi_m = \sum_r b_{mr} d_r \qquad (18)$$

$D_r = A d_r$ (*cf.* eq. 1). Each simple product d_r may be written as a product $d_r^{PQ} d_r^{(PQ)}$, the first factor containing all atomic spin orbitals associated with the diatomic fragment PQ only, the second factor containing all other atomic spin orbitals. The right half of the integrand in eq. 17 thus can be written

$$A_{PQ} A_{(PQ)} \psi_m = \sum_r b_{mr} D_r^{PQ} D_r^{(PQ)} \qquad (19)$$

since $A_{PQ} A_{(PQ)} d_r^{PQ} d_r^{(PQ)} = D_r^{PQ} D_r^{(PQ)}$; the latter two factors are determinantal functions totally antisymmetric with respect to those electrons in the set belonging to and not belonging to the diatomic fragment PQ, respectively.

Suppose that valence-bond approximations of the ground and excited states of the diatomic molecule PQ are available

$$\Psi_s^{PQ} = \sum_r c_{sr} D_r^{PQ} \qquad (20)$$

If the optimum coefficients c_{sr} in these expansions of the eigenfunctions Ψ_s^{PQ} have been determined, then the inverse of eq. 20

$$D_r^{PQ} = \sum_s (c^{-1})_{rs} \Psi_s^{PQ} \qquad (21)$$

should be good approximations of the determinantal functions in terms of eigenfunctions. If eq. 21 is substituted into 19 and then operated upon from the left by the diatomic Hamiltonian H_{PQ}, we obtain

(10) *Cf.* eq. 6.9–6.10 in ref. 2.

$$H_{PQ}A_{PQ}A_{(PQ)}\psi_m = \sum_r \sum_s b_{mr}(c^{-1})_{rt}E_s{}^{PQ}\Psi_s{}^{PQ}D_r{}^{(PQ)} \quad (22)$$

$$= \sum_s E_s{}^{PQ}\Psi_s{}^{PQ} \sum_r b_{mr}(c^{-1})_{rs}D_r{}^{(PQ)} \quad (23)$$

Equation 20 (with t replacing r) is now used to transform back to the determinantal wave function basis

$$H_{PQ}A_{PQ}A_{(PQ)}\psi_m =$$
$$\sum_s E_s{}^{PQ} \sum_t \sum_r c_{st}b_{mr}(c^{-1})_{rs}D_t{}^{PQ}D_r{}^{(PQ)} \quad (24)$$

The supplementary antisymmetrizer $A_{PQ}{}^{(PQ)}$ may then be applied to generate new determinants antisymmetric in all electrons belonging to the polyatomic

$$A_{PQ}{}^{(PQ)}H_{PQ}A_{PQ}A_{(PQ)}\psi_m = \sum_s E_s{}^{PQ} \sum_u g_{su}D_u \quad (25)$$

in this expression, the double sum over t and r has been accumulated into a single sum over independent determinants D_u.

If one begins with a *canonical set* of structures Ψ_n for the polyatomic molecule, the inverse of eq. 1 will yield equations for each D_u in terms of canonical structure wave functions[11]

$$D_u = \sum_v (b^{-1})_{uv}\Psi_v \quad (26)$$

Introducing this into eq. 25 gives

$$A_{PQ}{}^{(PQ)}H_{PQ}A_{PQ}A_{(PQ)}\psi_m = \sum_s E_s{}^{PQ} \sum_w h_{sw}\Psi_w \quad (27)$$

where again we have accumulated the double sum over u and v into a single sum over independent Ψ_w. Putting eq. 27 into 17 gives

$$H_{nm}{}^{PQ} = \sum_s E_s{}^{PQ} \sum_w h_{sw}S_{nw} \quad (28)$$

The integrals S_{nw} are simply overlap integrals between valence-bond structures as defined in eq. 3.

The energy integrals $H_{nm}{}^P$ appearing in eq. 15 may be expressed in a form similar to eq. 28

$$H_{nm}{}^P = \sum_s E_s{}^P \sum_w h_{sw}S_{nw} \quad (29)$$

in which the $E_s{}^P$ are experimental energies for electronic states of the atom P; the coefficients h_{sw} in eq. 28 and 29 will be different, of course.

Equations 28 and 29 are fundamental, in addition to eq. 13–15, in the method of diatomics in molecules. Used together, the general energy matrix element H_{nm} may be evaluated in terms of overlap integrals S_{nw} and experimental energies of diatomic and monatomic fragments which comprise the given polyatomic.

In practice, eq. 20 will be available only in approximation. Use of the inverse of eq. 20 in 22 followed by direct introduction of eq. 20 into 23 suggests a partial cancellation of concomitant errors, and thus a possibly effective way to bridge the gap between polyatomic structure and one- and two-atom structures using valence-bond theory.

The fundamental success of the theory depends, therefore, upon how well actual ground *and excited*

(11) Actually, the inverse of eq. 1 will not exist in general since the matrix b is not square for a canonical set of structures Ψ_n. If, however, the set Ψ_n is extended to include all possible structures (for a given basis set of valence atomic orbitals) having the same eigenvalue for S_z but all possible eigenvalues of S^2, there will be as many Ψ_n as D_r, and b^{-1} will exist (*e.g.*, see H. Eyring, J. Walter, and G. Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York, N.Y., 1944, pp. 232–235). Suppose that the operator S^2 is applied to both sides of eq. 27 from the left. The left-hand side is an eigenfunction of S^2 with eigenvalue $S_m(S_m + 1)h^2$; each term of the right-hand side is individually an eigenfunction of S^2 with eigenvalue $S_w(S_w + 1)h^2$. In order that the resulting equation be valid for all possible values of the electron coordinates, it is necessary that $h_{sw} = 0$ unless $S_w = S_m$. Therefore, the only valence-bond structures which will enter eq. 27 are those which belong to the *original* canonical set of valence-bond structures. In practice, we have not employed eq. 26, but rather have transformed from 25 to 27 by inspection using the original eq. 1.

states are represented by limited sets of valence-bond structures and how well valence-bond structures are represented by limited sets of actual ground *and excited* states. The derivative success of the theory depends upon how well the errors in the former representation cancel the errors in the latter representation. All errors will thus be contained in the use of a finite eq. 2 and in the adequacy of eq. 20 and 21; no integral approximations are introduced or needed in the entire theory.

Bond and Promotional Energies.—The total energy W of a polyatomic molecule represented by a resonance of two or more structures can be expressed

$$W = \sum_n \sum_m a_n a_m \bar{H}_{nm} \quad (30)$$

in which the a_n are optimum coefficients chosen so that W is minimized and so that Ψ is normalized. If the DIM Hamiltonian operator in the form of eq. 7 is used to partition the H_{nm}, we find that

$$W = \sum_P W_P - \sum_P \sum_{Q>P} B_{PQ} \quad (31)$$

where

$$W_P = \sum_n \sum_m a_n a_m \bar{H}_{nm}{}^P \quad (32)$$

$$B_{PQ} = \sum_n \sum_m a_n a_m (\bar{H}_{nm}{}^P + \bar{H}_{nm}{}^Q - \bar{H}_{nm}{}^{PQ}) \quad (33)$$

The first sum in eq. 31 is the total valence state energy of the atoms in the molecule as represented by the function Ψ; B_{PQ} may be interpreted as the valence state energy of the diatomic fragment PQ in the molecule relative to the energies of atoms P and Q in their appropriate valence states. It will be positive if the valence state energy of the diatomic PQ is less than the total valence state energy of atoms P and Q in the molecule; B_{PQ} may be defined as the bond energy of PQ in the polyatomic.

An alternative form of eq. 31 is

$$\Delta E_{at} = \sum_P W_P{}^\circ - W$$

$$= \sum_P \sum_{Q>P} B_{PQ} - \sum_P P_P \quad (34)$$

where ΔE_{at} is the energy of atomization of the polyatomic (for specified relative positions of the nuclei[5]), $W_P{}^\circ$ is the ground-state energy of atom P, and $P_P = W_P - W_P{}^\circ$ is the promotional energy of atom P in the molecule. Subtracting the total zero-point energy of the molecule from ΔE_{at} gives the experimental energy of atomization $\Delta E_{at}{}^\circ$.

Equation 34 thus provides us with a rigorous expression for the atomization energy of a polyatomic molecule as a sum of bond energies (over bonds and nonbonds) less the atomic promotional energy.

Application to Right-Angled H₂O

Theory.—We shall describe here a simple application to right-angled H_2O in which valence-bond wave functions corresponding to the two canonical structures

are considered. We denote the 1s orbitals on the two hydrogen atoms by h_1 and h_2, the 1s and 2s orbitals on oxygen by k and s, and select axes so that the $2pz = z$ oxygen orbital is directed toward h_2 and the $2py = y$ orbital is directed toward h_1; the $2px = x$ orbital is perpendicular to the molecular plane. All determinants in the valence bond wave functions Ψ_1 and Ψ_2

will contain the product of atomic orbitals $kkssxxyzh_1h_2$; spins associated with the first six orbitals will be $\alpha\beta\alpha\beta\alpha\beta$; spins associated with the last four orbitals will differ from determinant to determinant. The wave functions may be written

$$\Psi = {}^{1}\!/_{2}[|\alpha\alpha\beta\beta| - |\alpha\beta\beta\alpha| - |\beta\alpha\alpha\beta| + |\beta\beta\alpha\alpha|]$$
$$= {}^{1}\!/_{2}(D_1 - D_2 - D_3 + D_4) \qquad (35)$$
$$\Psi_2 = {}^{1}\!/_{2}[|\alpha\beta\alpha\beta| - |\alpha\beta\beta\alpha| - |\beta\alpha\alpha\beta| + |\beta\alpha\beta\alpha|]$$
$$= {}^{1}\!/_{2}(D_5 - D_2 - D_3 + D_6) \qquad (36)$$

where we have indicated the spins of yzh_1h_2 only.

The DIM Hamiltonian can be written

$$H = H_{01}{}^{0} + H_{02}{}^{0} + H_{12}{}^{0} - H_0{}^{0} - H_1{}^{0} - H_2{}^{0} \qquad (37)$$

where 0 refers to oxygen, 1 and 2 to the hydrogen. The following approximate valence-bond functions for H_2 and OH were utilized

$$\Psi_1{}^{HH} = 2^{-1/2}(|h_1\bar{h}_2| - |\bar{h}_1h_2|)$$
$$\Psi_2{}^{HH} = 2^{-1/2}(|h_1\bar{h}_2| - |\bar{h}_1h_2|)$$
$$\Psi_3{}^{HH} = |h_1h_2|, \ \Psi_4{}^{HH} = |\bar{h}_1\bar{h}_2| \qquad (38)$$
$$\Psi_1{}^{OH} = 2^{-1/2}(|\pi_+z\bar{h}| - |\pi_+\bar{z}h|)$$
$$\Psi_2{}^{OH} = 6^{-1/2}(|\pi_+\bar{z}h| + |\pi_+z\bar{h}| - 2|\bar{\pi}_+zh|)$$

Bars over orbitals denote β-spin, no bar denotes α-spin. The spin orbitals $k\bar{k}s\bar{s}\pi\bar{\pi}$, common to all of the OH determinants, have been omitted in writing eq. 38.

Applying eq. 18–27 to ψ_1 and ψ_2, we obtain the following expressions [in which the notation is simplified by letting $\mathcal{K}_{PQ} = A_{PQ}{}^{(PQ)}H_{PQ}A_{PQ(PQ)}$]

$$\mathcal{K}_{01}\psi_1 = E_{OH}\Psi_1$$
$$\mathcal{K}_{01}\psi_2 = {}^{1}\!/_{2}(E_{OH} - E_{OH}{}^{*})\Psi_1 + E_{OH}{}^{*}\Psi_2$$
$$\mathcal{K}_{12}\psi_1 = E_{HH}{}^{*}\Psi_1 + {}^{1}\!/_{2}(E_{HH} - E_{HH}{}^{*})\Psi_2$$
$$\mathcal{K}_{12}\psi_2 = E_{HH}\Psi_2 \qquad (39)$$
$$\mathcal{K}_0\psi_1 = E_0\Psi_1 + {}^{1}\!/_{2}(E_0{}^{*} - E_0)\Psi_2$$
$$\mathcal{K}_0\psi_2 = E_0{}^{*}\Psi_2$$
$$\mathcal{K}_1\psi_1 = E_H\Psi_1, \ \mathcal{K}_1\psi_2 = E_H\Psi_2$$

The eigenvalues appearing here are identified with molecular and atomic electronic states in Table I. Because of symmetry, $\mathcal{K}_{02}\psi_n$ gives results identical with $\mathcal{K}_{01}\psi_n$, and $\mathcal{K}_2\psi_n$ gives results identical with $\mathcal{K}_1\psi_n$.

TABLE I

DIATOMIC AND MONATOMIC ENERGIES USED IN H_2O CALCULATIONS

Eigenvalue	Eigenstate	Energy, kcal.
E_{OH}	X $^2\pi$, OH	-107^{a}
$E_{OH}{}^{*}$	A $^2\pi$, OH	45^{b}
E_{HH}	X $^1\Sigma_g{}^{+}$, H_2	-56^{c}
$E_{HH}{}^{*}$	a $^3\Sigma_u{}^{+}$, H_2	28^{c}
E_0	p^4 ^3P, O	0
$E_0{}^{*}$	p^4 ^1D, O	45^{a}
E_H	s ^2S, H	0

^{a} Ref. 12. ^{b} See text. ^{c} W. Kolos and C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 219 (1960).

All energies given in Table I are accepted observed values[12] except for the excited $^2\pi$ state of OH. It is highly probable that this state is repulsive: (1) according to simple valence-bond theory, it may be described as a "no-bond" structure $k^2s^2\pi_+{}^{2}(\pi\cdot z)h$ in resonance with a structure containing a $\sigma-\pi$ bond, $k^2s^2\pi_+{}^{2}z(\pi\cdot h)$, which would be repulsive since the exchange integral $K(h,\pi)$ is positive[13]; (2) according to simple molecular orbital theory, this state arises from the excited configuration $k^2(2s\sigma)^2(2p\sigma)(2p\pi)^3(3s\sigma)$, which also yields a $^4\pi$ state predicted by Mulliken[1] to be repulsive.[14] The O–H distance is taken equal to the equilibrium internuclear distance in ground-state OH; the H–H distance is appropriate to right-angled H_2O.

(12) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. I. D. Van Nostrand Co., Inc., New York, N. Y., 1950.

(13) R. S. Mulliken, *J. Phys. Chem.*, **56**, 295 (1952).

(14) R. S. Mulliken, *Rev. Mod. Phys.*, **4**, 1 (1932).

Expressions for the matrix elements $H_{nm}{}^{PQ}$ are obtained readily using eq. 39. The S_{nm} can be evaluated using the orbital descriptions of ψ_1 and ψ_2

$$S_{nm} = \alpha_1 + \alpha_2S_B{}^{2} + \alpha_3S_N{}^{2} + \alpha_4S_H{}^{2} + \alpha_5S_N{}^{2}S_H +$$
$$\alpha_6S_N{}^{2}S_B{}^{2} + \alpha_7S_B{}^{4} + \alpha_8S_N{}^{4} \qquad (40)$$

where $S_B = \int yh_2dv = 0.3479$, $S_N = \int sh_2dv = 0.4946$ $S_H = \int h_1h_2dv = 0.4440$. The coefficients α_i for S_{11} are 1, 2, −2, −$^1/_2$, 1, −2, 1, and 1; for S_{12} are $^1/_2$, 1, −1, $^1/_2$, −1, −1, $^1/_2$, and 1; and for S_{22} are 1, −1, −2, 1, −2, 1, 1, and 2. The diatomics-in-molecules theory can be applied either *with overlap* or *without overlap*. In the latter case, all determinantal functions appearing in eq. 35 and 36 are orthonormal, and $S_{11} = S_{22} = 1$ and $S_{12} = S_{21} = {}^{1}\!/_{2}$.

Results.—The energy of right-angled H_2O (relative to ground-state 2H + O) was calculated *without overlap* using $E_{OH}{}^{*} = 0$, 20, 45, and 60 kcal.; the results were −237.0, −233.6, −230.6, and −229.4 kcal. These may be compared with −231.6 kcal. obtained by subtracting 0.4 kcal. (the approximate energy needed to bend H_2O from 105 to 90°) from the observed ΔE_{at} = 232 kcal.[15] The results of the calculation using $E_{OH}{}^{*} = 45$ kcal. are employed in all considerations which follow.[16]

Including all overlap in evaluating eq. 40, the energy of right-angled H_2O was calculated to be −230.9 kcal., which is in remarkable agreement with the value obtained without overlap. The optimum coefficients in the resulting normalized wave function

$$\Psi = a_1\Psi_1 + a_2\Psi_2 \qquad (41)$$

turn out to be $a_1 = 0.9447$ and $a_2 = 0.3498$ with overlap, $a_1 = 0.8513$ and $a_2 = 0.2500$ without overlap. The structure projections or occupation numbers[17]

$$\nu_n = a_n \sum_m a_mS_{nm} \qquad (42)$$

are $\nu_1 = 0.8013$ and $\nu_2 = 0.1988$ with overlap, $\nu_1 = 0.8311$ and $\nu_2 = 0.1689$ without overlap.

The bond energies B_{OH} and B_{HH} and the promotional energy P_0 of the oxygen atom in H_2O can be computed for the individual structures Ψ_1 and Ψ_2 as well as for the resonance hybrid Ψ according to definitions given above. Results are displayed in Table II for the complete treatment and for the calculation in which overlap is neglected.

TABLE II

BOND AND PROMOTIONAL ENERGIES (KCAL.) FOR RIGHT-ANGLED H_2O STRUCTURES^{a} AND FOR OH

Structure	B_{OH}	B_{HH}	P_0	ΔE_{at}
OH	118		11	107
$\Psi_1(H_2O)$	119.1	−5.3	12.1	220.8
	(118.3)	(−7.0)	(11.3)	(218.3)
$\Psi_2(H_2O)$	57.5	56.0	45.0	126.1
	(38.0)	(56.0)	(45.0)	(87.0)
$\Psi(H_2O)$	120.4	11.2	21.0	230.9
	(120.4)	(10.3)	(20.5)	(230.6)

^{a} Numbers enclosed in parentheses are results obtained when overlap is neglected.

The bearing of promotional energies upon the significance of bond energies is well known.[18] Some time

(15) Experimental energies of atomization for H_2O and OH are 218.9[12] and 101.3 kcal. [P. A. Giguera, *J. Chem. Phys.*, **30**, 322 (1959)], respectively. Zero-point energies are 13.1 (ref. 12, Vol. 2) and 5.3 kcal.,[12] respectively.

(16) Since the excited $^2\pi$ state of OH is probably repulsive, and since it correlates with the ground state of H plus the excited p^4 ^1D state of O, $E_{OH}{}^{*}$ probably exceeds 45 kcal. Thus, our calculated energy of H_2O should be several kcal. higher than −230.6.

(17) A. C. Hurley, *Proc. Phys. Soc.* (London), **A69**, 49 (1946).

(18) L. Pauling, *Proc. Natl. Acad. Sci. U. S.*, **35**, 229 (1949); for the most recent and exacting analysis, see K. Ruedenberg, *Rev. Mod. Phys.*, **34**, 326 (1962).

ago, Moffitt[19] pointed out that the 18-kcal. discrepancy between $\Delta E_{at}(H_2O)$ and $2\Delta E_{at}(OH)$ is reduced if one properly accounts for promotional energies. First it was assumed that the energy of atomization can be separated into bond energies and promotional energies

$$\Delta E_{at}(H_2O) = 232 \text{ kcal.} = 2B_{OH} - P_{HOH} \quad (43)$$
$$\Delta E_{at}(OH) = 107 \text{ kcal.} = B_{OH} - P_{OH}$$

But $P_{HOH} = P_{OH} = 11$ kcal. for the simple valence-bond structures Ψ_1 and Ψ_1^{OH} (eq. 35 and 38). Therefore

$$\Delta E_{at}(H_2O) = 2\Delta E_{at}(OH) + P_{OH}$$
$$= 214 \text{ kcal.} + 11 \text{ kcal.} = 225 \text{ kcal.} \quad (44)$$

The 7-kcal. difference remaining is then attributed to hybridization, ionic–covalent resonance, H–H interaction, etc.

(19) W. Moffitt, *Rept. Progr. Phys.*, **17**, 173 (1959).

The diatomics-in-molecules theory leads to a quantitative explanation for the difference in atomization energies of H_2O and OH. It is seen that an important factor is the H–H interaction, which in fact contributes 11 kcal. to the binding in H_2O. The promotional energy for the oxygen atom is found to be almost twice as large in right-angled H_2O as in OH.

Questions relating to hybridization and/or ionic character cannot be answered by the present treatment. Addition of canonical *ionic* structures for H_2O to the starting set, necessitating valence-bond representations of OH ground and excited states more refined than eq. 38, would lead to explanations in terms of relative ionic characters. In any case, more detailed OH molecule descriptions will be necessary before the energy of H_2O can be determined by diatomics-in-molecules theory as a function of bond angle. Work is now in progress along these lines.

A Method of Diatomics in Molecules. II. H₃ and H₃⁺ [1]

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The diatomics-in-molecules theory described in the preceding paper[2] is used to calculate the potential energy surfaces for H₃ and H₃⁺. The energy of atomization ΔE_{at} of linear symmetrical ($R_{HH} = 1.8$ bohrs) H₃ is calculated to be 96.60 kcal., which corresponds to a classical activation energy of 13 kcal. (experimental, ~7.7 kcal.). The molecule-ion H₃⁺ is found to be most stable as an equilateral triangle, $\Delta E_{at} = 223.8$ kcal. The totally symmetrical A_1' and doubly degenerate E_1' vibrational wave numbers are determined to be 3450 and 2330 cm.⁻¹, respectively. The zero-point energy is thus 11.5 kcal. and $\Delta E_{at}° = 212.3$ kcal. The reaction H₂ + H₂⁺ = H₃⁺ + H is calculated to be exothermic by 48 kcal.; it is speculated that this result, as well as the atomization energies, may be about 10 kcal. too high.

Introduction

In the preceding paper (hereafter referred to as paper I),[2] there was proposed an approximate theory designed primarily to predict molecular stabilities and to provide understanding of the deviations from strict additivity of bond energies. In this paper we use the theory to calculate the potential energy surfaces for H₃ and H₃⁺, as well as the vibrational structure of the latter molecule-ion.

The H₃ Molecule

Theory.—We begin with the conventional valence-bond structures for H₃, which may be written A–B C and A B–C, the associated wave functions being

$$\Psi_1 = |a\bar{b}c| - |\bar{a}bc|$$
$$\Psi_2 = |a\bar{b}c| - |ab\bar{c}| \quad (1)$$

The a, b, and c represent 1s orbitals located on the three centers; a bar over the orbital denotes β-spin, no bar means α-spin. The wave functions are not normalized, even for infinite separation of the nuclei; experience has shown us that diatomics-in-molecules theory is easier to execute if functions are left nonnormalized.

The simplest valence-bond wave functions for H₂ are utilized; for example

$$\Psi_1^{AB} = |a\bar{b}| - |\bar{a}b|$$
$$\Psi_1^{AB} = |a\bar{b}| + |\bar{a}b| \quad (2)$$
$$\Psi_2^{AB} = |ab|, \Psi_4^{AB} = |\bar{a}\bar{b}|$$

These represent the ground $^1\Sigma_g^+$ state and excited $^3\Sigma_u^+$ states, respectively; analogous expressions for Ψ_s^{BC} and Ψ_s^{AC} are also needed.

The diatomics-in-molecules theory will be illustrated by evaluating two of the necessary integrals, H_{12}^{AB} and H_{22}^{AB}, where

(1) Supported in part by a grant from the National Science Foundation.
(2) F. O. Ellison, *J. Am. Chem. Soc.*, **85**, 3540 (1963).

$$H_{nm}^{PQ} = \int \Psi_n A_{PQ}^{(PQ)} H_{PQ} A_{PQ} A_{(PQ)} \psi_n d\tau \quad (3)$$

First, we may write

$$\psi_2 = a_1\bar{b}_2c_3 - a_1b_2\bar{c}_3$$
$$A_{AB}A_{(AB)}\psi_2 = |a\bar{b}|c - |ab|\bar{c} \quad (4)$$

Employing the inverse of eq. 2, we find that

$$A_{AB}A_{(AB)}\psi_2 = \frac{1}{2}(\Psi_1^{AB} + \Psi_2^{AB})c - \Psi_3^{AB}\bar{c} \quad (5)$$

Application of the diatomic hamiltonian H_{AB} yields

$$H_{AB}A_{AB}A_{(AB)}\psi_2 = [E_1^{AB}\Psi_1^{AB}c + E_2^{AB}(\Psi_2^{AB}c - 2\Psi_3^{AB}\bar{c})]/2 \quad (6)$$

where E_1^{AB} and E_2^{AB} are the ground singlet and excited triplet eigenvalues for H₂, the internuclear distance of which corresponds to the distance R_{AB} in H₃. We now use eq. 2 to transform back again to the determinantal function basis, and then apply the supplementary antisymmetrizer $A_{AB}^{(AB)}$

$$\mathcal{H}_{AB}\psi_2 = [E_1^{AB}(|a\bar{b}c| - |\bar{a}bc|) + E_2^{AB}(|a\bar{b}c| + |\bar{a}bc| - 2|ab\bar{c}|)]/2 \quad (7)$$

where $\mathcal{H}_{AB} = A_{AB}^{(AB)}H_{AB}A_{AB}A_{(AB)}$. Introducing eq. 1 gives

$$\mathcal{H}_{AB}\psi_2 = [E_1^{AB}\Psi_1 + E_2^{AB}(2\Psi_2 - \Psi_1)]/2 \quad (8)$$

from which we find that

$$H_{12}^{AB} = [E_1^{AB}S_{11} + E_2^{AB}(2S_{12} - S_{11})]/2$$
$$H_{22}^{AB} = [E_1^{AB}S_{21} + E_2^{AB}(2S_{22} - S_{21})]/2 \quad (9)$$

where $S_{nm} = \int \Psi_n \Psi_m d\tau$.

Similarly it can be shown that

$$\mathcal{H}_{AB}\psi_1 = E_1^{AB}\Psi_1$$
$$\mathcal{H}_{AC}\psi_1 = [E_1^{AC}(\Psi_1 - \Psi_2) + E_2^{AC}(\Psi_1 + \Psi_2)]/2$$
$$\mathcal{H}_{BC}\psi_1 = [E_1^{BC}\Psi_2 + E_2^{BC}(2\Psi_1 - \Psi_2)]/2 \quad (10)$$
$$\mathcal{H}_{AC}\psi_2 = [E_1^{AC}(\Psi_2 - \Psi_1) + E_2^{AC}(\Psi_1 + \Psi_2)]/2$$
$$\mathcal{H}_{BC}\psi_2 = E_1^{BC}\Psi_2$$
$$\mathcal{H}_A\psi_n = \mathcal{H}_B\psi_n = \mathcal{H}_C\psi_n = E_H\Psi_n$$