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Valence Bonds in the Main Group Elements. 2. The Sulfur Oxides

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Abstract: A new bonding description is presented for SO_2, S_2O, S_3, SO_3, H_2SO_4, and SO_4^{2-}, based on a *single* valence bond (VB) structure in each case. The results are derived from generalized valence bond (GVB) calculations, which provide accurate predictions of the experimental geometries, and contrast with the usual valence bond models for these species, which require more than one VB structure (i.e., resonance). The molecules SO_2, S_2O, and S_3 possess sulfur lone pairs that are angularly correlated. This angular separation of the two electrons within a lone pair occurs when charge is removed from the sulfur atom by electronegative atoms. Such a separation of lone pair electrons allows for the formation of additional bonds beyond that permitted by the Octet Rule. The role of d functions in the electronic structure of molecules containing second-row atoms is also considered. All calculations were performed within the GVB-PP method, i.e. incorporating the strong orthogonality and perfect pairing (SOPP) approximations.

A theoretical study of H_2S, SO_2, S_2O, S_3, SO_3, H_2SO_4, and SO_4^{2-} is reported. Several general treatments have been advanced previously for a description of their bonding,[1-4] and a number of detailed discussions concentrating on the role of d functions has been given.[1-11] Analyses of the bonding have been given in terms of "extent of hybridization",[2] bond orders,[3,10,11] or atomic orbital population densities.[3,4,11] The major thrust of this paper is to present a generalized valence bond (GVB) description of the electronic structures of these species. Each molecule or iron is described by one valence bond (VB) structure. A single VB structure is defined as a description in terms of a set of valence orbitals each containing one electron and having a unique spin coupling among the orbitals. In all calculations the atomic cores were treated at the Hartree-Fock (HF) level. The significance of the single set of valence orbitals is that there is a close correspondence between one of these VB structures and a classical valence bond (VB) "resonance" structure, except that here the orbitals are not confined to be atomic orbitals. The classical VB models for these molecules[4] (which have not had the benefit of being tested numerically) have restricted each atom to have four hybrid orbitals based on s and p atomic orbitals. Consequently two or more VB structures involving formal charge transfer are required for the total wave function to have the proper symmetry. In the present GVB description the orbitals are not restricted in their hybridization and the sulfur atoms in the molecules studied (except for H_2S and SO_4^{2-}) have *six* valence orbitals approximately arranged in a trigonal prism. The efficacy of the bonding description in terms of single VB structures is tested by the accuracy with which equilibrium geometries are predicted. If single VB structures predict equilibrium bond lengths and angles significantly different from their experimentally derived values the bonding concept described by the VB structure would have to be rejected. As shown below, not only does the GVB model based on a single VB structure provide good quantitative results for geometries, it also provides a description that has a simple logical framework because the relationships between bonding in one molecule and another are very direct.

There are certain consequences of representing each of these species by a single VB structure. The most obvious is that the Octet Rule of Lewis[12] and Langmuir[13] is violated at the sulfur atom for most of these VB structures since there are generally six orbitals localized on the central sulfur atom, earning these molecules the name "hypervalent". Furthermore, the concept of chemical bonds being formed by the overlap of atomic orbitals (AO's) is no longer tenable here as the orbitals localized on the sulfur atom are very different from the AO's of the sulfur atom. In a "bent bond" description of multiple bonds,[14,15] such as that presented here for sulfur-sulfur (S=S) and sulfur-oxygen (S=O) double bonds, s, p, and d "orbitals" no longer have any direct meaning and s, p, and d functions are better regarded merely as basis functions that compose the GVB orbitals.

As described below, angular correlation of lone pairs is an important feature of the electronic structures of these molecules. Lone pairs are usually thought of in a HF or "mean-field" sense, in which both electrons occupy the same spatial orbital. The GVB wave function permits electrons within a pair to occupy distinct orbitals so that the pair can be correlated *radially* or *angularly*. In the former case one orbital extends further from the nucleus than the other and in the latter case both orbitals have the same radial extent but split apart angularly. Angular correlation of lone pairs distinguishes these molecules from molecules containing first-row atoms that we find to have exclusively *radially* correlated lone pairs.

In a number of cases it is possible to obtain GVB wave functions for a particular molecule in which a lone pair is either radially or angularly correlated. On the basis of the variational principle it is possible to decide, within an independent-particle context, whether radial or angular correlation of the lone pair is favored. For all the sulfur oxide molecules studied, angular correlation was favored and the extent by which it was favored depended on the electronegativities of the atoms to which the sulfur atom containing the lone pair was bonded. For H_2S, radial correlation of the lone pairs was slightly favored, but by artificially increasing the

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(1) Schmiedekamp, A.; Cruickshank, D. W. J.; Skaarup, S.; Pulay, P.; Hargittai, I.; Boggs, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 2002.

(2) (a) Kutzelnigg, W. *Angew. Chem.* **1984**, *96*, 262. (b) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272.

(3) (a) Cruickshank, D. W. J. *J. Mol. Struct.* **1985**, *130*, 177. (b) Cruickshank, D. W. J.; Eisenstein, M. *J. Mol. Struct.* **1985**, *130*, 143. (c) Cruickshank, D. W. J.; Eisenstein, M. *J. Comput. Chem.* **1987**, *8*, 6.

(4) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; pp 514ff. (b) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 329.

(5) (a) Burton, P. G.; Carlsen, N. R.; Magnusson, E. A. *Mol. Phys.* **1976**, *32*, 1687. (b) Burton, P. G.; Carlsen, N. R. *Chem. Phys. Lett.* **1977**, *46*, 48.

(6) Marsden, C. J.; Smith, B. J. *J. Mol. Struct.* (*THEOCHEM*) **1983**, *105*, 385.

(7) Stromberg, A.; Wahlgren, U.; Pettersson, L.; Siegbahn, P. E. M. *Chem. Phys.* **1984**, *89*, 323.

(8) Magnusson, E.; Schaeffer, H. F. *J. Chem. Phys.* **1985**, *83*, 5721.

(9) Janszky, J.; Bartram, R. H.; Rossi, A. R.; Corradi, G. *Chem. Phys. Lett.* **1986**, *124*, 26.

(10) Yadav, A.; Surjan, P. R.; Poirier, R. A. *J. Mol. Struct.* (*THEOCHEM*) **1988**, *165*, 297.

(11) Ehrhardt, C.; Ahlrichs, R. *Theor. Chim. Acta* (*Berlin*) **1985**, *68*, 231.

(12) Lewis, G. N. *J. Am. Chem. Soc.* **1916**, *38*, 762.

(13) Langmuir, I. *J. Am. Chem. Soc.* **1919**, *41*, 868.

(14) Messmer, R. P.; Schultz, P. A. *Phys. Rev. Lett.* **1986**, *57*, 2653.

(15) Schultz, P. A.; Messmer, R. P. *J. Am. Chem. Soc.* **1988**, *110*, 8258.

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electronegativity of the H atoms, angular correlation became favored. Thus correlation in lone pairs is postulated to depend not only on atomic core size but also on the nature of the atoms bonded to the atom containing the lone pair.

There is much experimental evidence from the ground states of molecules to suggest the validity of a local approach to chemical bonding—e.g., force constants or bond lengths are generally transferable from molecule to molecule or even from molecular systems to covalently bonded solids. The preceding paper in this series presented an extension of current ideas of VB theory as the extended valence bond orbital (EVBO) model.[16] In it the localized orbitals are independent-particle probability amplitude functions or *wave packets*, one for each valence electron. The number or arrangement of wave packets around a particular atom is not limited to an octet in a tetrahedral arrangement (or 18 electrons in the case of a transition-metal complex) but is determined by the most energetically favorable means of arranging the wave packets, which are equal in number to the valence electrons. Since the Pauli principle allows electrons of opposite spin to form pairs, these wave packets are localized by pairs in "bonds" or "lone pairs", the strongest interactions are found within the pairs, and weaker interactions occur between them. This separation of orders of strength of interaction helps to rationalize why chemical bonds may be successfully considered as local entities. Their *shapes* are determined variationally and may be distorted when a wave packet is part of a bond between two atoms of significantly different electronegativity. Calculations on H_2S show that electronegativities of atoms bonded to the S atom determine the *arrangement* of the wave packets that make up the S lone pairs.

In the next section a GVB description of H_2S is given that demonstrates the importance of angular versus radial correlation in lone pairs. This is significant to the development of the ideas presented later regarding SO_2, etc. The description is initially given in terms of localized HF orbitals and this is used as an introduction to the GVB description of H_2S. This is followed by the results of GVB calculations on the remaining molecules in which geometry optimizations and discussions of bonding are given. Finally, the relevance of these results for a fuller understanding of the electronic structures of main group elements is discussed along with the role of d functions in calculations involving sulfur. Details of calculations and lone pair correlations in H_2S, SO_2, S_2O, and S_3 are given in Appendices A and B, respectively.

Electron Correlation in the Lone Pairs of H_2S

We begin by briefly reviewing the relationship between the approximate GVB wave function used in this work and the localized orbital Hartree–Fock (HF) wave function. The H_2S molecule is employed as an example. For H_2S, Ψ^{HF} is written as

$$\Psi^{HF} = \mathcal{A}[\{\text{core}\}\phi_1^2\phi_2^2\phi_3^2\phi_4^2(\alpha\beta\alpha\beta\alpha\beta\alpha\beta)] \qquad (1)$$

where $\mathcal{A}$ is the antisymmetrization operator, {core} is the set of doubly occupied core orbitals of the S atom, and ϕ_i^2 are the set of valence doubly occupied canonical molecular orbitals (CMO's) of the system. The CMO's of HF theory can be localized into bond-centered and lone pair orbitals for many molecules because the HF wave function is a single Slater determinant, and it is possible to take linear combinations of orbitals (columns) within the Slater determinant without changing the properties of the wave function. The Foster–Boys criterion[17] for localization of the CMO's is that the sum of squares of separations of centroids of localized orbitals should be a maximum. This is roughly equivalent to requiring that Coulomb repulsions between doubly occupied orbitals be minimized. When applied to a set of HF-CMO's for H_2S it results in a set of localized orbitals with two S–H bond orbitals and two lone pair orbitals. The resulting Hartree–Fock localized molecular orbital (HF-LMO) wave function is written as

$$\Psi^{HF\text{-}LMO} = \mathcal{A}[\{\text{core}\}\phi_{BP1}^2\phi_{BP2}^2\phi_{LP1}^2\phi_{LP2}^2(\alpha\beta\alpha\beta\alpha\beta\alpha\beta)] \qquad (2)$$

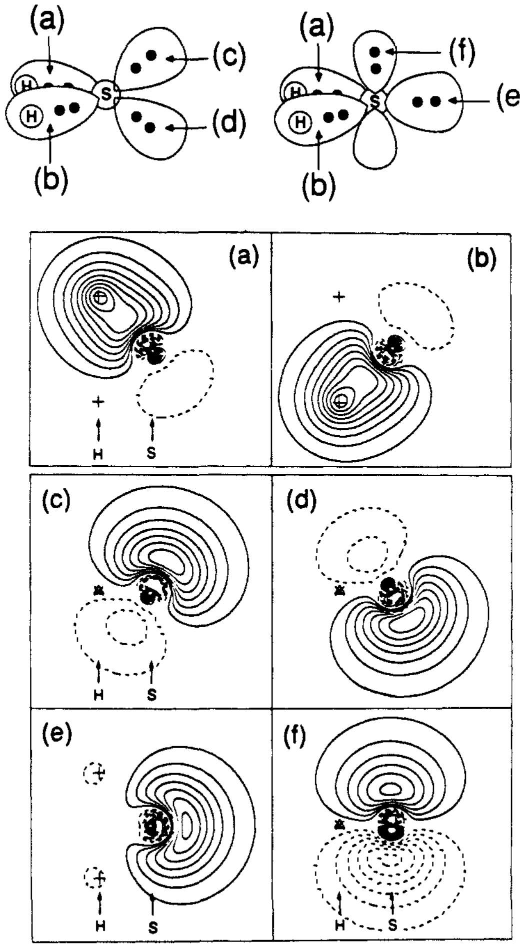

Figure 1. HF-LMO's for H_2S with a DZ+d(S) basis set: (a, b) S–H bond orbitals; (c, d) equivalent lone pair orbitals; (e, f) inequivalent lone pair orbitals. S–H bond orbitals (a, b) are common to wave functions with equivalent or inequivalent lone pair orbitals. In all orbital plots, atoms in the plane of the paper are indicated by +, atoms above the plane by ×, and atoms below the plane by Δ. Contours are separated by 0.04 au.

where ϕ_{BPi}^2 are the doubly occupied S–H bond pair orbitals and ϕ_{LPi}^2 are the lone pair orbitals. HF-LMO's for H_2S are shown in Figure 1. The two equivalent S–H bond orbitals are shown in panels a and b and the quasitetrahedral lone pairs are shown in panels c and d. Within a VB context, electron pairs in this molecule are generally considered to be in the quasitetrahedral arrangement shown in the schematic diagram at the top left of Figure 1. But it is possible to take linear combinations of the lone pair orbitals and hence represent them by a different set of orbitals. If the following transformation is applied to the lone pair orbitals, ϕ_{LPi}^2, in eq 2

$$\phi'_{LP1} = (\phi_{LP1} + \phi_{LP2})/\sqrt{2} \qquad (3a)$$

$$\phi'_{LP2} = (\phi_{LP1} - \phi_{LP2})/\sqrt{2} \qquad (3b)$$

then an equivalent HF-LMO wave function but with different lone pair orbitals results

$$\Psi^{HF\text{-}LMO} = \mathcal{A}[\{\text{core}\}\phi_{BP1}^2\phi_{BP2}^2\phi'^2_{LP1}\phi'^2_{LP2}(\alpha\beta\alpha\beta\alpha\beta\alpha\beta)] \qquad (4)$$

These transformed lone pair orbitals are shown in panels e and f of Figure 1 and consist of a p-type orbital perpendicular to the plane of the molecule and another orbital in the molecular plane. The reason for considering these two possibilities for the lone pair orbitals will become clear shortly.

In order to introduce the GVB wave function used in this study, it is convenient to regard a localized HF spatial orbital containing two electrons of opposite spin as two distinct spin orbitals with *unit spatial overlap*. The GVB wave function of interest emerges

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(16) Messmer, R. P. *Phys. Rev. A.* Submitted for publication.
(17) Foster, S.; Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 296.

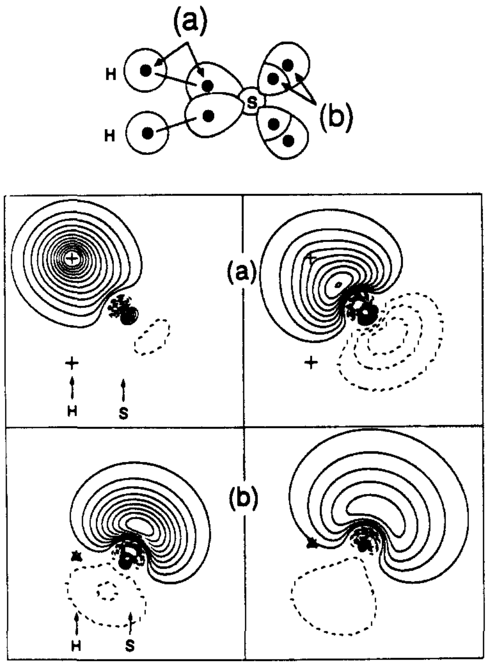

Figure 2. GVB orbitals for H_2S with DZ+d(S) and DZ basis sets for S and H, respectively: (a) left-right correlated S–H bond orbitals; (b) radially correlated S lone pair orbitals.

by allowing the orbitals within an HF-LMO pair to adjust their shapes self consistently (and thereby overlap to a variationally determined extent), which introduces *correlation* into the description of the electron pair. When the spatial orbitals of the electron pair are no longer identical the usual HF closed-shell spin function, $\alpha\beta$, must be changed to $(\alpha\beta-\beta\alpha)$ in order to assure a proper overall singlet wave function. Because the only spin coupling is within a pair and the only overlap of orbitals is within a pair, this wave function is referred to as the strongly orthogonal perfect-pairing (SOPP) approximation of the GVB wave function.[18] In the following when we refer to GVB wave functions the SOPP approximations are always employed unless otherwise stated.

The GVB wave function for H_2S is written as

$$\Psi^{GVB} = \mathcal{A}[\{\text{core}\}\varphi_{aBP1}\varphi_{bBP1}\varphi_{aBP2}\varphi_{bBP2}\varphi_{aLP1}\varphi_{bLP1}\varphi_{aLP2}\varphi_{aLP2}\theta^{PP}] \tag{5}$$

where {core} is a product of doubly occupied orbitals describing the S atomic core, φ_{aBP1} is one of the GVB orbitals, and θ^{PP} is a product of singlet spin coupling factors, $(\alpha\beta-\beta\alpha)$, one for each pair. The self-consistently determined GVB orbitals for H_2S, which are found to describe the electron pairs in a quasitetrahedral arrangement, are shown in Figure 2. There are two equivalent bond pairs and two equivalent lone pairs; one of each are shown in panels a and b, respectively, of Figure 2. A schematic representation of the orbitals is also shown at the top of the figure. The effects of introducing electron correlation within the electron pairs are apparent on comparing Figures 1 and 2; in the GVB description one orbital of the bond pair localizes on the H nucleus and the other in a lobe about the S core. In such a two center–two electron bond this is referred to as left-right correlation since the orbitals tend to localize on separate nuclei. The two lone pair orbitals must correlate in a different manner since they share a single nucleus. One electron occupies a more compact orbital closer to the nucleus and the other occupies a more diffuse orbital further from the nucleus; thus the lone pair exhibits radial correlation.

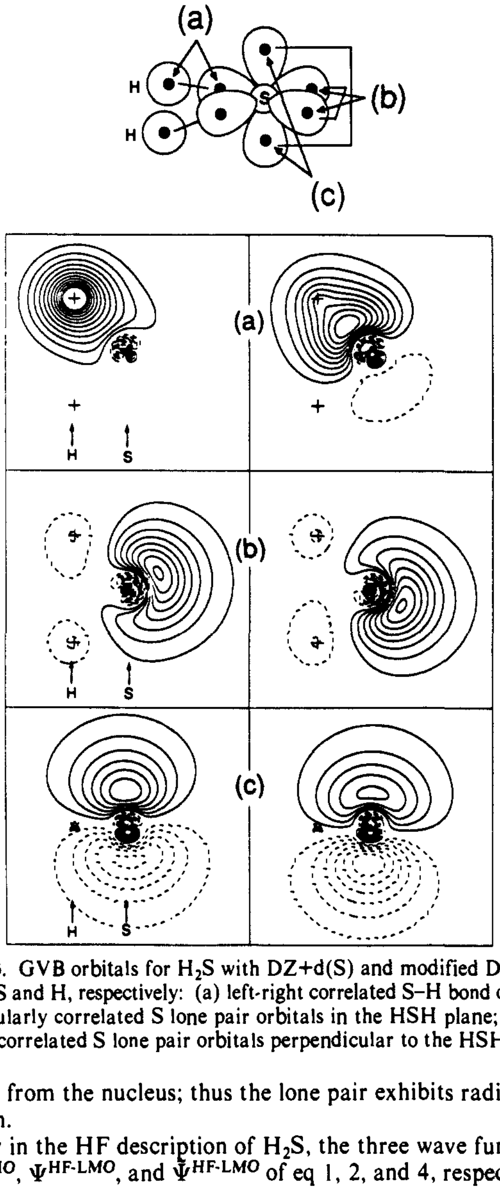

Figure 3. GVB orbitals for H_2S with DZ+d(S) and modified DZ basis sets for S and H, respectively: (a) left-right correlated S–H bond orbitals; (b) angularly correlated S lone pair orbitals in the HSH plane; (c) angularly correlated S lone pair orbitals perpendicular to the HSH plane.

Now in the HF description of H_2S, the three wave functions $\Psi^{HF\text{-}CMO}$, $\Psi^{HF\text{-}LMO}$, and $\Psi^{HF\text{-}LMO}$ of eq 1, 2, and 4, respectively, have identical properties since they each consist of the same single determinant. However, the GVB wave function, consisting of a sum of determinants, does not share the property that orbitals may be transformed without altering the total wave function—the orbitals of the GVB wave function are therefore unique. Introducing correlation into equivalent HF-LMO wave functions with different orbitals, i.e., the wave functions described by eq 2 and 4, respectively, results in different total energies for the correlated (GVB) wave functions. This difference in GVB total energies varies depending upon the electronegativity of the X atom in the X_2S molecule as described below.

If we consider a hypothetical molecule X_2S, in which H_2S is one limiting case and the electronegativity of "X" can be increased by augmenting its potential for attracting electrons from the S atom, then a simple physical effect may be illustrated. We will simply refer to this "theoretical" atom as an X atom. Consider the limiting case when correlation is introduced into the H_2S molecule, which is the situation described above and shown in Figure 2. This results in a correlated version of the HF-LMO lone pair orbitals of Figure 1c,d. If, however, we increase the electronegativity of H by using an X_2S molecule in the calculation,[19] we obtain the correlated orbitals shown in Figure 3. The

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[18] (a) The SO and PP approximations were first suggested in: Hurley, A. C.; Lennard-Jones, J. E.; Pople, J. A. *Proc. R. Soc. London, Ser. A* **1953**, *220*, 446. They were later implemented in the GVB method by Goddard and co-workers. (b) Hay, P. J.; Hunt, W. J.; Goddard, W. A., III *J. Am. Chem. Soc.* **1972**, *94*, 8293. (c) Hunt, W. J.; Hay, P. J.; Goddard, W. A., III *J. Chem. Phys.* **1972**, *57*, 738. (d) Bobrowicz, F. W.; Goddard, W. A., III *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Vol. 3, Chapter 4.

[19] The orbitals of Figure 3 were obtained in a calculation in which the electronegativity of the H atoms had been artificially increased by modifying the H atom basis set. In this case the octahedral arrangement of electrons was favored over the tetrahedral arrangement of electron pairs by ~0.05 eV; see Appendix B.

S–"H" bond pair orbitals are similar to those in Figure 2a except for the pronounced polarization of the S orbitals toward the X atoms. However, the lone pair orbitals are very different. One pair, shown in panel b, is *angularly correlated* in the HSH plane so that both GVB orbitals have the same radial extent but the orbitals are split apart angularly. The other pair resembles a pair of p orbitals in which one lobe or the other is alternately emphasized in the two correlated orbitals. Because of the arrangement of GVB orbitals around the S atom this is referred to as the "octahedral" arrangement of electrons compared to the previous "tetrahedral" arrangement of electron pairs.

Thus in a real molecule, A_2S, where A may be a F atom for example, we can expect the sulfur lone pairs to be very different than in the H_2S molecule. The consequence of this is that additional stable bonds may be formed in the former case (such as in SF_4) because the Pauli repulsions between bond pairs will be very much reduced over what they would be for additional bonds to the H_2S molecule.

Results of GVB Calculations

We have noted that each of the molecules studied can be described by a single VB structure in contrast to previous VB models for these molecules. There are three pertinent reasons for having a description that does not include resonance. First, and perhaps the most important, is the conceptual advantage. We seek the *simplest* possible model that accounts for the basic experimentally observed properties of the molecules. The need to include resonance in standard VB descriptions of these sulfur oxide molecules is an artifact introduced by requiring the electrons to occupy four valence s and p atomic or hybridized orbitals. Second, a resonating GVB calculation requiring several nonorthogonal VB structures for molecules of this size would require inordinate amounts of computer time. Third, if the single VB structure does capture the essential features of the electronic structure, improvements to the wave function may be accomplished by performing GVB-CI calculations to obtain improved properties or excited state energies. This is possible, of course, since the occupied natural orbitals and virtual orbitals are all mutually orthogonal.

We have already discussed the fact that there are two possible ways in which the lone pairs of H_2S can be correlated. In fact there is a third way of arranging six wave packets about the sulfur core, and with the exception of the sulfate anion this is the mode adopted in all the other molecules to be discussed here. This distribution of electron wave packets is the *trigonal prismatic* arrangement. The octahedral arrangement of electrons was preferred in the (modified-H) X_2S calculation. This may be the result of the fact that "triples" of electrons are *staggered* in the octahedron but *eclipsed* in the trigonal prism, resulting in lesser electron–electron repulsions in the octahedron. Nevertheless the trigonal prismatic lobes are better suited for formation of one, two, or three double bonds whereas the octahedral lobes are more appropriately oriented for formation of two, four, or six single bonds. In the description of bonding in sulfur oxides being presented here the S atom forms double bonds to two oxygen atoms with use of lobe orbitals in a quasitrigonal prismatic arrangement.

A. Sulfur Dioxide (SO_2). The sulfur dioxide molecule has been the subject of HF,[1,3c,5-10] GVB,[20] CI,[21] and MCSCF[21] studies. Total energies, predicted equilibrium geometries,[1,6,9,10] and a variety of electronic properties such as dipole moments,[21] polarizabilities,[21] and Raman activities[21] have been calculated. In this study we have optimized the molecular geometry using HF and GVB wave functions and investigated the effects of omitting d functions from the basis set and give a new interpretation of the bonding in SO_2. The experimental bond length and bond angle are respectively 1.432 Å and 119.5°.[22] Below we make comparison of equilibrium geometries and total energies (at the experimental geometry) using HF and GVB wave functions and various basis sets. The conclusion, that a double-ζ (DZ) plus single-ζ d function (d) basis set for each atomic site (O,S) was adequate to accurately reproduce the experimental geometry of SO_2, was applied to the other molecules studied and found to hold in those cases also. (See Appendix A for basis set details.)

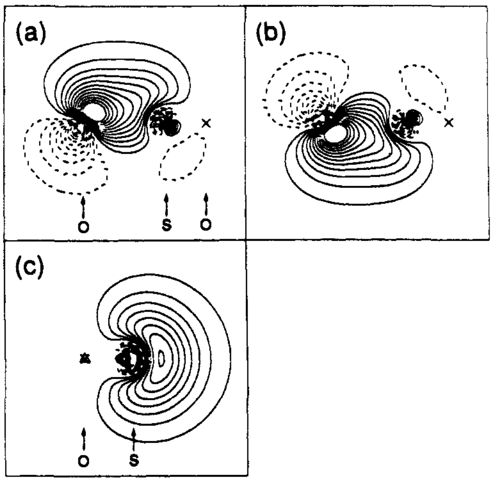

Figure 4. HF-LMO's for SO_2 with a DZ+d(O,S) basis set: bond orbitals representing the S=O double bond (a, b) and the S lone pair (c).

The experimental geometry was not well reproduced when only a DZ basis set was employed for S and O sites. At the HF level the equilibrium bond length and bond angle were determined to be r_{SO} = 1.534 Å and ∠O–S–O = 112.8°. Considerable improvement in the agreement between predicted geometry and experimental geometry was found at the HF level when a single d function was included on the S site alone (r_{SO} = 1.436 Å and ∠O–S–O = 117.8°). Supplementing this basis set with single d functions on the O site led to much smaller changes in geometry and total energy. The equilibrium geometry determined at the HF level for a single d function on each site was r_{SO} = 1.423 Å and ∠O–S–O = 118.1°. Thus, the HF wave function, when computed with a DZ+d basis on each site, accounts well for the equilibrium geometry of sulfur dioxide. This fact had already been established,[1,6,9,10] but these results are presented here to enable direct comparison to be made with the results of the GVB calculations presented below. When electron correlation was introduced via the GVB wave function the equilibrium geometry obtained with a DZ+d(O,S) basis set was r_{SO} = 1.436 Å and ∠O–S–O = 118.2°, also in good quantitative agreement with the experimental equilibrium geometry. The difference in SO equilibrium bond lengths of +0.013 Å between the HF and GVB wave functions is typical of a comparison of these two methods. As is well-known, the HF wave function typically *underestimates* bond lengths because it overemphasizes ionic terms in the wave function (which leads to the familiar HF problem of incorrect bond dissociation) whereas the GVB wave function typically *overestimates* bond lengths because it overemphasizes covalent terms in the wave function (this is a consequence of the fact that this wave function does not account for dynamic correlations). A geometry optimization of SO_2 with use of a GVB wave function has been reported previously.[20] In that case only three valence electron pairs (out of nine) were correlated and the equilibrium geometry predicted was r_{SO} = 1.450 Å and ∠O–S–O = 120.0°. In the present study all nine valence electron pairs are correlated. This previously reported GVB bond length in SO_2 is 0.014 Å longer than our calculated bond length, and this may be a consequence of the representation of the SO bonds in that calculation which differ significantly from our GVB description and the HF-LMO description. In the former case, with symmetry restrictions imposed, the SO bonds are each represented by a σ bond pair and one π pair which extends over both SO bonds. The HF-LMO description obtained according to the Foster–Boys localization criterion consists of two double SO bonds polarized toward the O atoms, two lone pairs on each O atom and one lone pair on the S atom (Figure 4). There is a one-to-one corre-

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(20) Dunning, T. H.; Raffenetti, R. C. *J. Phys. Chem.* **1981**, *85*, 1350.

(21) Backsay, G. B.; Rendell, A. P. L.; Hush, N. S. *J. Chem. Phys.* **1988**, *89*, 5721.

(22) Kivelson, D. *J. Chem. Phys.* **1954**, *22*, 904.

Table I. Optimized Geometries and Total Energies

(a) For SO_2, S_2O, S_3 (Thiazone), S_3 (Ring), SO_3, and SO_4^{2-}

molecule	W'Fn: basis set	$r_{S=O}$ (Å)	$r_{S=S}$ (Å)	bond angle (deg)	total energy (H)	molecule	W'Fn: basis set	$r_{S=O}$ (Å)	$r_{S=S}$ (Å)	bond angle (deg)	total energy (H)
SO_2	(expt)	1.432		119.5		SO_3	(expt)	1.4198		120.0	
SO_2	HF: DZ	1.534		112.8	−546.980957	SO_3^{b}	GVB: DZ+d(O,S)	1.423		120.0	−622.182144
SO_2	HF: DZ+d(S)	1.436		117.8	−547.150704	SO_4^{2-}	(expt)	1.486			
SO_2	HF: DZ+d(O,S)	1.423		118.1	−547.202598	SO_4^{2-}	HF: DZ+d(O,S)	1.494		109.5	−696.863803
SO_2^{a}	GVB: DZ+d(O,S)	1.436		118.2	−547.313676	SO_4^{2-}	HF: DZ+d,f(O,S)	1.485		109.5	−696.894573
S_2O	(expt)	1.465	1.884	118.0		$SO_4^{2-\,b}$	GVB: DZ+d(O,S)	1.507		109.5	−697.058331
S_2O^{b}	GVB: DZ+d(O,S)	1.460	1.885	117.1	−869.915663	$SO_4^{2-\,b}$	GVB: DZ+d,f(O,S)	1.499		109.5	−697.087773
S_3(thio)^{b}	GVB: DZ+d(O,S)		1.91 (6)	117.3	−1192.534275						
S_3(ring)^{b}	GVB: DZ+d(O,S)		2.134	60.0	−1192.559626						

(b) For $H_2SO_4^{b}$

W'Fn: basis set	$r_{S=O}$ (Å)	r_{S-O} (Å)	r_{O-H} (Å)	∠O=S=O (deg)	∠O-S-O (deg)	∠S-O-H (deg)	θ_1 (deg)^{c}	θ_2 (deg)^{d}	total energy (H)
(expt)	1.422	1.574	0.971	123.3	101.3	108.5	88.4	20.8	
HF: DZ+d(O,S)	1.419	1.572	0.961	123.6	101.9	111.1	88.8	25.5	−698.100078
GVB: DA+d(O,S)	1.426	1.592	0.976	123.1	102.0	106.1	88.3	22.3	−698.302862

[a] All nine valence electron pairs correlated. [b] All sixteen valence electron pairs correlated. [c] Angle between O(1)–S–O(2) and O(3)–S–O(4) planes in Chart I. [d] Dihedral angle H–O(1)–S–O(4) in Chart I.

Table II. Total Energy Dependence on Basis Set and Wave Function in SO_2^{a} and $H_2SO_4^{b}$

basis set	wave function	total energy (hartrees)	energy lowering (eV)
SO_2			
DZ	HF	−546.955413	0.00
DZ+d(S)	HF	−547.148754	−5.26
DZ+d(O,S)	HF	−547.200596	−6.67
DZ	GVB	−547.054468	−2.69
DZ+d(S)	GVB	−547.257140	−8.21
DZ+d(O.S)^{c}	GVB	−547.307840	−9.59
DZ+d(O.S)^{d}	GVB	−547.311305	−9.68
H_2SO_4			
DZ+d(O,S)^{e}	GVB	−698.297988	0.00
DZ+d(O,S)^{f}	GVB	−698.298465	−0.01

[a] All nine valence electron pairs correlated in GVB-SOPP wave function. [b] All sixteen valence electron pairs correlated in GVB-SOPP wave function. [c] Natural orbitals restricted to σ or π symmetries. [d] No restriction on natural orbital symmetries resulting in bent S=O bonds. [e] "Bent bond" description. [f] "Backbonded" description.

spondence between our GVB electron pairs and the HF localized orbitals, thus there is a bond order of ~2 in these cases whereas the three electron pair GVB description of Dunning and Raffenetti[20] makes no obvious provision for a bond order of 2. The HF and GVB geometry optimizations for SO_2 are summarized in Table Ia.

Total energies at the experimental geometry were investigated for the HF and GVB wave functions as a function of basis set. The reference zero is the HF wave function with a DZ basis set at each site. Energy lowerings on introducing more flexible basis sets and/or electron correlation are summarized in Table II. From the table it can be concluded that introduction of a d function on the S site causes the largest energy lowering for either the HF (5.26 eV) or GVB (5.52 eV) wave functions; introduction of a d function onto the O sites also results in further energy lowerings of 0.70 and 0.73 eV per O atom for the HF and GVB wave functions, respectively. Introduction of electron correlation via the GVB wave function with a DZ+d(O,S) basis set results in an energy lowering of 3.01 eV relative to the DZ+d(O,S) HF wave function. The importance of including d functions on hypervalent S atoms has been stressed many times before but we believe that the independent-particle GVB wave function (for which a unique pictorial representation is possible) used in this work provides additional insight into the reasons underlying these observations. Their importance is not due to population of atomic d orbitals, but the anomalously large energy lowerings found on including them are the result of an incomplete basis set that does not permit the valence bond orbitals within pairs to attain their optimum shapes while remaining orthogonal to those in other pairs. A fuller discussion of this subject is reserved for later. We now turn to an interpretation of the GVB description of bonding in SO_2.

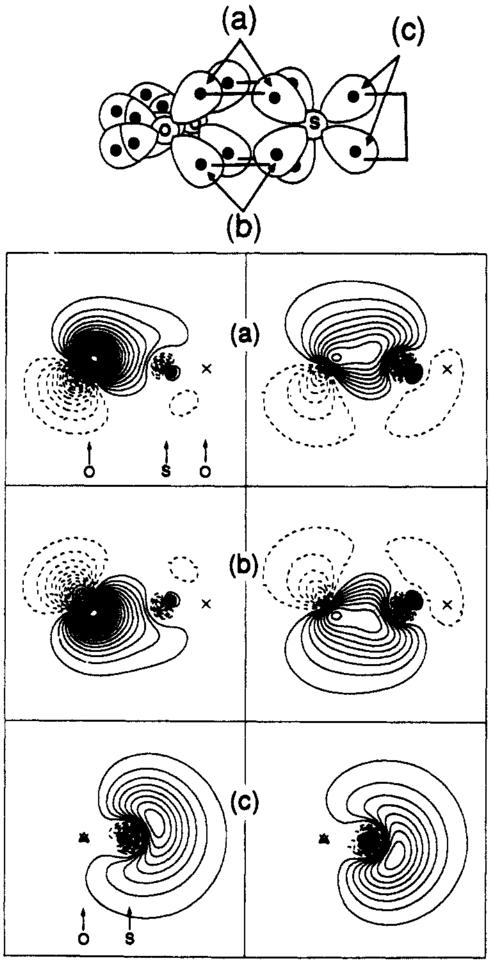

Figure 5. GVB orbitals for SO_2 with a DZ+d(O,S) basis set: orbitals representing the S=O double bond (a, b) and the angularly correlated S lone pair (c).

The HF-LMO's for SO_2 (Figure 4) employed the DZ+d(O,S) basis set. In this case each orbital is occupied by an electron *pair*. The SO bond is represented as a double bond strongly polarized toward the O atom (Figure 4a,b), consisting of two symmetrically equivalent bent bonds. Also shown is the S lone pair orbital (Figure 4c).

In the GVB description (Figure 5) each of the SO bent bonds is represented by two orbitals containing *one* electron each.

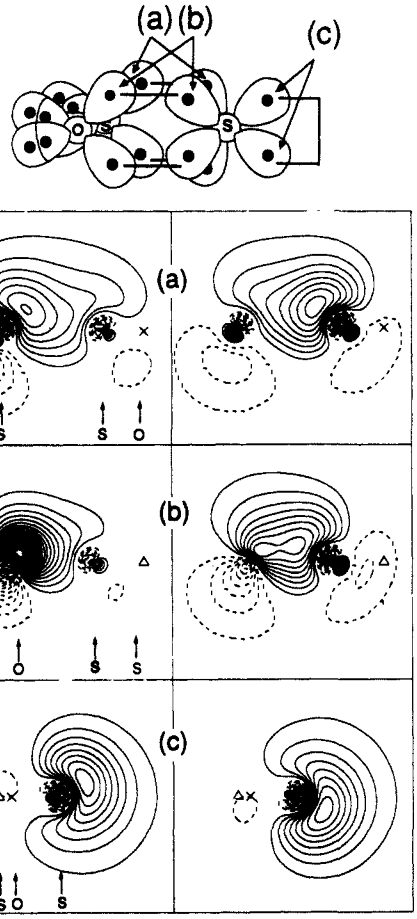

Figure 6. GVB orbitals for S_2O with a DZ+d(O,S) basis set: (a) orbitals representing part of the S=S double bond (the remaining two orbitals may be generated by reflecting those shown in the molecular plane); (b) orbitals representing part of the S=O double bond; (c) angularly correlated S lone pair.

Correlation has been introduced into orbitals a and b of Figure 4 and the result is two sets of unique orbitals describing the S=O double bond. For each of the bonds, one of the orbitals is localized on the O atom and the other on the S atom; however, the one localized on the S atom is severely polarized toward the O atom. Thus we have a GVB description of a polar-covalent bond that bears considerable resemblance to the HF-LMO description. Lone pair orbitals on the S atom are shown in Figure 5c. Note that these orbitals are angularly correlated. The lone pair orbitals localized on the O atom (not shown) were in the molecular plane and radially correlated, as expected (see schematic diagram at the top of Figure 5). Thus the arrangement of lobes around the O atom is quasitetrahedral and around the S atom it is quasitrigonal prismatic. The Octet Rule holds for the O atom but breaks down for the hypervalent S atom, which is formally surrounded by five electron pairs.

B. Disulfur Monoxide (S_2O). The molecule S_2O is similar in geometry to SO_2 having a bond angle of 118.0° and bond lengths of r_{SO} = 1.465 Å and r_{SS} = 1.884 Å.[23] HF[24] and CI[25] calculations have been performed for this molecule. The equilibrium geometry reported in a multireference double-excitation CI geometry optimization[25] (r_{SS} = 1.884 Å; r_{SO} = 1.500 Å; ∠SSO = 117.5°) is in good agreement with the experimental geometry except for an overestimate of the S=O bond length (+0.035 Å). The equilibrium geometry determined with the GVB wave function with a single-ζ d function on each site was r_{SS} = 1.885 Å, r_{SO} = 1.460 Å, and ∠SSO = 117.7°, again in good agreement with experiment.

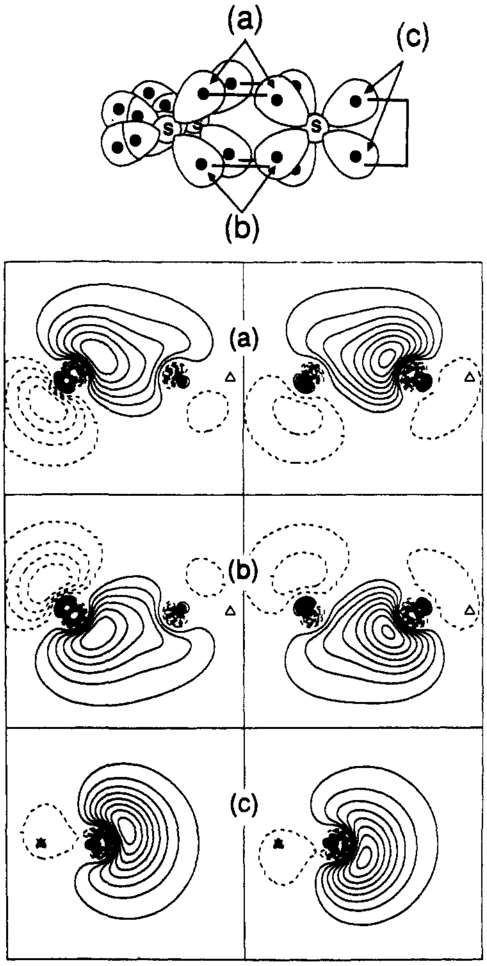

Figure 7. GVB orbitals for the S_3 thiozone structure with a DZ+d(S) basis set: (a, b) orbitals representing the S=S double bond; (c) angularly correlated S lone pair.

The total energy and optimized geometry are presented in Table Ia.

The S_2O molecule differs from SO_2 in that one of the bonds to the central S atom is replaced by one in which the atoms are of equivalent electronegativity instead of one being of significantly greater electronegativity. However, the qualitative (pictorial) description of bonding in SO_2 presented above also applies to S_2O (compare the schematic diagrams at the tops of Figures 5 and 6). The orbitals representing the S=O and S=S bonds in S_2O reflect the differing electronegativities of O and S. In the former case the orbitals are distorted toward the O atom and in the latter case they are more evenly distributed. There is, on inspection, a marked similarity between the S=O bonds in S_2O and SO_2. This demonstrates, at least, the transferability of "orbital shapes" if not that of "bonds" from molecule to molecule. Such orbital shape transferability is also found when the orbitals of the S=S bond in S_2O are compared to those of the thiozone form of S_3 in the next section and between the S=O bonds in SO_2, SO_3, and H_2SO_4! These similarities all point to the transferability of these chemical bonds and the value of the notion that bonds between atoms are well described by electron *wave packets*.

As a final note in this section the lone pair orbitals on the terminal S atom are radially correlated in contrast to the central S atom lone pair, which is angularly correlated. The terminal O atom was also found to have radially correlated lone pairs that give an overall tetrahedral arrangement of electron pairs about the O atom, as is the case in SO_2.

C. Trisulfur (S_3). There has been some debate over the structure of this molecule that has only recently[26] been studied

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[23] Tiemann, E.; Hoeft, J.; Lovas, F. J.; Johnson, D. R. *J. Chem. Phys.* **1974**, *60*, 5000.

[24] Rosmus, P.; Dacre, P. D.; Solouki, B.; Bock, H. *Theor. Chim. Acta* **1974**, *35*, 129.

[25] Fueno, T.; Buenker, R. J. *Theor. Chim. Acta* **1988**, *73*, 123.

[26] Lenain, P.; Piquenard, E.; Lesne, J. L.; Corset, J. *J. Mol. Struct.* **1986**, *142*, 355.

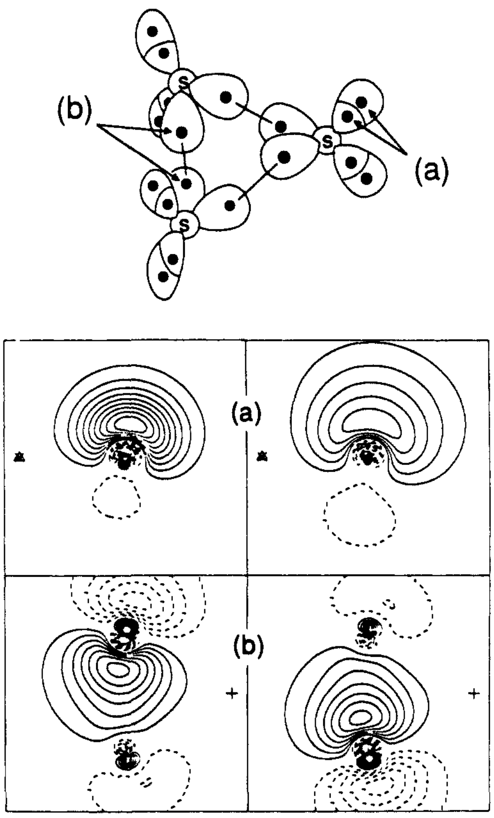

Figure 8. GVB orbitals for the S_3 ring structure with a DZ+d(S) basis set: (a) orbitals representing one of the six equivalent radially correlated S lone pairs; (b) orbitals representing one of the three S–S single bonds.

experimentally. From a VB point of view there are two structures that the molecule could adopt and these are illustrated schematically at the top of Figures 7 and 8. First of all there is a thiozone structure similar to that of SO_2 or S_2O, with a VB picture of the electronic structure resembling that of SO_2 or S_2O. The bond angle is expected to be slightly less than 120° and the bond length is expected to be around 1.9 Å, by comparison with S_2O. The second is a ring structure with a bond angle of 60° and an expected bond length similar to that in S_8 (mean value r_{SS} = 2.06 Å);[27] however, bond angle strain in the ring form must destabilize it somewhat and result in an elongated S–S bond length. The debate over this molecule's structure has been the result of conflicting predictions for the ground-state equilibrium geometry dependent on which theoretical method and basis set were applied. The issue is further complicated by the fact that, according to an MRDCI[25] calculation, there is a significant barrier (~1.3 eV) to interconversion between the thiozone and ring isomers, while there is a much smaller difference in their total energies (~0.3 eV).[25] Thermal interconversion of the isomers is therefore predicted to be negligible kinetically, and any experiment to determine the structure of the molecule cannot rely on the molecule being in its minimum energy geometry. Thus the recent IR study of the molecule by Lenain et al.,[26] which indicated that the molecule was in the thiozone form, is not conclusive proof that this form is the minimum energy geometry.

To date density functional[28,29] (DF), MRDCI,[25,30] and molecular dynamics–density functional[31] (MD–DF) geometry optimizations have been reported that find the thiozone form to be more stable. The estimate of the energy difference between the two isomers in these cases ranges between 0.11 and 0.32 eV for the DF[28] and one of the MRDCI[25] calculations, respectively. On the other hand, there are HF,[30,32] single and double CI[30] (CI–SD), and GVB calculations (this work) that support a ring isomer as the ground state. In this case the estimated energy difference between the isomers ranges from 0.10 to 1.12 eV below the thiozone structure for the CI–SD and one of the HF[32] calculations, respectively. The GVB estimate of energy difference between the isomers is 0.69 eV. Theoretically the evidence accumulated so far is probably in favor of the thiozone structure but, as has already been suggested,[32] the S_3 molecule may be experimentally observable in both geometries.

In this study we optimized the geometries of both VB structures of S_3 using the DZ+d(O,S) basis set and GVB wave function (Table Ia). The thiozone isomer was a local minimum in the potential energy surface, lying +0.69 eV above the minimum energy. The thiozone structure had an optimized bond length of 1.916 Å and bond angle of 117.3°. The ring isomer was predicted to have an equilibrium bond length of 2.134 Å, +0.07 Å longer than the mean single bond length in crystalline S_8. This seems reasonable in light of the fact that the bonds in the ring form of S_3 are expected to be severely strained (the bond angles in S_8 range between 105.3° and 107.2°).[27]

GVB oribtals of the thiozone and ring isomers of S_3 are shown in Figures 7 and 8. In the thiozine isomer the S=S double bond is represented by the four orbitals of Figure 7a,b and its angularly correlated lone pair is shown in Figure 7c. The VB description of the ring isomer has six equivalent, radially correlated lone pairs (Figure 8a) out of the molecular plane and three bent single bonds in the molecular plane (Figure 8b). The sulfur atoms in the ring isomer are surrounded by quasitetrahedral electron pairs, indicating that this form of the molecule is not actually "hypervalent".

There is one further point to be made when the strong orthogonality approximation is used for a comparison of the relative stabilities of two isomers such as these. This approximation will, of course, be better when the orbitals of different pairs in the full GVB wave function overlap to a small extent. It is well-known that the tetrahedral hybrids formed from linear combinations of an s and three p atomic orbitals are mutually orthogonal. In the full GVB wave function the electron pairs of the ring isomer are therefore likely to overlap to a small extent because of their approximately tetrahedral arrangement on all atoms, were the strong orthogonality constraint to be relaxed. The thiozone isomer has *six* GVB orbitals centered on one of the S atoms of which each must be orthogonal to at least four of the others since they belong to five different electron pairs. The strong orthogonality constraint is theerefore expected to be more severe in this case and so the SO approximation of the GVB wave function is expected to be biased against a thiozone ground state. To give an idea of the energetic cost of the strong orthogonality constraint, the energy lowering produced by relieving the strong orthogonality between the bent bonds in tetrafluoroethylene[15] was found to be 0.292 eV. Thus, it is not inconceivable that removing the strong orthogonality constraint in a full GVB calculation on both isomers could reverse the predicted order of stability.

D. Sulfur Trioxide (SO_3). We now proceed to describe two molecules, SO_3 and H_2SO_4, that can be formed by uncoupling the angularly correlated lone pair of SO_2 and forming one double or two single bonds to an O atom or two OH radicals, respectively. From the transferability of orbital shapes seen in the molecules above, we might expect the remaining orbitals that are common to both SO_2 and SO_3 to differ by only a small extent. This was indeed found to be the case in SO_3. A schematic diagram and GVB orbitals belonging to one of the three equivalent bonds of SO_3 are shown in Figure 9. The resemblance to orbitals of the S=O bonds in SO_2 is apparent.

The S=O bond length is slightly shorter in SO_3 than in SO_2, the experimental value being 1.4198 Å.[33] Bond angles in SO_3 are, of course, 120° by symmetry. The geometry-optimized GVB wave functions predicts an equilibrium bond length of 1.423 Å

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(27) *Elemental Sulfur, Chemistry and Physics*; Meyer, B., Ed.; Wiley: New York. 1966; p 29.

(28) Jones, R. O. *J. Chem. Phys.* **1985**, *84*, 318.

(29) Morin, M.; Foti, A. E.; Salahub, D. R. *Can. J. Chem.* **1985**, *63*, 1982.

(30) Rice, J. E.; Amos, R. D.; Handy, N. C.; Lee, T. J.; Schaefer, H. F., III *J. Chem. Phys.* **1986**, *85*, 963.

(31) Hohl, D.; Jones, R. O.; Car, R.; Parrinello, M. *J. Chem. Phys.* **1988**, *89*, 6823.

(32) Carlsen, N. R.; Schaefer, H. F., III *Chem. Phys. Lett.* **1977**, *48*, 390.

(33) Kaldor, A.; Maki, A. G. *J. Mol. Struct.* **1973**, *15*, 123.

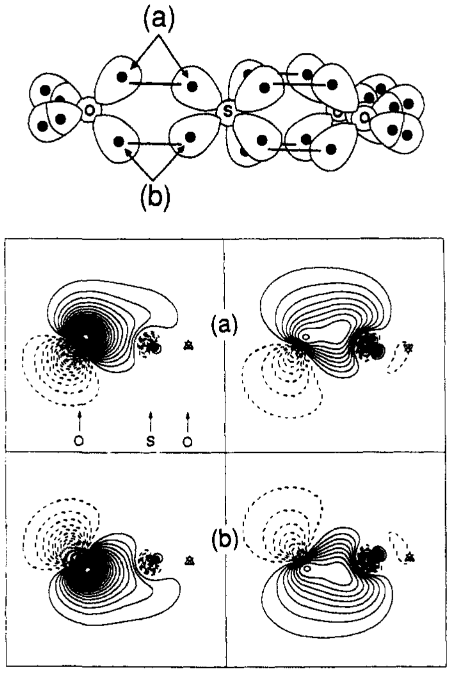
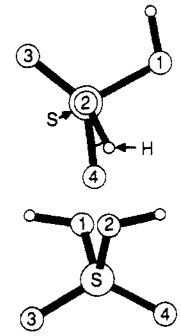


Figure 9. GVB orbitals for SO_3 with a DZ+d(O,S) basis set: (a, b) orbitals representing the S=O double bond.

Chart I



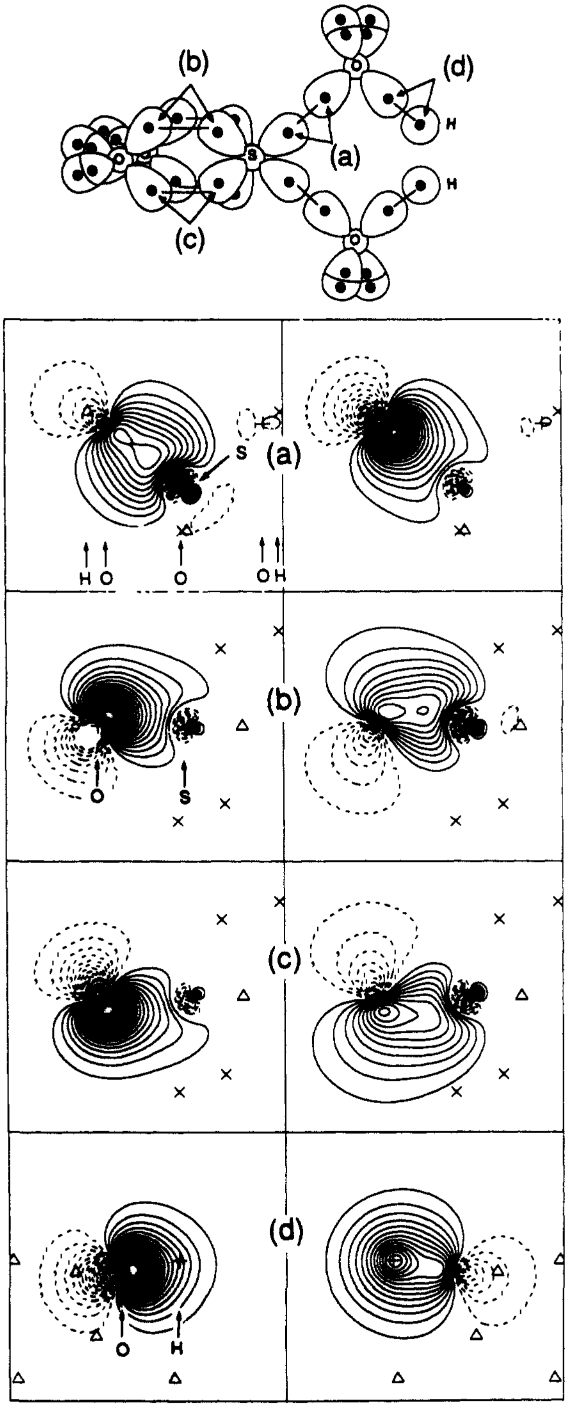


Figure 10. GVB orbitals for H_2SO_4 with a DZ+d(O,S) basis set: (a) orbitals representing the S—O single bond; (b, c) orbitals representing the S=O double bond (inequivalences in orbitals on S or O are introduced by the fact that the O=S=O plane is not a mirror plane); (d) orbitals representing the O—H bond.

(Table Ia). The oxygen lone pairs are not shown but are in radially correlated lone pairs in the plane of the molecule, as was the case for SO_2.

E. Sulfuric Acid Molecule (H_2SO_4). If the angularly correlated lone pair of SO_2 is uncoupled and new bonds are formed between two OH radicals and the dangling orbitals, a H_2SO_4 molecule is formed. Thus we might expect the S=O bonds in H_2SO_4 to resemble those in SO_2 as regards the shapes of their orbitals and the bond distances and angles. The geometry of this molecule in the gas phase has been determined[34] quite recently. The experimental S=O bond distance is 1.422 Å and the ∠O=S=O angle is 123.3°, which may be compared to r_{SO} = 1.432 Å and ∠O=S=O = 119.5° in SO_2. The molecule has C_2 symmetry. The simplest way to relate the structure of the molecule is to consider starting with a C_{2v} structure in which the O=S=O plane is perpendicular to the HO-S-OH plane containing all five of these atoms. This is in fact the geometry in the schematic diagram at the top of Figure 10. In order to obtain the actual C_2 structure, both OH bonds must be rotated in opposite senses by ~80° about the S-O bond resulting in a dihedral angle H-O(2)-S-O(4) of 20.8° (see top of Chart I). Finally the O-S-O plane is not quite perpendicular to the O=S=O plane. It must be rotated about the C_2 axis by 1.6° in a sense that displaces the O atom away from its bonded proton (see bottom of Chart I; the angle betwen planes O(1)-S-O(2) and (O)3-S-O(4) is 88.4°). Although one of the oxygen lone pairs on each protonated oxygen is oriented toward the other proton there can be little hydrogen bonding interaction between OH groups since the bond distance $r_{O..H}$ is 2.841 Å in H_2SO_4 compared to 1.75 Å[35] for deuterium oxide ice.

Geometry optimizations were carried out with both the HF and GVB wave functions and the DZ+d(O,S) basis set and a DZ basis set for H. Both wave functions yielded geometries in good agreement with experiment. For each of the S=O, S—O, and O—H bonds the HF geometry had bonds slightly shorter than experiment and the GVB geometry had bonds slightly longer than experiment. This is as expected (see section A, Sulfur Dioxide). Bond angles and dihedral angles were also close to experimental

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(34) Kuczkowski, R. L.; Suenram, R. D.; Lovas, F. J. *J. Am. Chem. Soc.* **1981**, *103*, 2561.

(35) Peterson, S. W.; Levy, H. A. *Acta Crystallogr.* **1957**, *10*, 70.

values. Geometries and total energies are summarized in Table Ib.

The S–O single bond orbitals are shown in Figure 10a. One is mainly localized near the S nucleus and the other is localized near the O nucleus. GVB orbitals for the S=O bond are shown in Figure 10b,c. The fact that S=O bonds in H_2SO_4 are expected to resemble those in SO_2 was mentioned above and it can clearly be seen that this is so by comparing Figure 10b,c to Figure 5a,b. Note that the S=O bonds above and below the bond axis in Figure 10 are inequivalent because there is no longer a σ_v mirror plane when the protons are rotated out of the (C_{2v}) $\sigma_{v'}$ mirror plane.

Finally we wish to point out an alternative GVB description for the S=O double bond in H_2SO_4. So far we have used a "bent bond" description of the S=O bond and the alternative will be referred to as the "backbonded" description. In the latter description there is a single bond between S and O leaving the oxygen atom with three lone pairs. These three lone pairs (instead of two in the bent bond description) participate in backdonation to the S atom—they distort toward the S atom to provide it with additional electron density and so form a "backbond". GVB calculations were carried out at the experimental geometry for both these descriptions and were essentially energetically indistinguishable—in fact the backbonding description was lower in energy by 0.01 eV (Table II). However, by the same reasoning as was applied to the S_3 molecule, the strong orthogonality approximation is expected to be more severe for the bent bond description than the backbonding description. Hence we expect the bent bond description to be favored in the full GVB wave function. Nevertheless, this result shows that the backbonding description is a reasonable description of the S=O bond. The importance of this observation will become clear as we consider the sulfate anion.

F. Sulfate Anion ($[SO_4]^{2-}$). *Resonance*, which is a concept closely associated with VB theory, was mentioned above in the context of the complexity which it introduces computationally. The ground states of all the molecules discussed so far are well described by a single VB (resonance) structure. In going from one molecule to another the shapes of orbitals changed little as did many of the molecular internal coordinates. The sulfate anion poses some more complex problems, however. Let us consider the issues regarding the question of whether it requires a description including resonance[36] or whether it will be well described by a single VB structure. We begin by comparing the structures of H_2SO_4 and SO_4^{2-}. In H_2SO_4 there are clearly two S=O double bonds and two S—O single bonds, judging by their respective bond lengths, 1.42 and 1.57 Å, and the orbital shapes in the GVB calculations above. The corrected bond length for the anion unperturbed by a surrounding field of ions is estimated to be 1.48 (6) ± 0.004 Å.[37] This bond length is nearly half-way between the double and single bond lengths in H_2SO_4, which is suggestive of a bond order of 1.5. Within the VB framework, non-integral bond orders are generally associated with resonance. For example, in benzene the C–C bond length is 1.40 Å, which is between a typical C–C single bond distance of 1.53 Å and a typical double bond length of 1.34 Å, and the importance of resonance in a VB description of benzene is well-known. Is it necessary to include resonance in a description of the sulfate anion or is it well described by a single resonance structure?

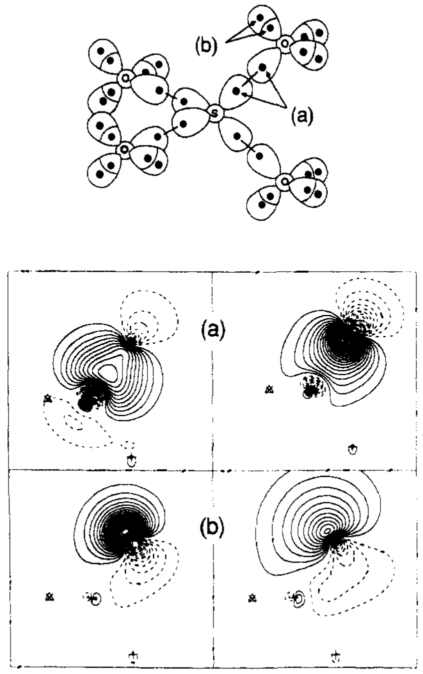
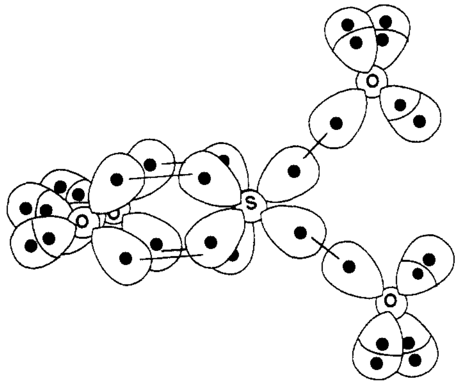


Figure 11. GVB orbitals for the backbonded representation of SO_4^{2-} with a DZ+d(O,S) basis set: (a) orbitals representing one of the S–O bonds; (b) one of the twelve equivalent radially correlated O lone pair orbitals. (Note the distortion toward the central S atom.)

Chart II



If we take as our starting point the sulfuric acid molecule in its equilibrium geometry and gradually remove the protons to infinity while keeping the SO_4^{2-} skeleton fixed, we can imagine that the arrangement of electron pairs would remain nearly constant as two double and two single S–O bonds. But this nuclear arrangement would probably not be the equilibrium geometry since relaxation to a tetrahedron with equivalent bond lengths would result in a lowering of the total energy by resonance. There are six such resonance structures that would then have an arrangement of electrons as shown in Chart II.

However, as was mentioned above in the section on H_2SO_4 it was found that a description of the S=O bonds with orbitals arranged to give a single bond and a significant back bond via the other three lone pairs was equally energetically favorable as the normal double bond description. For SO_4^{2-} there *is* a single resonance structure of the *back-bond* kind that has the full symmetry of the ion and therefore there is no need of resonance in this description of the electronic structure. This is shown schematically at the top of Figure 11 along with GVB orbitals representing one of the four equivalent S–O bonds and one of the backbonded lone pairs. The lone pairs are all staggered with respect to three S–O bonds. To demonstrate the extent of backdonation of the lone pair in Figure 11b, it is compared in

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(36) Reference 4b, p 320.

(37) McGinnety, J. A. *Acta Crystallogr.* **1972**, *B28*, 2845. The anion is only known in solution or the solid state where it is stabilized by solvation or surrounding counterions. At the DZ basis set level the dianion (SO_4^{2-}) was unbound with respect to the monoanion (SO_4^-) by 0.7 eV, but at the DZ + d(O,S) + f(S) level it was unbound by 1.4 eV. Negative ion functions are of much less importance than d and f functions in this model of the sulfate anion (and in HF calculations also) since augmenting the DZ basis set with single-ζ s,p(O,S) negative ion functions lowered the total energy of the dianion by 1.1 eV compared to a lowering of 10.9 eV when the DZ basis set was augmented with d and f functions. Crystal structures of many sulfates have been determined but it is not possible to directly compare S–O bonds lengths from the solid state to computed bond lengths since forces due to the surrounding ions must modify the bond lengths. However, McGinnety has calculated how the bond lengths of several oxo anions would change if the field due to the surrounding ions were removed. In solid anhydrous K_2SO_4 the S–O bond length is 1.46 Å, but the results of McGinnety's calculations indicate that the bond lengths of "free" sulfate anion would be 1.48 (6) ± 0.004 Å. We have adopted this distance for comparison with the results of our calculations.

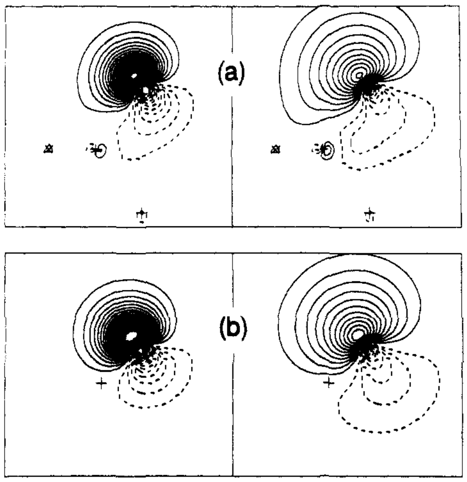

Figure 12. A comparison of backbonding lone pair orbitals and normal lone pair orbitals: (a) an O lone pair from the backbonded representation of SO_4^{2-}; (b) an O lone pair from the OH^- ion.

Figure 12 to the oxygen lone pair from the hydroxide ion in which there is no backbonding. This backbond orbital representation is also the one obtained by localizing HF orbitals from a calculation that employed the DZ+d(O,S) basis set according to the Boys–Foster criterion (this work) but differs from one obtained in a HF calculation that employed a single-ζ s,p(O,S)+d(S) basis set.[38] In that case the Boys–Foster localization procedure was also employed and each S–O bond was represented by three equivalent orbitals and the O atom had a single lone pair. These authors also found that the localized orbitals obtained for SO_2[39] depended on the basis set. This illustrates the importance of including a sufficiently flexible basis set in calculations on second-row molecules (occasionally a DZ+single d function basis set provides the S atom with insufficient flexibility, see Appendix B).

The geometry of the SO_4^{2-} anion was optimized with both the HF and GVB wave functions. When a DZ+d(O,S) basis set was employed in the geometry optimizations the HF and GVB equilibrium bond lengths were 1.494 and 1.507 Å, respectively (Table Ia). Since the HF geometry has a *longer* bond length than experiment we have reason to be suspicious of this description of the bonding. However, there are now 12 electron pairs simultaneously forming backbonds to the S atom. It will therefore require additional functional flexibility in order to accept electron density from the electron lone pairs. We therefore require 12 functions on the S atom that can adopt the appropriate spatial arrangement about the S atom so as to have significant amplitude where the electron pairs are to be donated. Formally we may assume that the s and p valence functions are employed in the four S–O single bonds of the backbonding description. The 12 orthogonal functions that form an appropriate basis set to accept electron density from the 12 lone pair orbitals with a T_d point group symmetry are a single set of d functions and a single set of f functions. In the backbonding description of the sulfate anion the d functions are not important in the same sense as in the bent bond description of SO_2 where there are six lobes originating on the S atom that must be mutually orthogonal. Here there are only four lobes originating on the S atom and the d functions will primarily be involved in accepting electron density from the oxygen lone pairs. Adding the f function to the basis set resulted in a reduction of the S–O bond length in both HF and GVB geometry optimizations. These were respectively 1.485 and 1.499 Å (Table Ia), which lie on either side of the "experimental" bond length. Thus this single VB structure results in a bond length in good agreement with the best available estimate of the bond length of an isolated sulfate anion.

Discussion

The results of the above GVB calculations can be discussed in terms of the extended valence bond orbital (EVBO) model and the latter used to rationalize the chemical stability of sulfur molecules that have more bonds than allowed by the Octet Rule. Also, the essential role of d functions in non-Octet molecules is illustrated with GVB calculations on SO_2.

The EVBO approach to electronic structure is based on localized independent-particle orbitals arranged in three dimensions. Application of this model to the species considered in this work leads to a simple picture of electronic structures in which electron correlation is included and enables us to derive relationships among their electronic structures. Ironically the EVBO approach bears more resemblence in its interpretation to the ideas put forward by Lewis and Langmuir before the advent of quantum mechanics than to the concepts associated with molecular orbitals. It is interesting to observe how Langmuir[40] describes his theory on the arrangements of electrons in molecules which formed the basis of his contribution to the Octet Rule: "There is much chemical evidence, especially in the field of stereochemistry, that the primary valence forces between atoms act in directions nearly fixed with respect to each other. This can only be satisfactorily accounted for by electrons arranged in three dimensions." Much current thinking about bonding is based on delocalized orbitals resulting from *linear combinations of atomic orbitals* (LCAO). Such orbitals form the basis of general configuration interaction (CI) and multiconfiguration self-consistent-field (MCSCF) methods, both of which include electron correlation, and are frequently used to obtain accurate geometries, energies, and wave functions. However, neither of these approaches has an independent-particle picture and therefore cannot be interpreted in the same way as the GVB method. The GVB method being of intermediate complexity and accuracy between Hartree–Fock and general CI and MCSCF methods can be used to test simple concepts because of its interpretability.

The arguments put foward for the Octet Rule by Langmuir and Lewis were based on empirical observations of the inert gases and a wide variety of mainly first-row-element molecules. We observe from the calculations described here that there are additional arrangements of electron pairs that can exist around an atomic core. Although in the first-row elements there is usually only sufficient space to accommodate tetrahedra of electron pairs, in second-row and heavier elements there is additional space in which trigonal prismatic, octahedral, etc. arrangements of electron pairs are possible. Angular correlation of lone pairs is an indicator that this additional space is available. If an angularly correlated lone pair were energetically highly unfavorable because of interpair Coulombic repulsions, then it would collapse and become radially correlated. When the lone pair is sufficiently angularly correlated the spins of the singlet pair may uncouple and the resulting orbitals may form either two single bonds or one double bond. An important factor in deciding what arrangement of electron pairs will be adopted and whether extra bonds can be formed is the difference in electronegativity of the atoms composing the molecule. Neighboring atoms of greater electronegativity withdraw electrons from a central atom, distorting its wave packets and increasing angular correlations of lone pairs thereby enabling more electron pairs to be packed around the central atomic core when extra bonds are formed. There observations are summarized within the postulates of the EVBO model: (1) *correlations* in the motions of valence electrons around atomic cores in a molecule result in the valence electrons becoming localized in *wave packets* that surround the core; (2) the *number of bonds* an atom can form is governed by the amount of angular space available to the wave packets—this is affected by the electronegativities of atoms to an extent that can radically alter the arrangement of wave packets and determine whether a molecule is stable or not; (3) normal, two center-two electron covalent "bonds" consist of a pair of largely overlapping wave packets and are transferable because the in-

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(38) Guest, M. F.; Hillier, I. H. *Int. J. Quantum Chem.* **1972**, *6*, 967.

(39) Guest, M. F.; Hillier, I. H.; Saunders, V. R. *J. Chem. Soc., Faraday Trans II* **1972**, *68*, 114.

(40) Reference 13, p 869.

(41) Reference 13, p 889.

teractions *within a bond* are much stronger than interactions *between bonds*; and (4) "*oxidation*" of lone pairs consists of unpairing the spins of electrons in the lone pair and recoupling them to spins of electrons of other atoms.

Accordingly, in the EVBO model a single bond is formed when two wave packets, initially on different atoms, overlap along the internuclear axis while multiple bonds result when two, three, or four pairs of wave packets overlap *off* the internuclear axis. The wave packet description of a single covalent bond has obvious similarities to a σ bond based on atomic orbitals (AO), but the resemblence to double ($\sigma + \pi$), triple ($\sigma + \pi + \pi$), or quadruple ($\sigma + \pi + \pi + \delta$) bonds is not clear at all. However, owing to the single determinant properties of the HF wave function, these AO model bonds may be transformed to localized, bent, multiple bonds, with which they are, of course, energetically equivalent. The GVB wave function distinguishes energetically between these two descriptions. Recently an investigation was carried out[15] to determine which was the better description of carbon–carbon double and triple bonds in a variety of molecules, using "lower total energy" as the criterion for "better". It was found that only when the strong orthogonality restriction was relaxed between orbitals in the multiple bonds of ethylene and acetylene was the bent bond description of these molecules favored over the σ/π counterparts. The perfect pairing restriction was also relaxed but was relatively unimportant at the experimental geometries.

This finding is important to the wave packet description of molecules because we should expect the wave packets to be *nodeless*. The σ/π descriptions of multiple bonds in the AO model introduces nodes a priori into π and δ orbitals whereas there are no atomic symmetry nodes in "bent bond" orbitals. This reasoning implies that the atomic symmetry nodes of the AO model are an unnecessary restriction that should lead to a higher total energy. Thus, if the nodes in SOPP-GVB orbitals presented above are enforced by the strong orthogonality approximation then relaxation of this restriction should lead to nodeless orbitals.

In one GVB calculation mentioned above the natural orbitals in SO_2 were restricted to σ or π symmetries. This had a higher total energy by +0.09 eV (Table II) showing that, again, the bent bond description was favored—this time at the SOPP level of GVB. It should be noted that a single VB structure using a σ/π description of SO_2 does not possess the full molecular symmetry because it is impossible to construct two sets of symmetrically equivalent, orthogonal π orbitals on three atoms. The energy quoted in Table II is for a single VB structure; the "resonance" energy calculated by including the mirror image VB structure in the total wave function is 0.10 eV. Thus the σ/π description with two VB structures is only 0.01 eV lower in energy than the single VB structure "bent bond" description. The latter is preferred because of its simplicity.

We now consider the circumstances necessary for formation of additional bonds to lone pairs. The important factors that determine whether a lone pair may be "oxidized" or not are (1) the size of the atomic core and (2) the electronegativity of the substituent atoms. This is well illustrated by the stability of phosphine and amine oxides. There are many stable phosphine oxides known, such as R_3PO,[42] but only one amine oxide F_3NO exists.[42] The ease with which the P lone pair in a phosphine is oxidized contrasts sharply with oxidation of an N lone pair in an amine. A phosphorus atom has a large atomic core and so an angularly separated pair of electrons is easily energetically accessible for oxidation. On the other hand extreme conditions are necessary before an amine lone pair can be oxidized. F is a very electronegative substituent and is capable of withdrawing sufficient charge that a "double" bond may be formed between the N and O atoms in F_3NO[16] and a "triple" bond between the P and O atoms in F_3PO.[16] A second example of the oxidizibility of lone pairs of second-row atoms is provided by the S_n rings (where n = 6–8). In the molecules S_nO[43] (and others with more than one O atom bonded) the S=O bond is pointed in the direction one would expect if the oxidized S atom had a trigonal prismatic arrangement of electrons. Finally, the role that atomic core size plays in determining the chemistry of isovalent molecules is illustrated by SO_2 and O_3. The GVB description of SO_2 was given above and a trigonal prismatic arrangement of electrons was established for it. The central atom in O_3, on the other hand, is not able to extend its octet to have a similar description to SO_2. In O_3 each O atom has two *radially* correlated lone pairs and each terminal O atom is bonded to the central atom by a normal covalent bond and a two center-three electron bond. Since it has no energetically accessible lone pair on the central O atom, ozone is not able to combine with another O atom to form "O_4", unlike SO_2 which does and can readily form SO_3.

We would like to be able to predict from simple calculations when "oxidation" of a lone pair to form a molecule with extra bonds is likely to occur. Arguments given above dictate that a state where the electrons in the lone pair are highly angularly correlated should be energetically accessible in order for "oxidation" to occur. This avoids large Pauli repulsions between the new bonds to be formed. The way in which electron-withdrawing power of substituent atoms bonded to an atom with a lone pair influences its correlations is now illustrated with use of a simple physical picture based on orbital overlap residuals, and the predictions of that model are compared to overlap residuals of GVB orbitals.

Consider a HF-LMO lone pair compared to a radially correlated lone pair. What will be the effect of introducing radial correlation into the pair on the electron nuclear attraction of the pair? We may obtain a rough estimate by the following procedure. If a representative volume element of the HF-LMO is at a distance r from a nucleus in an unscreened potential $-eZ/r$, then the electron–nuclear attraction for the pair is $-2e\langle Z/r\rangle$. If radial correlation of the pair is introduced and the volume elements move radially inwards and outwards to an extent δr then the electron nuclear attraction of the pair will be $\{-e\langle Z/(r + \delta r)\rangle -e\langle Z/(r - \delta r)\rangle\}$. If this is expanded as a power series and subtracted from the uncorrelated electron–nuclear attraction and terms to $1/r^{+}$ are collected, the electron–nuclear attraction energy recouped from radial correlation is $\Delta E \sim 2e(\delta r)^2\langle Z/r^3\rangle$. Including screening in the electron–nuclear attraction, $-e^{-\zeta r}(eZ/r)$, changes the lowering in energy by a factor of $\sim 1/(1 + \zeta r)^2$, i.e., screening *decreases* the radial correlation energy. The effect of a more electronegative substituent atom is to *de-screen* the lone pair of electrons. This raises the correlation energy of the pair, enabling it to be more highly correlated. There is a parallel between the extent of radial correlation (δr) and the residual $(1 - S)$ of the overlap (S) of a pair of GVB orbitals, i.e., the extent to which they do not overlap completely. The factor $(1 - S)$ is directly available from calculations and may be used as a measure of δr when discussing radial correlation. Consider H_2S with a valence electron arrangement as shown in Figure 2. For the lone pair (b) the overlap residual of the GVB orbitals is 0.101; when the calculation is repeated with the more electronegative modified hydrogen (having the same arrangement of lone pairs as in Figure 2 except that the orbital exponent scaling factor is 0.50) the overlap residual is 0.116, i.e., radial correlation of the lone pair is *increased* by the more electronegative hydrogen as predicted above by the simple argument. A similar trend with electronegativity was observed in the molecules SO_2, S_2O, and S_3. The molecule with the most electronegative atoms bonded to it (SO_2) had the largest overlap residual of its angularly correlated lone pair, 0.120 versus 0.115 and 0.113 for S_2O and S_3, respectively. This naive model focuses on just one aspect of the problem, namely electron–nuclear attraction, and neglects very important quantities such as kinetic energy. Nevertheless trends observed in the quantity $(1 - S)$ do follow those predicted by the model: as the core at which the lone pair is located becomes more and more descreened the radially correlated pair is drawn toward that core and is more highly correlated. At some point, however, angular correlation of the pair becomes favored because then *both* electrons in the pair can approach the nucleus separately and hence can come closer than

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(42) Reference 4a. p 384.

(43) *Gmelin Handbuch der Anorganische Chemie*: *Schwefeloxyd*; System 9. 8th ed.: Springer-Verlag: Berlin. 1980; pp 5 ff.

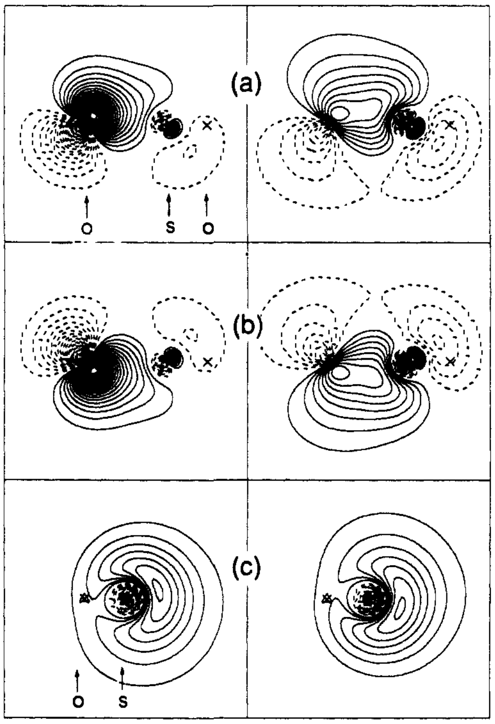

Figure 13. GVB orbitals for SO_2 with use of an unpolarized DZ basis set: (a, b) orbitals representing the S=O double bond; (c) angularly correlated S lone pair. (Note that the orbitals have much greater amplitude outside the region of the bond compared to the same calculation using a polarized basis set; also note that the orbitals do not "wrap around" the nuclei as effectively as when a polarized basis set is used; see Figure 5.)

if they were radially correlated. We expect to find a correlation between the point at which angular correlation becomes favored and the orbital overlap residual. Hence it may be possible to predict whether a lone pair is "oxidizable" and, more likely, *which* lone pair in a molecule is most readily oxidizable.

Table III. Total Energies

(a) For H_2S and Modified-H X_2S with Radially or Angularly Correlated Lone Pair Orbitals[a,b]

molecule	scaling factor	lone pair corr	total energy (hartrees)	ΔE^d (eV)
H_2S	1.00	radial	−398.700073	+0.027
H_2S	1.00	angular	−398.699050	
X_2S	0.50	radia	−398.626617	−0.047
X_2S	0.50	angular	−398.628367	

(b) For SO_2, S_2O, and S_3 (Thiazone) with Radially or Angularly Correlated Lone Pair Orbitals[e]

molecule	lone pair corr	total energy (hartrees)	ΔE^h (eV)
SO_2	none[f]	−547.305601	−0.109
SO_2	radial[g]	−547.309611	
SO_2	angular[g]	−547.311305	−0.155
S_2O	none[f]	−869.907689	−0.122
S_2O	radial[g]	−869.912169	
S_2O	angular[g]	−869.913290	−0.152
S_3	none[f]	−1192.528875	−0.132
S_3	radial[g]	−1192.533592	
S_3	angular[g]	−1192.534275	−0.147

[a] DZ(H) and DZ + 2d(S) basis sets used. [b] All four valence electron pairs correlated. [c] See Appendix B for details of hydrogen basis set modification. [d] Energy differences are with respect to the radially correlated lone pair. [e] DZ + d(O,S) basis sets used. [f] Eight valence electron pairs correlated; HF central S lone pair. [g] All nine valence electron pairs correlated. [h] Energy differences are with respect to the HF lone pair.

The Role of d Functions in Hypervalent Molecule Electronic Structures

In Figure 13 we present orbitals for a GVB calculation on SO_2 in which all d functions have been omitted from the basis set. When compared to the orbitals in Figure 5 that were obtained in an exactly similar calculation, except that d functions had been included in the basis set of each atom, it can be seen that there are two major differences between orbitals with or without d functions. These differences in the orbital shapes are as follows: the orthogonality "tails" are much larger in the DZ basis set, and the DZ+d(O,S) basis set orbitals are more *flexible* and are wrapped around the cores more effectively than the DZ orbitals. Thus there are two ways in which d functions are important. First, they reduce orthogonality tails (this is important because higher wave function curvature implies higher kinetic energies), and second, they enable orbitals to attain their optimum shapes and maximize electron–nuclear attraction. The following observation confirms the conclusion that the role of d functions on the S atom is primarily in *allowing the orbitals to attain their optimum shapes while remaining mutually orthogonal*. We note that the self-consistent orbitals obtained without d functions are rather different in shape to those obtained with d functions, but when d function coefficients in the orbitals obtained with a DZ+d(O,S) basis set were zeroed out in the converged self-consistent wave function and the orbitals replotted, the orbitals changed almost imperceptibly. Therefore the d functions are providing flexibility within the orthogonality constraints placed on the orbitals and this enables the s and p functions composing the orbitals to adopt more energetically favorable combinations. This additional flexibility is all the more important for molecules with extra bonds that have more than four orbitals centered on one atom. In normal molecules a DZ set of s and p functions is sufficient to allow the four orbitals on an atom to attain their optimum shape and d functions act as the usual polarization functions, whereas in atoms with extra bonds the orthogonality constraints between six or possibly more orbitals centered on one site place severe constraints on the shapes of orbitals that can be made less severe by adding functions of higher angular momentum into the basis. This analysis of the role of d functions in molecules such as SO_2 and SO_3 differs markedly from those proposed previously.

Conclusions

Each of the species listed in the abstract are well described by a single VB structure according to the condition that they produce optimized geometries in agreement with experimentally determined geometries. This includes the sulfate anion. In this latter case the apparent bond order of 1.5 (deduced from the corrected experimental geometry of the anion) is accounted for by each O atom being bonded to the S atom via a single bond and three back bonds from the lone pairs on the O atom.

For the molecules studied in this work the sulfur atom has its valence electrons arranged in either an octet (a tetrahedron of pairs), a trigonal prismatic arrangement, or an octahedral arrangement. The arrangement adopted in any particular molecule is determined by the bonds to be formed (single or double) and the electronegativities of bonded atoms. Angular correlation of lone pairs is an important feature of some of these molecules; orbital shapes in a given bond are transferable from one molecule to another.

The role of d functions in electronic structure calculations of hypervalent molecules (those with trigonal prismatic or octahedral arrangements of electrons) differs from that in normal molecules (those with tetrahedral octets). In hypervalent molecules d functions provide additional flexibility so that the orbitals may attain their optimum shapes while remaining mutually orthogonal, whereas in normal molecules they act as polarization functions. This is a very different conclusion than reached by many previous authors who have argued that *atomic d orbitals* play a part in bonding in hypervalent molecules.

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Appendix A: Details of Computations

All calculations employed the GVB-PP methods;[45] those reported in Table Ia,b employed the GAMESS program,[44] which was used to perform the geometry optimizations, and all calculations reported in Tables II and IIIa,b employed the GVB2P5 program.[45] Small differences in total energy between results obtained from GVB2P5 and GAMESS calculations (0.059 eV for SO_2 in a GVB calculation with a single d function on each atom) arise because the symmetric combination of d functions was excluded from GVB2P5 calculations whereas no restrictions on combinations of d or f functions were enforced in GAMESS calculations. In all cases the [11s7p/6s4p] and [9s5p/3s2p] contractions[46] of Dunning of the basis sets of Huzinaga[46] were employed for sulfur and oxygen, respectively. A combination of these two basis sets has been referred to as DZ in the text above. The nomenclature used when polarization functions were included is as follows: where a single d function was included on the sulfur and/or oxygen site(s), the basis set name, DZ, was supplemented by +d(S) or +d(O,S), indicating a single d function on the S site or both O and S sites, respectively. Here the d exponent was always 0.53 for S and 0.80 for O. The basis set for H was the unscaled [3s/2s] contraction of the basis set of Huzinaga.[47] When a single f function was included in calculations on the sulfate anion, the exponent used was 0.80, which was the exponent that produced the lowest total energy when the f exponent was varied in a HF calculation on the sulfate anion at the corrected experimental geometry (1.486 Å). The negative ion functions used in calculations on the sulfate anion had s and p exponents: 0.060 (0.041) and 0.088 (0.060) for S (O), respectively.

Appendix B: Lone Pair Correlations in H_2S and SO_2

Calculations were performed on H_2S and SO_2 with lone pairs correlated radially or angularly. The electron-withdrawing potential or "electronegativity" of the H atoms in H_2S was varied to determine what effect electron-withdrawing potential had on the relative stabilities of radially versus angularly correlated lone pairs for that molecule. This was effected by uniformly scaling the [3s/2s] H basis set exponents by $1/\sqrt{2}$, $1/\sqrt{3}$, and $1/2$ in separate calculations. In this way the H nucleus is descreened (charge is thrust away from the H nucleus by having the smaller exponent). Charge can then be more effectively drawn from a neighboring atom and so the effective electronegativity of the modified H atom is greater than that of normal H. A scaling factor of $1/\sqrt{2}$ resulted in a diminution of the difference in energies of the tetrahedral and octahedral electronic arrangements, whereas scaling factors of $1/\sqrt{3}$ or $1/2$ resulted in the octahedral electron arrangement being favored. Energies are given for a scaling factor of $1/2$ in Table IIIa.

In calculations on H_2S a double-ζ d function (referred to in Table IIIa as +2d(S)) was used on the sulfur site; the exponents were 0.70 and 0.30. Double-ζ polarization flexibility on the S site was found to be necessary to obtain the octahedral electron arrangement of Figure 3—the single-ζ (0.53) polarization function resulted in one lone pair being radially correlated and the other angularly correlated when the electron-withdrawing power of the H atoms was increased. Additional d exponents greater than 1.00 or a single f function were found to contribute to a very small extent.

Differences in total energy between GVB-SOPP wave functions with angularly or radially correlated lone pairs for SO_2, S_2O, and S_3 were found to be small (as was the case for H_2S), but in contrast to H_2S, *angular* correlation of the lone pair is always favored. The energy differences between radially and angularly correlated lone pair wave functions were −0.046, −0.030, and −0.015 eV, respectively, diminishing as the number of *more electronegative* atoms bonded to the central S atom decreased. A more meaningful comparison is the relative energy lowering obtained by either radial or angular correlation of the lone pair referenced to an uncorrelated (HF) lone pair. This comparison is made in Table IIIb where it is shown that the relative importance of angular correlation decreases in the order $SO_2 > S_2O > S_3$ and the small differences in total energy between radially and angularly correlated lone pairs reflect the fact that the correlation energy for one of these lone pairs within the SOPP-GVB wave function is itself rather small (~0.15 eV). (In all of these lone pair calculations the S=O and S=S bond orbitals are essentially unchanged except for small changes required to maintain orthogonality between the natural orbitals.)

Registry No. SO_2, 7446-09-5; S_2O, 20901-21-7; S_3, 12597-03-4; SO_3, 7446-11-9; H_2SO_4, 7664-93-9; SO_4, 14808-79-8.

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(44) Dupuis, M.; Spangler, D.; Wendoloski, J.; Elbert, S.; Schmidt, M. GAMESS program Version 1.02, Revision 10 (1987), National Resource for Computation in Chemistry Software Catalog Vol. 1 Program QG01 (1980). Lawrence Berkeley Lab., USDOE.

(45) Bair, R. A.; Goddard, W. A., III; Voter, A. F.; Rappé, A. K.; Yaffe, L. G.; Bobrowicz, F. W.; Wadt, W. R.; Hay, P. J.; Hunt, W. J. GVB2P5 program (unpublished).

(46) (a) Dunning, T. H., Jr.; Hay, P. J. *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Vol. 3, Chapter 1. (b) Huzinaga, S. *Approximate Atomic Functions II*; Report from the Department of Chemistry, The University of Alberta, Canada, 1971.

(47) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

(48) (a) Redondo, A.; Goddard, W. A., III; Swarts, C. A.; McGill, T. C. *J. Vac. Sci. Technol.* **1981**, *19*, 498. (b) Schultz, P. A.; Messmer, R. P. *Phys. Rev. B.* **1986**, *34*, 2532.