lone pair and the LUMO of the adjacent substrate is controlled by the variation of the matrix element when the LUMO of the substrate lies high in energy but will tend to become energy-gap controlled when the LUMO of the adjacent π system lies low in energy.

(iii) The destabilization energy associated with the four-electron interaction between the heteroatom lone pair and the HOMO of the adjacent π system increases in going from a more electronegative heteroatom to a less electronegative heteroatom when the heteroatom is changed from one column to another, i.e., in going from F to OH and from Cl to SH, but decreases in going from a more electronegative heteroatom to a less electronegative heteroatom when the heteroatom is changed from one row to another, i.e., in going from OH to SH and from F to Cl.

(iv) The overall π effect of the substituents OH, SH, F, and Cl, i.e., the energy effect associated with the π interactions occurring between the lone pair of these substituents and the π system of the substrate, is stabilizing in the $^+CH_2$—X and BH_2—X systems, where the only interaction occurring is the stabilizing n–π^* interaction, and destabilizing in the CH_2=CH—X systems, where also the destabilizing interaction n–π occurs since the substrate has vacant and doubly occupied π MO's. It is important to point out that the overall π effect of a substituent depends critically on the adjacent substrate. As we have already seen, the π overall effect of a substituent, except in the simple cases of the $^+CH_2$—X and BH_2—X systems, is the result of the combination of two effects of opposite sign. In neutral systems, the destabilizing effects seem to dominate, while in other species such as charged species or transition states, the stabilizing effects may dominate.

(v) The overall π effect in the CH_2=CH—X systems has been found to be more destabilizing for OH than for F and basis-set dependent in the comparison OH vs. SH, F vs. Cl, and SH vs. Cl. Therefore, while the trend of the two-electron stabilization and of the four-electron destabilization is the same at the two computational levels, the result of the combination of the two effects varies in the majority of cases going from a minimal to an extended basis set. It can be expected that the results obtained at the 4-31G level are more reliable, but this point requires further investigation.

References and Notes

(1) (a) Istituto di Chimica Organica, Università di Bologna. (b) Department of Chemistry, University of Washington, A. P. Sloan Fellow (1976–1978).
(2) F. Bernardi, A. Mangini, N. D. Epiotis, J. R. Larson, and S. Shaik, *J. Am. Chem. Soc.*, **99**, 7465 (1977).
(3) F. Bernardi, A. Bottoni, N. D. Epiotis, and M. Guerra, *J. Am. Chem. Soc.*, **100**, 6018 (1978).
(4) M. H. Whangbo, H. B. Schlegel, and S. Wolfe, *J. Am. Chem. Soc.*, **99**, 1296 (1977).
(5) N. C. Baird, *Theor. Chim. Acta*, **16**, 239 (1970).
(6) C. Muller, A. Schweig, and H. Vermeer, *Angew. Chem., Int. Ed. Engl.*, **13**, 273 (1974).
(7) The standard SCF-MO calculations have been carried out using the GAUSSIAN 70 program: W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, "Gaussian 70", Quantum Chemistry Program Exchange, No. 236, Indiana University, Bloomington, Ind.
(8) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
(9) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).
(10) (a) The expression of the two-electron stabilization is a result of perturbational molecular orbital theory. See, for instance, M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969. (b) The dependence of the four-electron overlap repulsion upon the mean of the energy of the interacting levels has been discussed previously in the literature: N. C. Baird and R. M. West, *J. Am. Chem. Soc.*, **93**, 4427 (1971); K. Müller, *Helv. Chim. Acta*, **53**, 1112 (1970).

Comment on a Symmetry Criterion for the Necessity of Including Atomic d Orbitals in Computational Basis Sets

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Abstract: A recently proposed symmetry criterion for characterizing a qualitative as opposed to a quantitive need for including higher angular momentum functions in computational basis sets is examined. In typical numerical examples "symmetry required" d orbitals are not found to be of qualitatively different importance to other d orbitals.

I. Introduction

Recently Ratner and Sabin[1,2] have discussed a criterion based on symmetry considerations for characterizing the need for higher angular momentum functions (d orbitals on first- and second-row atoms, p orbitals on hydrogen) in atomic orbital basis sets for molecular LCAO SCF calculations. According to this criterion,[1] for each occupied molecular orbital there should be at least one basis orbital per atomic center of a symmetry appropriate to contribute to the molecular orbital. Put another way, orbital population on a particular center should not be precluded in a molecular orbital because of the absence of basis functions spanning the irreducible representation of the molecular point group carried by the molecular orbital. If a nonpolarized atomic basis set is deficient in this respect, then there is a symmetry requirement for the inclusion

of higher angular momentum basis functions on the center concerned. This requirement is seen[1] to be "of fundamental importance in the *qualitative* bonding picture", and is distinguished from the *quantitative* effect resulting from the addition of higher angular momentum functions when they are not required by the symmetry criterion. The latter effect is regarded as "primarily numerical in nature".

While it seems reasonable that the proposed symmetry criterion should be taken into account in assessing the requirement for higher angular momentum functions in a particular application, the distinction drawn between the *qualitative* effect of symmetry-required functions and the *quantitative* effect of those not so required appears to require computational justification. It is argued here that this has not been provided by the previous[1] illustrative computations, and some alternative calculations bearing on the issue are presented.

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Confidence in general distinctions between qualitative and quantitative aspects of including higher angular momentum basis functions inferred from Ratner and Sabin's (RS)[1] numerical examples is undermined by two main features.

(1) The qualitative aspects are illustrated by a hypothetical highly (doubly) excited, $1b_1^2 \rightarrow 1a_2^2$, state of water. This example is untypical of the usual situations in which the question of the need for higher angular momentum functions arises, and is also shown below to be more fundamentally unsuitable.

(2) d functions (p's on hydrogens) are included in complete sets, whereas usually only one component is required by the symmetry criterion. It is therefore not easy to distinguish the effects of this component from those of the non-symmetry-required components.[3] If the *qualitative/quantitative* classification is well founded then it should be possible to observe a clear distinction between the effects of the symmetry-required components of higher angular momentum functions and the effects of the remaining components. The extent of this distinction is examined in computational results presented below (section IIB).

II. Numerical Examples

A. RS's Hypothetical Excited State of Water. To illustrate the qualitative aspects of including higher angular momentum functions RS[1] consider a hypothetical doubly excited, $1b_1^2 \rightarrow 1a_2^2$, state of water. To form the a_2 orbital it is necessary to include in the basis set a d_{xy} orbital on oxygen and/or a p_y function on each hydrogen (the coordinate axes are those used by RS[1]). The energy calculated for this state is 62.8 eV (2.31 au) above the corresponding ground-state energy.[1] The second ionization potential of water ($H_2O \rightarrow H_2O^{2+}$) is only 39.2 eV,[4] so that the hypothetical state is embedded in the doubly ionized continuum of H_2O, some $\sim$20 eV above its onset. The state would thus be expected to lose the two $1a_2$ electrons to form an H_2O^{2+} ion. In an SCF calculation using square integrable basis functions this would be simulated by the occurrence of a very diffuse $1a_2$ molecular orbital,[5] provided that appropriate diffuse functions were present in the basis set. In the absence of such diffuse functions the orbital populations and calculated molecular properties may be expected to show particular sensitivity to modifications to the basis functions spanning the a_2 irreducible representation. This is probably the major cause of the large changes in the calculated molecular properties observed by RS upon variation of their basis set.

To illustrate these points we have performed some additional SCF calculations on the hypothetical doubly excited state of water. Our molecular geometry (R_{OH} = 1.8111 au, $\angle HOH$ = 104.45°) and initial basis set {(9s5p1d/4s1p) contracted to [4s3p1d/2s1p]} is that used by Dunning[6] for the ground state of water. This basis set gives a ground-state wave function of similar quality to that from the larger uncontracted basis used by RS.[1] The SCF energy of the hypothetical doubly excited $1b_1^2 \rightarrow 1a_2^2$ state is much higher (Table I) relative to the ground state than obtained by RS, no doubt because of our single ζ representation of the oxygen d and hydrogen p part of the basis set compared to RS's double ζ representation. However, if we add a single diffuse d_{xy} orbital (a_2 symmetry) with an exponent of 0.03[7] centered on the oxygen atom we observe a marked change. The SCF energy is lowered by 67.5 eV (2.48 au) and is now only 32.3 eV (1.19 au) above the ground-state energy, so that the state has become more stable than the H_2O^{2+} ion.[8] The results of these calculations are shown in Table I. It can be seen that with the inclusion of a diffuse d_{xy} (a_2) basis function, the calculated properties of the hypothetical state are quite different from those obtained by RS.[1]

It can be argued that for this excited state the oxygen d orbitals and hydrogen p orbitals are qualitatively important in that an a_2 orbital cannot be constructed at all if neither set is

Table I. Calculations[29] on a $1b_1^2 \rightarrow 1a_2^2$ Excited State of Water[a]

case	RS[b]	no diffuse d[c]	diffuse d[c]
O d function exponents	1.0, 0.5	0.88	0.88, 0.03[d]
E_{tot}	−73.73913	−72.37852	−74.86067
eigenvalues $1a_1$	−20.9572	−20.8296	−21.5053
$2a_1$	−1.4989	−1.3266	−2.0942
$1b_2$	−0.8954	−0.7268	−1.4713
$3a_1$	−0.8094	−0.6588	−1.3534
$1a_2$	0.6519	1.3735	−0.0578
μ (dipole moment)	0.063	0.305	1.399
$\langle r^2 \rangle$[e]		18.53	126.86
population[f] in $1a_2$ O	0.560	0.977	1.997
H	0.720	0.511	0.001

[a] Atomic units throughout. [b] Reference 1. The geometry used differs slightly from that of the present work. [c] See text for geometry and basis set. [d] Single d_{xy} (a_2) orbital with exponent of 0.03. [e] Electronic component to second moment. [f] Calculated according to Mulliken's scheme.

present. This is so obvious a truism that such a characterization does not appear useful. Moreover, in this particular case, the symmetry criterion for requiring a contribution to the a_2 molecular orbital from each atomic center is not relevant as the diffuse basis functions necessary to describe such a Rydberg-type orbital are essentially *molecular* basis functions and their precise placement within the framework of a small molecule is not chemically significant.[9]

More interesting and typical tests of the symmetry criterion are those in which it is possible to construct molecular oribtals of all required symmetries without recourse to higher angular momentum basis functions. Higher angular momentum functions added in this situation would generally be thought of as *polarization* functions, and the question then is whether the polarization functions required by the symmetry criterion have a characteristically different effect from other polarization functions.

B. Further Examples, O_3 and SO_2. Ground-state SCF wave functions for both ozone and sulfur dioxide have an occupied a_2 orbital to which, in an s and p only basis, no orbital on the central atom can contribute. According to the symmetry criterion a d_{xy} orbital which transforms like the a_2 irreducible representation of C_{2v} is therefore required on the central O (S) atom of $O_3(SO_2)$. (We take the z axis to be collinear with the C_2 axis and the molecule to lie in the yz plane.)

We have performed calculations on these systems using Huzinaga's oxygen (9s5p)[10] and sulfur (11s7p)[11] primitive Gaussian basis sets contracted to [4s2p] and [6s4p], respectively, according to Dunning's schemes.[6,12] These atomic bases were augmented in various ways with d polarization functions with "standard" exponents[12] (ζ_{dO} = 0.85, ζ_{dS} = 0.60) as follows: (A) no d functions; (B) a symmetry-required single d_{xy} (a_2) function on the central atom; (C) the set of four non-symmetry-required ($\neq a_2$) d orbitals on the central atom; (D) a complete set of five d orbitals on the central atom; (E) complete sets of d functions on all atoms.

Since the "standard" d exponents are based on experience using full sets of d functions on all centers and thus represent some average value of the optimum exponents for the individual d orbitals, we also examined the effect of optimizing the d exponents for cases B, C, and D. All the calculations were carried out at the experimental geometries: O_3,[13] R_{OO} = 2.415 au, $\angle OOO$ = 116.8°; SO_2,[14] R_{SO} = 2.704 au, $\angle OSO$ = 119.3°. Results of these calculations are shown in Tables II and III. For comparison the results of Rothenberg and Schaefer's[17] calculations on SO_2 are also included in Table III.

These tables do not indicate any obvious marked *qualitative* differences between the effects of adding a symmetry-required

Table II. Calculations[29] on Ozone Using Various d Orbital Sets[a]

		A[c]	B[d]	C	D	E[c]
d functions[b] in basis	central O	none	d_{xy} (a₂)	4d's (not d_{xy})	complete set	complete set
	terminal O's	none	none	none	none	complete set
E_{tot}[e]		−0.20724	−0.22040 (−0.22266)	−0.25566[f]	−0.26842[g]	−0.30706
eigenvalues[h]	3a₁	−1.7840	−1.7800 (−1.7779)	−1.7672	−1.7632	−1.7480
	2b₂	−1.4546	−1.4522 (−1.4506)	−1.4478	−1.4455	−1.4300
	4a₁	−1.0973	−1.0949 (−1.0940)	−1.0968	−1.0944	−1.0924
	5a₁	−0.8369	−0.8344 (−0.8333)	−0.8342	−0.8318	−0.8293
	3b₂	−0.7939	−0.7921 (−0.7916)	−0.7929	−0.7911	−0.7963
	1b₁	−0.7905	−0.7886 (−0.7869)	−0.7859	−0.7840	−0.7787
	4b₂	−0.5793	−0.5779 (−0.5772)	−0.5701	−0.5687	−0.5625
	6a₁	−0.5615	−0.5597 (−0.5589)	−0.5591	−0.5574	−0.5507
	1a₂	−0.4941	−0.5009 (−0.5018)	−0.4833	−0.4900	−0.4854
μ (dipole moment)		0.281	0.257 (0.231)	0.395	0.371	0.326
Q_{xx} (quadrupole moment)		1.853	1.846 (1.812)	1.655	1.648	1.335
Q_{yy}		−2.177	−2.105 (−2.023)	−2.164	−2.092	−1.631
Q_{zz}		0.324	0.259 (0.211)	0.509	0.442	0.296
d orbital populations[i] on central O						
d_{xy} (a₂)			0.033 (0.067)		0.033	0.029
d_{yz} (b₂)				0.042	0.042	0.034
d_{xz} (b₁)				0.009	0.009	0.007
$d_{x^2 - y^2}$ (a₁)				0.022	0.022	0.019
d_{z^2} (a₁)				0.018	0.018	0.016
total			0.033 (0.067)	0.092	0.124	0.105[j]

[a] Atomic units. See text for geometry and basis set details. [b] Oxygen d exponent = 0.85 except where noted otherwise. [c] Calculations A and E differ from the work of ref 16 only in the representation and exponent of the d function sets for calculation E. A six-component set of Cartesian d functions, ζ_d = 0.80, was used in ref 16. [d] Figures in parentheses refer to use of optimized d_{xy} exponent, ζ_d = 0.56. [e] E_{tot} = total energy − 224.0. [f] With optimized d exponent, ζ = 0.77, E_{tot} = −0.256 06. [g] With optimized d exponent, ζ = 0.71, E_{tot} = −0.269 91. [h] Only valence orbital energies shown. [i] Calculated according to Mulliken's scheme. [j] Total d orbital population on each terminal atom = 0.041.

Table III. Calculations[29] on Sulfur Dioxide Using Various d Orbital Sets[a]

		A	B[c]	C	D	E	ref 17[d]
d functions[b] in basis	S	none	d_{xy} (a₂)	4d's (not d_{xy})	complete set	complete set	six (none)
	O's	none	none	none	none	complete set	six (none)
E_{tot}[e]		−0.95538	−1.01051 (−1.01316)	−1.10187[f]	−1.15191[g]	−1.20688	−1.2089 (−0.9512)
eigenvalues[h]	5a₁	−1.5730	−1.5636 (−1.5625)	−1.5438	−1.5353	−1.5115	−1.5095
	3b₂	−1.4442	−1.4389 (−1.4379)	−1.4323	−1.4274	−1.4047	−1.4038
	6a₁	−0.8919	−0.8838 (−0.8833)	−0.8775	−0.8700	−0.8705	−0.8695
	7a₁	−0.7178	−0.7122 (−0.7115)	−0.7085	−0.7034	−0.6969	−0.6959
	4b₂	−0.6955	−0.6949 (−0.6951)	−0.9646	−0.6938	−0.6983	−0.6986
	2b₁	−0.6939	−0.6884 (−0.6874)	−0.6786	−0.6740	−0.6671	−0.6665
	5b₂	−0.5504	−0.5518 (−0.5517)	−0.5435	−0.5444	−0.5405	−0.5400
	1a₂	−0.5034	−0.5310 (0.5320)	−0.4955	−0.5202	−0.5167	−0.5161
	8a₁	−0.4928	−0.4885 (−0.4880)	−0.5056	−0.5006	−0.4928	−0.4917
μ (dipole moment)		1.112	0.979 (0.943)	1.144	1.020	0.921	0.90 (1.11)
Q_{xx} (quadrupole moment)		5.144	4.980 (4.903)	4.514	4.368	3.891	3.84 (5.23)
Q_{yy}		−6.961	−6.542 (−6.423)	−6.345	−5.938	−5.139	−5.12 (−7.11)
Q_{zz}		1.817	1.562 (1.520)	1.830	1.570	1.248	1.27 (1.87)
d orbital populations[i] on S							
d_{xy} (a₂)			0.140 (0.181)		0.129	0.118	
d_{yz} (b₂)				0.156	0.152	0.134	
d_{xz} (b₁)				0.022	0.022	0.019	
$d_{x^2 - y^2}$ (a₁)				0.129	0.124	0.110	
d_{z^2} (a₁)				0.084	0.081	0.074	
total			0.140 (0.181)	0.391	0.509	0.455[j]	0.425[k] (0.0)

[a] Atomic units. See text for geometry and basis set details. [b] ζ_{dS} = 0.60, ζ_{dO} = 0.85 except where noted otherwise. [c] Figures in parentheses refer to use of optimized d_{xy} exponent, ζ_d = 0.486. [d] Calculations performed using sulfur (12s 9p)/[6s 4p] and oxygen (10s 5p)/[4s 2p] basis sets augmented with six component sets of Cartesian d functions, ζ_{dS} = 0.60, ζ_{dO} = 0.80. Figures in parentheses refer to calculations without the d functions. [e] E_{tot} = total energy −546.0. [f] With optimized d exponent, ζ = 0.654, E_{tot} = −1.102 80. [g] Optimization of the d exponent gives essentially the "standard" exponent, ζ = 0.6. [h] Only valence orbital energies shown. [i] Calculated according to Mulliken's scheme. [j] Total d orbital population on each terminal oxygen atom = 0.036. [k] Total d orbital population on each terminal oxygen atom = 0.063.

d_{xy} orbital and those of adding other d function components to the central atom.[15]

Using the "standard" exponents the energy lowering produced by the addition of a single d_{xy} (a₂) orbital to the central

atom is ∼22 and ∼28% for O₃ and SO₂, respectively, of the total energy lowering obtained by adding a full set of five d orbitals. In other words, the proportional effect of the symmetry-required d component on the total energy is little more

than would be expected on the assumption of an equal effect from all five d components.[18]

A similar pattern is observed in the d orbital populations. When a full set of d orbitals is added to the central atom the population of the d_{xy} (a_2) orbital is ~27 and ~28% of the total central atom d orbital population for O_3 and SO_2, respectively, and is in both cases qualitatively similar to the population of, for example, the d_{yz} component.

It has been argued[19] that, in "first order", basis set expansion serves to raise all the orbital energies, and that an observed lowering of an orbital energy indicates a strong interaction involving higher order effects. In the case of SO_2 comparatively large lowerings of the $1a_2$ orbital energy are observed on the addition of any d orbital set which includes the d_{xy} (a_2) component, and this may be taken to indicate a strong mixing of the d_{xy} function with the $1a_2$ molecular orbital. Note, however, that some other orbital energy lowerings are also observed, the $8a_1$ in calculations C and D, the $4b_2$ in calculation E, and the $5b_2$ in calculation B (Table III), although these energy lowerings are smaller than for the $1a_2$ molecular orbital. The effects of the d functions on the orbital energies of O_3 are less clear cut, and in neither example do they lead to qualitative changes in the predicted photoelectron spectrum obtained using Koopmans' theorem.[20]

Optimization of the central atom d function exponent in cases B, C, and D for both O_3 and SO_2 leads to a more diffuse d_{xy} (a_2) function when the exponent is optimized for this component alone than when a common exponent is optimized for the full set of d orbitals. However, the optimization in general only results in changes that are small relative to the total effect of the addition of the d_{xy} (a_2) orbital. The largest change is in the gross atomic population of the d_{xy} orbital, but we still find that the difference between the behavior of the symmetry-required d_{xy} orbital and that of the other d components remains quantitative rather than qualitative.

III. Other Considerations

In the above examples we have confined our attention to the addition of d functions to sp basis sets of around double ζ quality, since this is the level of sp basis set at which the addition of polarization functions is nowadays normally invoked. Although RS regard their results illustrating the symmetry criterion as "representative of minimal and extended basis LCAO–MO type calculations", it is well known that the *total* effect of polarization functions is dependent on the quality of the underlying sp basis. In particular the effects of polarization functions are generally larger with minimal basis sets than with more extended ones, and it might be asked whether for minimal sp basis sets the differences between the effects of symmetry-required and other higher angular momentum functions might be more significant. We note, however, that in such cases it is not clear that any large, "qualitative" effects can necessarily be properly ascribed particularly to the inclusion of polarization functions since similar effects may also result from a conventional improvement in the sp basis set.

Neglecting this last point, a broad range of examples of the influence on predicted molecular geometries (and binding energies) of d functions added to minimal basis sets for second-row atoms is provided in the recent work of Collins et al.[24] These authors find that a particularly large effect on the predicted geometry (and binding energy) results from the use of d functions for SO_2, ClF_3, and OPF_3, and this is correlated with the "hypervalent" nature of these molecules.[24,25] It can also be noted that for these systems higher angular momentum functions on the second-row atom are symmetry required, and, indeed, for SO_2 the effect of d functions on the calculated bond angle has been correlated with the involvement of the symmetry-required d_{xy} (a_2) function in the a_2 molecular orbital.[26] However, in ClF_3 (C_{2v}) detailed studies[27] of the dependence

of the orbital energies on the bond angle ($\angle F_{ax}ClF_{eq}$) do not point to the symmetry-required d (a_2) orbital being specially significant in determining the angle, and it is also found[24] that adding d functions to the minimal basis leads to similar changes in both axial and equatorial ClF bond lengths, again suggesting that the symmetry-required and the remaining d orbitals have similar effects. In the case of the third hypervalent molecule, OPF_3 (C_{3v}), the large effect of the d orbitals cannot be ascribed to the symmetry requirement since the d orbitals only provide bases for the irreducible representations already spanned by the s and p functions, and f functions on the P atom are required for a contribution from this center to the occupied a_2 molecular orbital! By comparison d functions are found[24] to have only a relatively small effect on the calculated bond length for AlF_3 (D_{3h}), yet for this molecule both d and f functions are symmetry required on the Al atom to contribute to the occupied e'' and a_2' orbitals, respectively.

IV. Summary

We emphasize that here we have not been concerned with the much discussed *general* problem of the need for d orbitals in SCF calculations, but solely with the question of whether the symmetry criterion provides a reliable characterization of a qualitative as opposed to a quantitative requirement for their use.

There is *no* evidence from the above numerical examples of O_3 and SO_2 that, in typical systems, components of higher angular momentum functions required by the symmetry criterion have a *qualitatively* different importance in ab initio SCF calculations from other components of higher angular momentum functions. (There is, however, some evidence that the symmetry-required d_{xy} orbital in O_3 and SO_2 has among the larger effects of the central atom d orbitals.) An analysis of some results in the literature supports the conclusion that the symmetry requirement for a polarization function does not necessarily imply a qualitatively more significant magnitude to its effect. We note that even in the case of SF_6, which has been regarded as one of the "extremes for the contribution of d orbitals and symmetry considerations",[2] recent calculations have indicated[28] that d functions are not of fundamental *qualitative* importance to the description of the bonding. The symmetry criterion can, of course, still be a useful consideration in assessing the *quantitative* need for polarization functions in a particular application.

References and Notes

(1) M. A. Ratner and J. R. Sabin, *J. Am. Chem. Soc.*, **99**, 3954 (1977).
(2) M. A. Ratner and J. R. Sabin, *J. Am. Chem. Soc.*, **93**, 3542 (1971).
(3) This point is of importance in constructing numerical examples for the study of the *symmetry criterion*, although in RS's water example[1] the problem associated with the inclusion of complete sets of higher angular momentum functions is overshadowed by those due to the omission of diffuse functions (see section IIA).
(4) W. E. Moddeman, T. A. Carlson, M. O. Krause, B. P. Pullen, W. E. Bull, and G. K. Schweitzer, *J. Chem. Phys.*, **55**, 2317 (1971).
(5) See, for example, R. Ahlrichs, *Chem. Phys. Lett.*, **34**, 570 (1975).
(6) T. H. Dunning, *J. Chem. Phys.*, **53**, 2823 (1970).
(7) No precise exponent optimization has been carried out but test calculations show that the value of 0.03 is close enough to the optimum value for our present purposes.
(8) A physical meaning still cannot, of course, realistically be ascribed to the hypothetical state, which remains embedded in the *singly* ionized continuum of the water molecule. However, variational collapse of our SCF solutions onto a singly ionized state is prevented by the constraint of doubly occupied orbitals.
(9) We assume that all basis functions would normally be sited so as to transform, singly or in linear combinations, like irreducible representations of the molecular point group.
(10) S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965).
(11) S. Huzinaga, "Approximate Atomic Wavefunctions II", University of Alberta, Edmonton, Alberta, Canada, 1971.
(12) T. H. Dunning and P. J. Hay, "Modern Theoretical Chemistry", Vol. 3, H.

F. Schaefer, Ed., Plenum Press, New York, N.Y., 1977, p 1.
(13) R. H. Hughes, *J. Chem. Phys.*, **24**, 131 (1956).
(14) Y. Morino, Y. Kikuchi, S. Saito, and E. Hirota, *J. Mol. Spectrosc.*, **13**, 95 (1964).
(15) The previously noted[16,17] greater importance of central atom d functions in calculations on SO_2 compared to O_3 is, however, apparent.
(16) S. Rothenberg and H. F. Schaefer, *Mol. Phys.*, **21**, 317 (1971).
(17) S. Rothenberg and H. F. Schaefer, *J. Chem. Phys.*, **53**, 3014 (1970).
(18) If the energy lowerings produced by adding single d components are roughly additive, then the 28% contribution to the total SO_2 energy lowering produced by the d_{xy} orbital can at most be ~1.5 times the next largest contribution from a single d function, and this figure is only obtained in the unlikely event that the four non-symmetry-required components have equal energy lowering effects.
(19) H. Nakatsuji and J. I, Musher, *Chem. Phys. Lett.*, **24**, 77 (1974).
(20) Analogous results have been observed[21] in studies of ethylene episulfide, episulfoxide, and episulfone, although cases can be found in which the addition of d functions to similar sp bases does lead to changes in the ordering of the orbital energies. For example, for SF_6 calculations apparently comparable to those of section IIB lead to a change in the relative position of the $3e_g$ orbital energy.[22] Sulfur d functions are symmetry required to contribute to this orbital orbital pair. With a minimal basis much larger changes in the SF_6 orbital energies are observed on adding d functions[23] (compare, however, section III).
(21) M.-M. Rohmer and B. Roos, *J. Am. Chem. Soc.*, **97**, 2025 (1975).
(22) B. Roos, unpublished results quoted in ref 23.
(23) F. A. Gianturco, C. Guidotti, U. Lamanna, and R. Moccia, *Chem. Phys. Lett.*, **10**, 269 (1971).
(24) J. B. Collins, P. v. R. Schleyer, J. S. Binkley, and J. A. Pople, *J. Chem. Phys.*, **64**, 5142 (1976).
(25) I. H. Hillier and V. R. Saunders, *Chem. Commun.*, 1183 (1970).
(26) I. H. Hillier and V. R. Saunders, *Mol. Phys.*, **22**, 193 (1971).
(27) M. F. Guest, M. B. Hall, and I. H. Hillier, *J. Chem. Soc., Faraday Trans. 2*, **69**, 1829 (1973).
(28) P. J. Hay, *J. Am. Chem. Soc.*, **99**, 1003 (1977).
(29) All calculations were performed using the ATMOL3 suite of programs: V. R. Saunders and M. F. Guest, "ATMOL3 Users Guide", Science Research Council, Daresbury, Warrington, England.

A Simple Model of Bond Geometry and the Stereoactivity of Lone Pairs

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Abstract: Bond angles and the stereoactivity of lone-pair electrons are predicted using a simple quantum mechanical model consisting of orbitals on a circle or ring, with Dirac δ functions representing bonds. Treatment of bonding in a plane is simple enough to be handled on a small minicomputer. The pattern of energetically favored bond angles shows the effect of stereoactive lone pairs and the expected changes with ligand electronegativity. The bond angle in water is predicted as 104.9° (experimental 104.5°). Predictions for other small molecules compare favorably with those from other simple treatments. The model intentionally omits Coulomb repulsions: the bond angle trends would appear to result from the Pauli exclusion principle.

I. Introduction

An understanding of the geometries of molecules and ions is basic to almost every field of chemistry. Accordingly, the configurations of covalent bonds around atoms have been studied extensively, and there are available today not only a vast body of experimental data, but also a number of well-documented and useful generalizations. Important among these is the effect of lone electron pairs upon the bond geometry about an atomic kernel. Concepts used to explain observed trends include hybridization,[1] valence-shell electron-pair repulsion (VSEPR),[2] second-order Jahn-Teller effects,[3] and ligand-pair vs. lone-pair electrostatic repulsions.[4] These schemes possess in common a recognition that bond geometries can generally be predicted from (1) the number of bond and lone pairs about each atom in a Lewis-type description and (2) the relative electronegativities of the atoms involved.

Two sources of the apparent stereoactivity of lone-pair electrons have been suggested: electrostatic repulsions and effects of the Pauli exclusion principle. Extreme partisans of each view can be cited.[5] In this paper we explore the simplest model we can imagine which might simulate the effect of the number of valence electrons on a bond angle. This model intentionally omits electrostatic repulsions. We believe that the success of this model in mimicking observed stereochemistry may be important in assessing the role of the Pauli principle, and in discussing bonding concepts in general.

A very preliminary report on this model has been published.[6] We here present it in detail, and dissect it in terms of localized orbitals, electron densities, and kinetic vs. potential energy contributions. We calculate bond angles for several simple molecules, and compare results with those from other models.

II. The Model and Its Exact Solutions

In this model the electrons are placed on a ring, that is, on the circumference of a circle, so that the position of each electron is defined by the value of a single angular coordinate, ϕ. This circle can be thought of as centered at the nucleus, and as having some radius appropriate for the purpose of examining angular electron–electron interactions, such as a typical bond radius. We are thus replacing orbital functions involving three coordinates by functions of only one angle: that in the plane of the bond. For a single electron the Schroedinger equation has the familiar solutions:

$$\psi_0^0 = 1/\sqrt{2\pi} \qquad\qquad W_0^0 = 0$$
$$\psi_{c,k}^0 = \cos(k\phi)/\sqrt{\pi} \qquad\qquad (1)$$
$$\psi_{s,k}^0 = \sin(k\phi)/\sqrt{\pi} \qquad W_k^0 = k^2 W_1^0$$

where k is an integer. The natural unit of energy in this model is W_1^0: all energies will be expressed in this unit, and this symbol will be omitted for the remainder of this paper. W_1^0 is approximately 6.104×10^{-39} J m$^2/r^2$, where r is the radius of our circle.

For this discussion we shall ignore Coulomb electron–electron repulsions. Equations 1 then give a set of orbitals to be doubly occupied by electrons. It was early pointed out by Lennard-Jones[7] that for three electrons of like spin occupying the three lowest orbitals on a circle or ring, the most probable electron–electron angular separation is 120°. Since the electrons of each spin move independently of those of opposite spin, it might be argued that if one electron of each spin (i.e., one pair) is pinned down at a given position by formation of a bond, electron density might pile up at positions 120° from that bond,