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Ab initio Valence-Bond Calculations of H_2O

I. Bond Dissociation Energies

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The first and second bond dissociation energies for H_2O have been calculated in an *ab initio* manner using a multistructure valence-bond scheme. The basis set consisted of a minimal number of non-orthogonal atomic orbitals expressed in terms of gaussian-lobe functions. The valence-bond structures considered properly described the change in the molecular system as the hydrogen atoms were individually removed to infinity. The calculated equilibrium geometry for the H_2O molecule has an O—H bond length of 1.83 Bohrs and an HOH bond angle of 106.5°. With 49 valence-bond structures the energy of H_2O at this geometry was -76.0202 Hartrees. The calculated equilibrium bond length for the OH radical was 1.86 Bohrs and the energy, using the same basis set, was -75.3875 Hartrees. After correction for zero point energies the calculated bond dissociation energies are: $H_2O \rightarrow OH + H$, $D_1 = 75.38$ kcal/mole and $OH \rightarrow O + H$, $D_2 = 54.79$ kcal/mole.

Die ersten und zweiten Dissoziationsenergien der Bindungen von H_2O wurden mit einem *ab initio* Verfahren nach der Valenzstrukturmethode berechnet. Die Basis bestand aus einer minimalen Anzahl von nicht-orthogonalen Atomorbitalen, die durch Gaußfunktionen ausgedrückt wurden. Die beteiligten Valenzstrukturen beschrieben in geeigneter Weise den Wechsel in der Molekülstruktur bei Abspaltung der einzelnen Wasserstoffatome. Die berechnete Gleichgewichtsgeometrie des H_2O-Moleküls hat eine O—H-Bindungslänge von 1,83 Bohr und einen HOH-Winkel von 106,5°. Mit 49 Valenzstrukturen betrug die Energie des H_2O bei dieser Geometrie $-76{,}0202$ Hartree. Die berechnete Bindungslänge des OH-Radikals für das Gleichgewicht betrug 1,86 Bohr und die Energie wurde mit derselben Basis zu $-75{,}3875$ Hartree berechnet. Nach Korrekturen für die Nullpunktenergien betrugen die berechneten Dissoziationsenergien der Bindungen: $H_2O \rightarrow OH + H$, $D_1 = 75{,}38$ kcal/Mol und $OH \rightarrow O + H$, $D_2 = 54{,}79$ kcal/Mol.

1. Introduction

Ab initio valence-bond (VB) calculations for polyatomic molecules with inclusion of all electrons are rare. Previous studies on polyatomic systems have usually involved integral approximations [1] or other assumptions such as $\sigma - \pi$ separability [2]. The major difficulty in using an *ab initio* approach in VB calculations is the vast number of multiple exchange integrals that must be evaluated when a basis set of non-orthogonal atomic orbitals is used in making up the VB structures. However the use of orthogonalized atomic orbitals [3], while decreasing computational difficulties, also decreases the chemical interpretability of the results [4]. The non-orthogonal basis was therefore retained in the present study and the formulation derived by Löwdin [5] and discussed by Slater [6] was used to evaluate the necessary matrix elements.

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In order to study the process of bond dissociation in the H_2O molecule the wave function must be of sufficient flexibility to correctly describe the change in electronic structure as the hydrogen atoms are individually removed to infinity. As is well known a proper description of this process cannot in general be given by a single configuration (unless the reactants and products are closed-shell species) which is usually constrained to dissociate into a sum of ground and excited state atomic species. It is a simple matter however to obtain correct dissociation results using VB methods by including among the valence structures in the configuration interaction scheme those structures which at infinite internuclear separations represent the atoms in their ground states. If the VB structures do not represent spectroscopic states at infinite internuclear separations then additional structures must be added to allow intra-atomic configuration interaction [7]. A variational calculation will then automatically increase the contribution of these structures to the wavefunction as the internuclear distance is increased.

2. Basis Set and Computer Program

The atomic orbital basis set for these calculations consists of gaussian-lobe functions with Whitten's [8] exponents and coefficients. The H(1*s*) orbital was represented by a linear combination of five gaussian functions and for calculations at the equilibrium geometry of H_2O this orbital was scaled by 1.4. No polarization functions such as *d*-type orbitals on the O atom or *p*-type orbitals on the H atoms were used in the present study. Although the basis set is therefore "minimal" it has had excellent success in yielding molecular geometries in close agreement with experiment [9].

The program used in these calculations was an early version of the MOLE Quantum Chemistry System developed by Rothenberg and co-workers [10]. Particular use was made of the non-orthogonal configuration interaction subprogram developed by Erdahl and Lesk [11]. In this program each Slater determinant is written in terms of two "primary" functions each of which is a product function of all the spin-orbitals in the determinant having similar spin. Only matrix elements between "primary" functions of the same spin value need be calculated. The resulting blocking of the overlap matrix leads to similar blocking in the matrices of the first and second order minors which appear in the energy expressions developed by Löwdin [5]. By focusing on "primary" structures rather than the entire Slater determinant computational time is considerably shortened by reducing the number of *different* interaction matrix elements between VB structures. For example in the H_2O calculations reported here 15 "primary" functions have been combined in various ways to give 101 different Slater determinants which appear in the 49 VB structures considered.

3. Valence Bond Structures

The 49 VB wavefunctions used in these calculations are given in Table 1. The O(1*s*) orbital is doubly occupied in each of these structures and only the $O(2s) \equiv \Phi_s$, $O(2px) \equiv \Phi_x$, $O(2py) \equiv \Phi_y$, $O(2pz) \equiv \Phi_z$, $H_1(1s) \equiv h_1$, and $H_2(1s) \equiv h_2$ are shown.

A bar over the orbital indicates β spin, no bar indicates α spin. All of the wavefunctions in Table 1 either individually or in linear combinations transform as the A_1 representation of the C_{2v} point group. Wavefunctions $\Psi_1 - \Psi_{10}$ represent covalent bonding schemes; wavefunctions $\Psi_{11} - \Psi_{49}$ represent ionic bonding schemes. Intra-atomic configuration interaction occurs among both the covalent and ionic functions except for those wavefunctions which dissociate to an O^- configuration. The importance of the lack of intra-atomic configuration interaction for this configuration will be discussed later.

This set of 49 wavefunctions includes all the structures of A_1 symmetry that may be formed from the configurations:

$$O^+(1s^2 2s^2 2p^3),\ O^+(1s^2 2s 2p^4),\ O^+(1s^2 2p^5),\ O(1s^2 2s^2 2p^4),\ O(1s^2 2s 2p^5),$$
$$O(1s^2 2p^6),\ O^-(1s^2 2s^2 2p^5),\ O^-(1s^2 2s 2p^6),\ \text{and}\ O^=(1s^2 2s^2 2p^6).$$

4. Results

A) *Calculated Equilibrium Geometry and Energy for* H_2O

A number of preliminary calculations using a set of 30 VB functions were performed to establish the equilibrium conformation of H_2O. These calculations predicted the HOH bond angle to be 106.5° and the O–H bond length to be 1.83 Bohrs [12]. This geometry was used in the more extensive calculations

Table 1. Valence bond wave functions

$$\Psi_1 = |\Phi_s\bar{\Phi}_s\Phi_x\Phi_y\Phi_z\bar{\Phi}_z\bar{h}_1\bar{h}_2| - |\Phi_s\bar{\Phi}_s\bar{\Phi}_x\Phi_y\Phi_z\bar{\Phi}_z\bar{h}_1 h_2| - |\Phi_s\bar{\Phi}_s\Phi_x\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_1\bar{h}_2| + |\Phi_s\bar{\Phi}_s\bar{\Phi}_x\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_1 h_2|$$
$$\Psi_2 = |\Phi_s\bar{\Phi}_s\Phi_x\Phi_y\Phi_z\bar{\Phi}_z\bar{h}_1\bar{h}_2| - |\Phi_s\bar{\Phi}_s\Phi_x\bar{\Phi}_y\Phi_z\bar{\Phi}_z\bar{h}_1 h_2| - |\Phi_s\bar{\Phi}_s\bar{\Phi}_x\Phi_y\Phi_z\bar{\Phi}_z h_1\bar{h}_2| + |\Phi_s\bar{\Phi}_s\bar{\Phi}_x\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_1 h_2|$$
$$\Psi_3 = |\Phi_s\bar{\Phi}_s\Phi_x\bar{\Phi}_x\Phi_z\bar{\Phi}_z h_1\bar{h}_2| - |\Phi_s\bar{\Phi}_s\Phi_x\bar{\Phi}_x\Phi_z\bar{\Phi}_z\bar{h}_1 h_2|$$
$$\Psi_4 = |\Phi_s\bar{\Phi}_s\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_1\bar{h}_2| - |\Phi_s\bar{\Phi}_s\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z\bar{h}_1 h_2|$$
$$\Psi_5 = |\Phi_s\bar{\Phi}_s\Phi_x\bar{\Phi}_x\Phi_y\bar{\Phi}_y h_1\bar{h}_2| - |\Phi_s\bar{\Phi}_s\Phi_x\bar{\Phi}_x\Phi_y\bar{\Phi}_y\bar{h}_1 h_2|$$
$$\Psi_6 = |\Phi_s\Phi_x\bar{\Phi}_x\Phi_y\Phi_z\bar{\Phi}_z\bar{h}_1\bar{h}_2| - |\Phi_s\Phi_x\bar{\Phi}_x\bar{\Phi}_y\Phi_z\bar{\Phi}_z\bar{h}_1 h_2| - |\bar{\Phi}_s\Phi_x\bar{\Phi}_x\Phi_y\Phi_z\bar{\Phi}_z h_1\bar{h}_2| + |\bar{\Phi}_s\Phi_x\bar{\Phi}_x\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_1 h_2|$$
$$\Psi_7 = |\Phi_s\Phi_x\bar{\Phi}_x\Phi_y\Phi_z\bar{\Phi}_z\bar{h}_1\bar{h}_2| - |\bar{\Phi}_s\Phi_x\bar{\Phi}_x\Phi_y\Phi_z\bar{\Phi}_z\bar{h}_1 h_2| - |\Phi_s\Phi_x\bar{\Phi}_x\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_1\bar{h}_2| + |\bar{\Phi}_s\Phi_x\bar{\Phi}_x\bar{\Phi}_y\Phi_z\ \bar{}_z h_1 h_2|$$
$$\Psi_8 = |\Phi_s\Phi_x\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z\bar{h}_1\bar{h}_2| - |\Phi_s\bar{\Phi}_x\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z\bar{h}_1 h_2| - |\bar{\Phi}_s\Phi_x\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_1\bar{h}_2| + |\bar{\Phi}_s\bar{\Phi}_x\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_1 h_2|$$
$$\Psi_9 = |\Phi_s\Phi_x\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z\bar{h}_1\bar{h}_2| - |\bar{\Phi}_s\Phi_x\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z\bar{h}_1 h_2| - |\Phi_s\bar{\Phi}_x\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_1\bar{h}_2| + |\bar{\Phi}_s\bar{\Phi}_x\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_1 h_2|$$
$$\Psi_{10} = |\Phi_x\bar{\Phi}_x\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_1\bar{h}_2| - |\Phi_x\bar{\Phi}_x\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z\bar{h}_1 h_2|$$
$$\Psi_{11} = |\Phi_s\bar{\Phi}_s\Phi_x\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z\bar{h}_2| - |\Phi_s\bar{\Phi}_s\bar{\Phi}_x\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_2|$$
$$\Psi_{12} = |\Phi_s\bar{\Phi}_s\Phi_x\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z\bar{h}_1| - |\Phi_s\bar{\Phi}_s\Phi_x\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_1|$$
$$\Psi_{13} = |\Phi_s\bar{\Phi}_s\Phi_x\bar{\Phi}_x\Phi_y\Phi_z\bar{\Phi}_z\bar{h}_2| - |\Phi_s\bar{\Phi}_s\Phi_x\bar{\Phi}_x\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_2|$$
$$\Psi_{14} = |\Phi_s\bar{\Phi}_s\Phi_x\bar{\Phi}_x\Phi_y\Phi_z\bar{\Phi}_z\bar{h}_1| - |\Phi_s\bar{\Phi}_s\Phi_x\bar{\Phi}_x\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_1|$$
$$\Psi_{15} = |\Phi_s\Phi_x\bar{\Phi}_x\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z\bar{h}_2| - |\bar{\Phi}_s\Phi_x\bar{\Phi}_x\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_2|$$
$$\Psi_{16} = |\Phi_s\Phi_x\bar{\Phi}_x\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z\bar{h}_1| - |\bar{\Phi}_s\Phi_x\bar{\Phi}_x\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_1|$$
$$\Psi_{17} = |\Phi_s\bar{\Phi}_s\Phi_x\bar{\Phi}_x\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z|$$
$$\Psi_{18} = |\Phi_s\bar{\Phi}_s\Phi_x\bar{\Phi}_x\Phi_y\bar{\Phi}_y h_2\bar{h}_2|$$
$$\Psi_{19} = |\Phi_s\bar{\Phi}_s\Phi_x\bar{\Phi}_x\Phi_z\bar{\Phi}_z h_2\bar{h}_2|$$
$$\Psi_{20} = |\Phi_s\bar{\Phi}_s\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_2\bar{h}_2|$$
$$\Psi_{21} = |\Phi_s\bar{\Phi}_s\Phi_x\bar{\Phi}_x\Phi_y\bar{\Phi}_y h_1\bar{h}_1|$$
$$\Psi_{22} = |\Phi_s\bar{\Phi}_s\Phi_x\bar{\Phi}_x\Phi_z\bar{\Phi}_z h_1\bar{h}_1|$$
$$\Psi_{23} = |\Phi_s\bar{\Phi}_s\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_1\bar{h}_1|$$
$$\Psi_{24} = |\Phi_x\bar{\Phi}_x\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_2\bar{h}_2|$$
$$\Psi_{25} = |\Phi_x\bar{\Phi}_x\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_1\bar{h}_1|$$

Table 1 (continued)

$$\begin{aligned}
\Psi_{26} &= |\Phi_s\bar{\Phi}_s\Phi_x\bar{\Phi}_x\Phi_y\bar{h}_1h_2\bar{h}_2| - |\Phi_s\bar{\Phi}_s\Phi_x\bar{\Phi}_x\bar{\Phi}_y h_1h_2\bar{h}_2|\\
\Psi_{27} &= |\Phi_s\bar{\Phi}_s\Phi_x\Phi_y\bar{\Phi}_y\bar{h}_1h_2\bar{h}_2| - |\Phi_s\bar{\Phi}_s\bar{\Phi}_x\Phi_y\bar{\Phi}_y h_1h_2\bar{h}_2|\\
\Psi_{28} &= |\Phi_s\bar{\Phi}_s\Phi_y\Phi_z\bar{\Phi}_z\bar{h}_1h_2\bar{h}_2| - |\Phi_s\bar{\Phi}_s\bar{\Phi}_x\Phi_z\bar{\Phi}_z h_1h_2\bar{h}_2|\\
\Psi_{29} &= |\Phi_s\bar{\Phi}_s\Phi_x\Phi_z\bar{\Phi}_z\bar{h}_1h_2\bar{h}_2| - |\Phi_s\bar{\Phi}_s\bar{\Phi}_x\Phi_z\bar{\Phi}_z h_1h_2\bar{h}_2|\\
\Psi_{30} &= |\Phi_s\Phi_x\bar{\Phi}_x\Phi_y\bar{\Phi}_y\bar{h}_1h_2\bar{h}_2| - |\bar{\Phi}_s\Phi_x\bar{\Phi}_x\Phi_y\bar{\Phi}_y h_1h_2\bar{h}_2|\\
\Psi_{31} &= |\Phi_s\Phi_x\bar{\Phi}_x\Phi_z\bar{\Phi}_z\bar{h}_1h_2\bar{h}_2| - |\bar{\Phi}_s\Phi_x\bar{\Phi}_x\Phi_z\bar{\Phi}_z h_1h_2\bar{h}_2|\\
\Psi_{32} &= |\Phi_s\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z\bar{h}_1h_2\bar{h}_2| - |\bar{\Phi}_s\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_1h_2\bar{h}_2|\\
\Psi_{33} &= |\Phi_s\bar{\Phi}_s\Phi_x\bar{\Phi}_x\Phi_y h_1\bar{h}_1\bar{h}_2| - |\Phi_s\bar{\Phi}_s\Phi_x\bar{\Phi}_x\bar{\Phi}_y h_1\bar{h}_1h_2|\\
\Psi_{34} &= |\Phi_s\bar{\Phi}_s\Phi_x\Phi_y\bar{\Phi}_y h_1\bar{h}_1\bar{h}_2| - |\Phi_s\bar{\Phi}_s\bar{\Phi}_x\Phi_y\bar{\Phi}_y h_1\bar{h}_1h_2|\\
\Psi_{35} &= |\Phi_s\bar{\Phi}_s\Phi_y\Phi_z\bar{\Phi}_z h_1\bar{h}_1\bar{h}_2| - |\Phi_s\bar{\Phi}_s\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_1\bar{h}_1h_2|\\
\Psi_{36} &= |\Phi_s\bar{\Phi}_s\Phi_x\Phi_z\bar{\Phi}_z h_1\bar{h}_1\bar{h}_2| - |\Phi_s\bar{\Phi}_s\bar{\Phi}_x\Phi_z\bar{\Phi}_z h_1\bar{h}_1h_2|\\
\Psi_{37} &= |\Phi_s\Phi_x\bar{\Phi}_x\Phi_y\bar{\Phi}_y h_1\bar{h}_1\bar{h}_2| - |\bar{\Phi}_s\Phi_x\bar{\Phi}_x\Phi_y\bar{\Phi}_y h_1\bar{h}_1h_2|\\
\Psi_{38} &= |\Phi_s\Phi_x\bar{\Phi}_x\Phi_z\bar{\Phi}_z h_1\bar{h}_1\bar{h}_2| - |\bar{\Phi}_s\Phi_x\bar{\Phi}_x\Phi_z\bar{\Phi}_z h_1\bar{h}_1h_2|\\
\Psi_{39} &= |\Phi_s\Phi_y\,\overline{}_y\Phi_z\bar{\Phi}_z h_1\bar{h}_1\bar{h}_2| - |\bar{\Phi}_s\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_1\bar{h}_1h_2|\\
\Psi_{40} &= |\Phi_s\bar{\Phi}_s\Phi_x\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_2\bar{h}_2| - |\Phi_s\bar{\Phi}_s\bar{\Phi}_x\Phi_y\Phi_z\bar{\Phi}_z h_2\bar{h}_2|\\
\Psi_{41} &= |\Phi_s\bar{\Phi}_s\Phi_x\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_1\bar{h}_1| - |\Phi_s\bar{\Phi}_s\bar{\Phi}_x\Phi_y\Phi_z\bar{\Phi}_z h_1\bar{h}_1|\\
\Psi_{42} &= |\Phi_s\bar{\Phi}_x\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_2\bar{h}_2| - |\bar{\Phi}_s\Phi_x\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_2\bar{h}_2|\\
\Psi_{43} &= |\Phi_s\bar{\Phi}_x\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_1\bar{h}_1| - |\bar{\Phi}_s\Phi_x\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_1\bar{h}_1|\\
\Psi_{44} &= |\Phi_s\Phi_x\bar{\Phi}_x\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_2\bar{h}_2| - |\bar{\Phi}_s\Phi_x\bar{\Phi}_x\Phi_y\Phi_z\bar{\Phi}_z h_2\bar{h}_2|\\
\Psi_{45} &= |\Phi_s\Phi_x\bar{\Phi}_x\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_1\bar{h}_2| - |\bar{\Phi}_s\Phi_x\bar{\Phi}_x\Phi_y\Phi_z\bar{\Phi}_z h_1\bar{h}_1|\\
\Psi_{46} &= |\Phi_x\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z\bar{h}_1h_2\bar{h}_2| - |\bar{\Phi}_x\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_1h_2\bar{h}_2|\\
\Psi_{47} &= |\Phi_x\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_1\bar{h}_1\bar{h}_2| - |\bar{\Phi}_x\Phi_y\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_1\bar{h}_1h_2|\\
\Psi_{48} &= |\Phi_x\bar{\Phi}_x\Phi_y\Phi_z\bar{\Phi}_z\bar{h}_1h_2\bar{h}_2| - |\Phi_x\,_x\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_1h_2\bar{h}_2|\\
\Psi_{49} &= |\Phi_x\bar{\Phi}_x\Phi_y\Phi_z\bar{\Phi}_z h_1\bar{h}_1\bar{h}_2| - |\Phi_x\bar{\Phi}_x\bar{\Phi}_y\Phi_z\bar{\Phi}_z h_1\bar{h}_1h_2|
\end{aligned}$$

Table 2. H_2O energies at calculated equilibrium geometry[a, b]

Nuclear repulsion	9.0842
Kinetic	76.5737
Nuclear attraction	−199.6371
Electron repulsion	37.9590
Total	− 76.0202
Virial ratio	0.9964

[a] O–H bond = 1.83 Bohr; HOH angle 106.5°.
[b] All energies in Hartrees.

reported in Table 2 for which the full set of 49 VB functions was used. The total energy, −76.0202 Hartrees, was only slightly superior to that obtained by using smaller preliminary sets; 30 functions gave an energy of −76.0163 Hartrees and 39 functions gave an energy of −76.0182 Hartrees. Both of the smaller sets contained all 10 covalent VB functions but only part of the ionic functions in Table 1. The results reported in Table 2 should be quite close to the limit obtainable with a minimal atomic basis since additional functions would represent atomic configurations of such high energies that they should not contribute significantly to the molecular wavefunction. These results for the three sets of functions emphasize the slowly convergent nature of configuration interaction with a minimal atomic basis.

Table 3. Contributions of the most important VB structures to H_2O at the calculated equilibrium geometry

Structure	Structure projection
Ψ_{11}	0.1412
Ψ_{12}	0.1412
Ψ_{1}	0.0977
Ψ_{2}	0.0977
Ψ_{17}	0.0915
Ψ_{13}	0.0655
Ψ_{14}	0.0655
Ψ_{4}	0.0561
Ψ_{8}	0.0514
Ψ_{9}	0.0514
Ψ_{15}	0.0391
Ψ_{16}	0.0391
Ψ_{3}	0.0142
Ψ_{20}	0.0081
Ψ_{23}	0.0081
Ψ_{40}	0.0081
Ψ_{41}	0.0081

Table 4. Calculated and experimental excitation energies (Hartrees)

Configuration	Calculated energies	Experimental energies
$O(1s^2 2s^2 2p^4, {}^1D)$	0.0805	0.0724
$O(1s^2 2s^2 2p^4, {}^1S)$	0.2038	0.1540
$O^-(1s^2 2s^2 2p^5, {}^2P)$	0.1594	−0.0540
$O^-(1s^2 2s 2p^6, {}^2S)$	0.8596	0.4924
$O^+(1s^2 2s^2 2p^3, {}^2P)$	0.6501	0.6846
$O^+(1s^2 2s^2 2p^3, {}^2D)$	0.7306	0.6222

The relative importance of the ionic functions in describing H_2O is shown in Table 3 which contains the structure projections or occupation numbers [13] of the most important contributing functions in the set of 49 structures. For a given structure N, the structure projection v_N is given by, $v_N = C_N \sum_M C_M S_{NM}$, where C_I is the coefficient of structure I in the molecular wavefunction, the S_{IJ} are overlap integrals $S_{IJ} = \int \Psi_I \Psi_J d\tau$, $M = 1, 2, \ldots, 49$, and $\sum_N v_N = 1$. This type of population analysis ascribes over 60% ionic character to the bonding in H_2O with the largest contributions coming from the O^- and $O^=$ configurations.

The importance of the ionic contributions to the molecular wavefunction is somewhat unfortunate since atomic and ionic excitation energies are poorly represented by a minimal atomic basis set. In Table 4 the calculated excitation energies using the gaussian-lobe basis are compared to experimental energies [14] for various O, O^-, and O^+ configurations. The errors in the calculated values of the electron affinity are particularly large.

Table 5. OH + H energies at calculated equilibrium geometry[a, b]

Nuclear repulsion	4.3013
Kinetic	76.2211
Nuclear attraction	− 189.4010
Electron repulsion	32.9913
Total	− 75.8873
Virial ratio	0.9978

[a] O–H bond = 1.86 Bohr; H at 50000 Bohr.
[b] All energies in Hartrees.

Table 6. Contributions of the most important VB structures to OH + H at the calculated equilibrium geometry

Structure	Structure projection
Ψ_2	0.2936
Ψ_{14}	0.2302
Ψ_1	0.1462
Ψ_{11}	0.1283
Ψ_3	0.0529
Ψ_4	0.0528
Ψ_6	0.0466
Ψ_8	0.0257
Ψ_7	0.0081

B) First Bond Dissociation Energy: $H_2O \rightarrow OH + H$

To obtain the dissociation energy involved in breaking one of the O–H bonds in H_2O calculations were performed with a H removed by 50000 Bohrs from the OH fragment. Preliminary calculations indicated that the bond length in the OH fragment was 1.86 Bohrs. The results for the total energy and its components for this geometry using the set of 49 VB functions are presented in Table 5. The H within the OH radical was scaled by 1.4 while the H at 50000 Bohrs was unscaled. Comparing the results in Tables 2 and 5, and using zero point energies of 13.25 kcals for H_2O [15] and 5.29 kcals for OH [16], the calculated bond dissociation energy is 75.38 kcals. The recommended experimental value is 118.0 ± 0.2 kcals (0° K) [17].

As shown in Table 6 the VB functions contributing to the OH + H system all require the leaving H to be in the ^2S state thus insuring proper dissociation products. The energy of the separated H is −0.4998 Hartrees indicating an energy of −75.3875 Hartrees for the OH radical. Freeman [18] obtained an energy of −75.327 Hartrees for OH using 10 VB functions and a Hartree-Fock atomic basis. Table 6 also indicates an ionic contribution to the OH bond of 36% arising from structures Ψ_{11} and Ψ_{14} which represent the $O^-(1s^2 2s^2 2p^5)$ configuration at infinite internuclear separation.

C) Second Bond Dissociation Energy: $OH + H \rightarrow O + 2H$

In this calculation the second H is removed to 50000 Bohrs such that the two H atoms are separated by ~ 100000 Bohrs. The calculated energies for the separated atoms are O(−74.7919 Hartrees) + 2H(−0.9996 Hartrees). The wavefunction consists of equal weights of structures Ψ_1 and Ψ_2. Using the tables of Companion and Ellison it may be shown that the wavefunction represents O in its ^3P state and each H in a ^2S state. As expected the VB method gives the correct dissociation products. The calculated second bond dissociation energy is 54.79 kcals compared to the recommended experimental value of 101.3 ± 0.5 kcals [17]. Freeman obtained a dissociation energy of 23.95 kcals using ten VB functions.

5. Discussion

The basis set used in these calculations is often referred to as being of double-zeta quality [8, 19] since atomic energies calculated with this set are found to be quite close to those given by Clementi's [20] double-zeta Slater basis. For molecular calculations however the lack of true double-zeta flexibility in the present basis set is exemplified by an SCF calculation for H_2O which gives an energy of −75.97516 Hartrees [21] while a calculation by Dunning [19] using a [42/2] basis derived from Huzinaga's [22] uncontracted set of gaussian functions gave an energy of −76.0093 Hartrees and a calculation by Guidotti and Salvetti [23] using Clementi's [20] set of Slater functions gave an energy of −76.0054 Hartrees. This deficiency in our basis set makes it difficult to compare the results of this paper with the LCAO-MO-CI calculations of Schaefer and Bender [24] which gave an energy for H_2O of −76.13497 Hartrees using 224 configurations with Dunning's [19] [42/2] basis and the calculations of Hosteny *et al.* [25], which gave an energy for H_2O of −76.14225 Hartrees using 6779 configurations and Dunning's [19] [42/2] basis set.

A major difficulty with LCAO-MO-CI calculations arises in attempting to calculate potential energy surfaces leading to correct dissociation products. For diatomic molecules the "optimized-valence configurations" method of Das and Wahl [26, 27] has led to satisfactory potential curves for a rather limited number of species. Their approach has not yet been extended to polyatomic molecules. Schaefer and Harris [28] used a complete set of configurations formed from a minimal STO basis to ensure correct dissociation behavior for O_2. With such a restricted basis set, however, good dissociation energies cannot be expected. Using an extended [421] basis Schaefer [29] has obtained an improved dissociation energy for O_2 and a potential curve parallel to the experimental curve. In this calculation 128 configurations were used which included one quadruple excitation needed to ensure dissociation to ^3P O atoms.

For polyatomic calculations it would seem that ensuring correct dissociative behavior would be quite difficult for any MO-CI calculation employing an extended basis set. For valence-bond calculations of the type we report here, however, it is a fairly simple matter to include structures in the configuration interaction whose dissociative properties are such as to allow correct molecular dissociation. For example structures Ψ_1 and Ψ_2 of Table 1 combine at infinite internuclear separation to yield O(^3P) and H(^2S) atoms. Thus as long as we include these two structures among our trial configurations we know that the potential surface will be at least qualitatively correct. A previous valence-bond-like calculation on H_2O has been reported by Guberman and Goddard [30] using a spinprojected Hartree-Fock wave function followed by orbital optimization. This procedure gives a proper account of molecular dissociation by making sufficient orbitals available to describe not only H_2O but also $OH + H$ and $O + 2H$. Their results for H_2O, $OH + H$, and $O + 2H$ using the [42/2] basis set of Dunning [19] are -76.05269, -75.89331, and -75.80525 Hartrees respectively. Their values for the first and second bond dissociation energies are thus 0.15938 Hartrees and 0.08806 Hartrees respectively compared to the comparable results of 0.1332 Hartrees and 0.0958 Hartrees obtained in the present calculation. As mentioned previously the difference in flexibility between the [42/2] basis and our minimal basis set makes comparison difficult but it does seem that the two calculations would give similar results if our basis was of true [42/2] flexibility.

Although a large number of configurations have been included in the present calculations only about 60–65% of each of the two bond dissociation energies was obtained. The deficiencies in the results are inherent in any calculation utilizing atomic basis functions incapable of permitting intraatomic configuration interaction. The particular difficulty in reproducing the electron affinity of O has its counterpart in previous *ab initio* studies where difficulty in describing F^- relative to F was encountered [31, 32]. Various semiempirical techniques have been proposed such as the "atoms-in-molecules" method of Moffitt [33] and the "interatomic correlation correction" method of Hurley [34] to compensate for these errors in relative atomic and ionic excitation energies but they must be applied with caution [32].

The importance of ionic structures in H_2O and to a lesser extent in the OH radical requires that basis functions be chosen to give at least the correct sign to the electron affinity for O and H. One procedure is to reoptimize the atomic basis functions for the negative ion of a given atom until the electron affinity is positive. Usually however the energy of the neutral atom is increased by this procedure and some compromise basis must be chosen that gives a satisfactory energy for the neutral atom but still predicts a positive electron affinity. A second procedure is to include polarization functions in the atomic basis by using a double-zeta set or by including d-type functions on O and p-type functions on H [35]. It would seem likely that the second procedure would be more effective in that it should lead to significant improvement in molecule energies [36] as well as to improved atomic and ionic excitation energies. The disadvantage to the second procedure would be the large number of additional VB structures that could be created from the expanded basis set. A selective configuration interaction calculation would then be necessary wherein the configurations necessary to ensure the proper dissociation products were combined with a judicious number of other configurations important for intraatomic correlation.

Finally the present study comments on the difference between the first and second bond dissociation energies of H_2O. The calculated difference reported here is 20.59 kcals/mole while experimentally the difference is 16.7 ± 0.7 kcals/mole. Pauling [37] and Moffitt [38] ascribe the difference to the stabilization energy of the O atom in the ^3P ground state relative to the energy of the O atom in its valence state in the OH radical and H_2O molecule. Moffitt [38] found that the valence state of O was the same in both OH and H_2O when both species were represented by a single, perfect pairing, VB structure and then assumed that the two bond dissociation energies would be identical if the O atom, after complete dissociation, existed in its valence state rather than as the ^3P state. Inspection of the structure projections for H_2O and OH in Tables 3 and 6 indicates that it is highly unlikely that the valence state of O is the same in both OH and H_2O. It is certain that the description of the valence state is more complicated than the simple mixture of ^3P and ^1D spectroscopic states proposed by Moffitt. An analysis of the valence state of O in OH and H_2O is currently being carried out along the lines suggested by Craig and Thirunmachandran [39] to determine if the calculated difference in dissociation energies can indeed be explained by valence state energies.

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