

greatly improved by the use of linear combinations of two or more functions to represent each AO (multiple  $\zeta$  basis sets). In such a treatment, the electron density at the nucleus depends not only on the electron distribution in the valence shell region but also on the relative contributions of the corresponding suborbital functions to each AO, in particular to each s AO. The latter factor is neglected in all current semiempirical SCF-MO treatments (including MINDO/3) since they all use minimum basis sets. It is therefore not surprising that MINDO/3 reproduces all the "chemical" properties that depend on the valence shell electron distribution but is much less successful for NMR coupling constants. This argument suggests that attempts to calculate the latter accurately by any LCAO-MO procedure are doomed to failure unless a multiple  $\zeta$  basis set is used. To attempt this in a semiempirical treatment would raise obvious and formidable problems.

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## Some Symmetry Considerations Concerning the Role of Atomic d Orbitals in Chemical Bonds: Discussion and Some Computational Examples

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**Abstract:** The problem of the necessity for the inclusion of d orbitals in a computational basis set is discussed, with emphasis placed on the symmetry of the system under consideration. The distinction between qualitative and quantitative necessity for such inclusion is drawn on the basis of symmetry and illustrative examples, both computational and conceptual, for several simple systems are presented.

### I. Introduction

Since the classic work of Pauling,<sup>1</sup> there have been many papers dealing with participation of orbital basis functions of atomic d-like character in molecular orbitals<sup>2-42</sup> for systems containing nontransition elements. The current literature contains papers in which the relative merits of inclusion or omission of atomic d orbitals in an LCAO basis set are debated.<sup>43</sup> Unfortunately, the question as generally stated is not precise, and consequently it is impossible to answer in any meaningful way. It is the purpose of this paper to restate the basic question, to relate this to the problem of chemical bonding, to present some heuristically helpful examples, and to develop guidelines for the desirability of including such basis functions in a quantum chemical calculation or explanation.

The addition of any linearly independent function to a basis set will result in a wave function which is better, variationally, than a wave function in the smaller basis. Thus the addition of 4f functions will improve a calculation on H<sub>2</sub>, although 4f

functions on an H atom are physically unimportant. One would like to understand the role of these higher angular momentum functions in orbital bases. Much misunderstanding comes from the idea that d functions (abstract mathematical constructs) can contribute to, or participate in, a chemical bond, an idea rooted in too close adherence to the simple minimal basis LCAO approximation. In LCAO theory the inclusion of higher angular momentum orbitals can be required or justified by appeals to arguments of orbital population, energy lowering, or improvement in computed one-electron properties. This works because the prescription for choosing a basis is well defined: one Slater-type orbital (STO) per occupied atomic orbital in the constituent atoms. In this situation, the addition of any basis orbital means the addition of an orbital of the next higher angular momentum, as lower angular momentum functions have already been saturated in the scheme. Since *any* basis orbital thus included will contribute to all the one-electron wave functions it is allowed to by symmetry, the added function will have a nonzero population. The result always is lowering

of the total energy of the system and improvement in the computed one-electron properties.

Most studies of the role of higher angular momentum functions in chemical bonding of nontransition elements concern cases involving atoms which expand the octet or form nonclassical Lewis structure molecules.<sup>44</sup> These involve the second row nonmetals (Si, P, S), their higher congeners, and the halogens. These are the atoms which have low-lying virtual d orbitals (<1 eV above the highest occupied AO<sup>45</sup>) and which might thus be expected to mix d orbitals strongly into the basis if they were to be added to a single  $\zeta$  or to a more extended, basis. One might expect a significant energy lowering, property improvement, and d-orbital occupation in such cases. Such is frequently observed and taken as evidence of the importance of d orbitals. The magnitudes of the observed effects depend on the system under consideration, and it has been difficult to formulate rules governing the necessity for inclusion of d orbitals in the basis. The nonmetals of the second and higher rows are of most interest in this context, but a large number of basis functions (and much computing time) is necessary to describe molecules including these atoms. We therefore take as illustrative examples various states of H<sub>2</sub> and H<sub>2</sub>O. These molecules illustrate the points to be made, which are general and based on symmetry arguments.

The problem is double faceted. We neglect the cases of molecules involving atoms with occupied d levels, as it is generally agreed that such systems should have d orbitals included. We concentrate on systems with no occupied valence d levels.<sup>67</sup> We ask when the inclusion of d orbitals in the computational basis set (not necessarily a minimal basis set) for some system is qualitatively necessary. If they are not necessary, what is the quantitative effect of inclusion of such functions if they were included anyway? We also seek conclusions from such calculations about orbital populations, energy lowering, changes in values of computed properties, etc.

The qualitative problem deals with which of the irreducible representations of the molecular point group must be spanned for a correct description of the system; the quantitative problem is one of completeness of the basis set spanning the qualitatively necessary irreducible representations. We consider qualitative importance to reflect major stereochemical differences or orbital occupation changes (not just inversion of two nearly degenerate orbitals, but rather changes in symmetry of occupied orbitals and of the symmetry state of the system) attendant on d-function addition to the basis. Quantitative effects are primarily numerical in nature, and do not change the excitation description of the system. The symmetry of the system is the overriding consideration when discussing the qualitative aspects of inclusion of higher angular momentum basis functions in a basis. If an occupied molecular orbital transforms according to an irreducible representation of the point group of the system for which the usual s and p functions on first and second row atoms, and s functions on hydrogen, do not provide a basis, then one must include functions of higher azimuthal quantum number in the computational basis. If, however, the s and p functions do provide an appropriate basis, the inclusion of higher orbitals in the basis is not of fundamental importance in the qualitative bonding picture. In this case, the normal overlap criteria of importance<sup>46</sup> can be used. One should be sure that there are functions of the appropriate symmetry on *each center* in the molecule, to ensure that density is not excluded from a center in a molecular orbital by exclusion of an appropriate basis function. For example, in H<sub>2</sub>S (C<sub>2v</sub>) one might conceive of a state where the 1a<sub>2</sub> orbital is occupied (see example in section II below). This orbital transforms according to an irreducible representation which is spanned only by d functions on sulfur and p functions on hydrogen. If both are omitted, it is impossible to construct the orbital. If the sulfur d functions are excluded, the orbital cannot have any density

**Table I.** Total Energies and Orbital Occupations of Some Singlet States of Water with a Doubly Occupied 1a<sub>2</sub> Orbital

State	Occupation	-E <sub>tot</sub>
<sup>1</sup> A <sub>1</sub> ground	1a <sub>1</sub> <sup>2</sup> 2a <sub>1</sub> <sup>2</sup> 3a <sub>1</sub> <sup>2</sup> 1b <sub>1</sub> <sup>2</sup> 1b <sub>2</sub> <sup>2</sup>	76.046 402
<sup>1</sup> A <sub>1</sub> '	1a <sub>1</sub> <sup>2</sup> 2a <sub>1</sub> <sup>2</sup> 1a <sub>2</sub> <sup>2</sup> 1b <sub>1</sub> <sup>2</sup> 1b <sub>2</sub> <sup>2</sup>	73.544 539
<sup>1</sup> A <sub>1</sub> ''	1a <sub>1</sub> <sup>2</sup> 2a <sub>1</sub> <sup>2</sup> 3a <sub>1</sub> <sup>2</sup> 1a <sub>2</sub> <sup>2</sup> 1b <sub>2</sub> <sup>2</sup>	73.739 132
<sup>1</sup> A <sub>1</sub> '''	1a <sub>1</sub> <sup>2</sup> 2a <sub>1</sub> <sup>2</sup> 3a <sub>1</sub> <sup>2</sup> 1a <sub>2</sub> <sup>2</sup> 1b <sub>1</sub> <sup>2</sup>	73.329 588

centered on the sulfur, but must be located primarily on the hydrogens. Similarly, exclusion of hydrogen p functions effectively excludes 1a<sub>2</sub> orbital density on those atoms.

## II. Qualitative Aspects

To illustrate the qualitative aspects of d-function inclusion in a basis, we need a molecule that has an occupied molecular orbital which transforms as an irreducible representation of the molecular point group that is spanned only by d functions on the central atom and p functions on the ligands (such as the A<sub>2</sub> orbital in ground state SO<sub>2</sub> or ClO<sub>2</sub> (C<sub>2v</sub>)). Here we assume for the sake of simplicity that we are dealing with a molecule of AB<sub>n</sub> or AX<sub>n</sub>Y<sub>m</sub> type. For simplicity, we would also like to have a singlet state derived from a closed shell. Most of the ground state singlet molecules satisfying these criteria are MX<sub>4</sub> or MX<sub>6</sub> systems, where the central atom is a transition metal, or heavier polyatomic systems such as SO<sub>2</sub>, SF<sub>6</sub>, and PCl<sub>5</sub>. We take an example from the excited states of small molecules. There is an A<sub>2</sub> irreducible representation of the C<sub>2v</sub> point group that has the desired properties. We can thus produce a model system by preparing a C<sub>2v</sub> molecule with the 1a<sub>2</sub> orbital occupied. Calculations<sup>47</sup> were thus carried out on a variety of hypothetical states of the water molecule, using an uncontracted (10s, 5p, 2d; 4s, 2p) basis constructed from the s-p basis of Neumann and Moskowitz<sup>48</sup> augmented by two sets of d functions on oxygen with orbital exponents of 1.5 and 0.5, and two sets of p functions on hydrogen with orbital exponents also of 1.5 and 0.5. All calculations were done at the ground state minimum energy geometry of Smith et al.<sup>49</sup> R<sub>OH</sub> = 1.779 bohr, and  $\theta = 106.1^\circ$ . The total energies and orbital occupations for the ground state and for the three lowest lying excited states of water having a doubly occupied 1a<sub>2</sub> orbital are presented in Table I.<sup>50</sup>

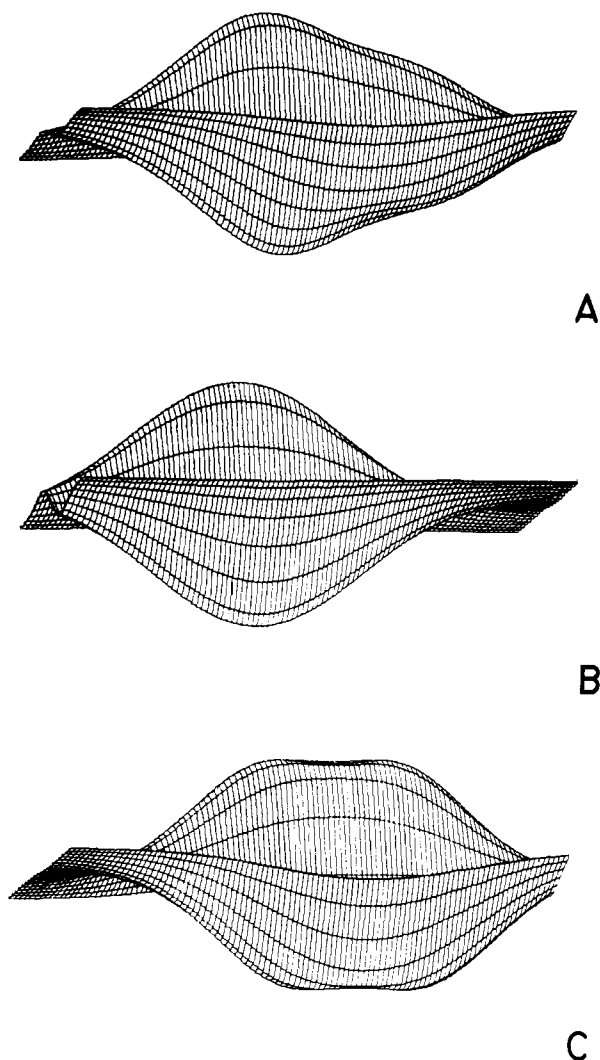
Calculations were restricted to the lowest energy <sup>1</sup>A<sub>1</sub>'' state. Although it is difficult to estimate the quality of the basis for this hypothetical state, the ground state energy is at least encouraging (cf., e.g., ref 49). The results obtained for calculations on the <sup>1</sup>A<sub>1</sub>'' state of water with the full basis (case A), with the full basis after the p functions had been deleted from hydrogen (case B), and the full basis after the d functions had been deleted from oxygen (case C) are displayed in Table II.

The C<sub>2v</sub> character table shows that for the z axis taken along the bisector of the H-O-H angle and in the molecular plane, and the x axis perpendicular to the molecular plane, only the d<sub>xy</sub> orbitals on oxygen and the antisymmetric sums of p<sub>x</sub> orbitals on the hydrogen transform as A<sub>2</sub>. If these orbitals were not included, it would be impossible to form a molecular orbital with the required symmetry, thus forcing a different orbital occupancy from the desired one. This is a qualitative change in the description of the molecule. The four orbitals (two of each) included in case A seem to comprise a nearly minimal set. The population of the 1a<sub>2</sub> orbital shows that deletion of the p orbitals on hydrogen forces population onto oxygen, as there are no longer functions of A<sub>2</sub> symmetry on hydrogen. Deletion of the d orbitals on oxygen forces population onto hydrogen. The charge transfer is not complete as the functions on one of the centers do provide a basis, however poor, for representation of the orbital on other centers. The effect of the orbital deletion

**Table II.** Calculated Properties<sup>a</sup> for <sup>1</sup>A<sub>1</sub>'' Water (*R*<sub>OH</sub> = 1.779 bohr, *θ* = 106.1°) with and without p Functions on H and d Functions on O

		Case		
		A	B	C
Deletions		None	p on H	d on O
<i>E</i> <sub>tot</sub>		-73.739 132	-73.280 246	-73.637 756
Eigenvalues	1a <sub>1</sub>	-20.957 179	-20.915 281	-20.989 721
	2a <sub>1</sub>	-1.498 948	-1.434 955	-1.547 294
	3a <sub>1</sub>	-0.809 418	-0.718 744	-0.854 221
	1a <sub>2</sub>	0.651 910	0.896 218	0.698 010
	1b <sub>2</sub>	-0.895 435	-0.833 720	-0.936 636
Atomic population	O	7.793	9.261	7.121
	H	1.104	0.370	1.440
Overlap population	O-H	0.427	0.231	0.283
	H-H	-0.101	-0.011	-0.182
<i>μ</i> (dipole moment)		0.063 3	1.165 8	0.549 9
Population in 1a	O	0.559 5	2.000 0	
	H	0.720		1.000 0
<i>Q</i> <sub>xx</sub> (quadrupole moment)		-0.482 5	-1.578 0	0.163 4
<i>Q</i> <sub>yy</sub>		-0.532 7	0.454 4	0.972 4
<i>Q</i> <sub>zz</sub>		1.015 2	1.123 7	0.808 9

<sup>a</sup> Calculated in principal axis coordinates; atomic units.



**Figure 1.** Plot of the 1a<sub>2</sub> orbital of the hypothetical <sup>1</sup>A<sub>1</sub>'' state of water using basis 4, plotted 0.25 bohr above the yz plane: A, the full basis; B, p orbitals on H omitted from the calculation; C, d orbitals on O omitted from the calculation.

is presented pictorially in Figure 1, where the value of the 1a<sub>2</sub> orbital is plotted for each of the three cases. Another manifestation of the lack of available orbitals is the drastic lowering of the O-H overlap population in cases B and C. This is attributable to the inability of the 1a<sub>2</sub> orbital to have any O-H overlap when there are no orbitals of proper symmetry on one of the centers. In case B, where the p orbitals are deleted from the hydrogens, the H-H overlap population is lowered for the same reasons.

There are large, qualitative changes in the values of the moments of the charge distribution as one goes from case A to case B to case C. The components of the quadrupole moment, especially the off axis components, *Q*<sub>xx</sub> and *Q*<sub>yy</sub>, change their sign as a function of the basis. Similarly, the dipole moment varies by a factor of 20 over the variation in basis. The quantitative changes should also be noted. The total energies increase when basis functions are deleted. However, the energy variation does not indicate the qualitative necessity for inclusion of d functions on the oxygen, and p functions on the hydrogen. The total and orbital energies serve only to indicate that the p orbitals on the hydrogen are more important than the d orbitals on oxygen. Similarly, the basis function population in the oxygen d orbitals is no more significant physically than the population in the p orbital on hydrogen.

The qualitative necessity for the use of valence basis functions with higher azimuthal quantum numbers than those of the highest occupied atomic orbitals in computations of this type is illustrated above. These results are representative of minimal and extended basis LCAO-MO type calculations, as well as of other orbital methods such as X<sub>α</sub>,<sup>52-53</sup> as the arguments on which they are based are general and derived from symmetry considerations alone.

These considerations are also important when dealing with dynamical processes, as the symmetry of the problem may change during the process, necessitating different basis orbitals at different points on the reaction path. Consider the inversion of ammonia or phosphine. Both are pyramidal (*C*<sub>3v</sub>) in the ground state, but pass through a planar (*D*<sub>3h</sub>) transition state. In the ground state, only the A<sub>1</sub> and E irreducible representations are occupied, so the addition of d orbitals to the basis will increase the degree of completeness of the basis (vide infra), but will not change the qualitative aspects of the basis.

**Table III.** Population Analysis and Energetics of  $H_2$  ( $^1\Sigma_g^+$ ) Calculated with Various Basis Sets ( $R_{HH} = 1.40$  bohr)

Basis <sup>a</sup>	Deleted orbitals	$E_{1\sigma}$	Population in orbital types			Overlap population	$E_{tot}$
			s	p	d		
1a	None	-0.591 824	1.992	0.019	-0.011	0.414	-1.131 238
1b	p	-0.593 043	2.021		-0.021	0.401	-1.126 747
1c	d	-0.591 677	1.981	0.019		0.415	-1.131 200
1d	p,d	-0.592 778	2.000			0.404	-1.126 589
1e	s'	-0.355 714	1.628	0.009	0.363	0.384	-0.857 112
1f	s',p	-0.358 052	1.642		0.360	0.378	-0.856 351
1g	s',d	-0.314 667	1.998	0.002		0.312	-0.811 818
1h	s',p,d	-0.315 341	2.000			0.310	-0.811 774
2a	None	-0.591 961	1.990	0.019	-0.008	0.414	-1.131 244
2b	p	-0.592 248	2.033		-0.033	0.399	-1.126 951
2c	d	-0.591 999	1.981	0.019		0.416	-1.131 225
2d	p,d	-0.592 417	2.000			0.404	-1.126 622
3		-0.592 827					-1.130 308
4a	None	-0.576 832	1.775	0.0	0.225		-1.081 685
4b	p	-0.576 832	1.775		0.225		-1.081 685
4c	d	-0.556 560	2.000	0.0			-1.033 124

<sup>a</sup> See text for explanation.

In the transition state there are orbitals of  $E''$  symmetry which are spanned only by higher  $\ell$  functions. If these orbitals are occupied, it is necessary to include the appropriate higher  $\ell$  functions in the basis in order to describe the planar transition state correctly. This problem has been investigated for ammonia<sup>38</sup> using configuration interaction methods, and similar conclusions were reached.

A similar situation is encountered in chemical reactions which involve changes in symmetry at some central atom. This problem arises in work on the  $SiH_5^-$  intermediate.<sup>54</sup> These specific symmetry-dictated examples are aspects of a more general problem which occurs whenever a basis set is not of the same quality for all nuclear configurations of the constituent atoms of a system. A basis of a given quality for description of a supermolecule near its putative quasistable equilibrium state will not necessarily be of the same quality for description of the separated fragments. This is true even when the symmetry considerations do not apply. If an inadequate basis is used (less than near-Hartree-Fock quality) strong numerical effects may appear which are apparently symmetry dependent, but are in fact consequences of space spanning problems. The remarks in the above two paragraphs should thus be taken in the context of an adequate s,p basis.

### III. Quantitative Aspects

Consider an occupied molecular orbital that transforms according to one of the irreducible representations spanned by s and p functions on the central atom, and at least s functions on the ligands. We investigate the effect of adding functions of higher azimuthal quantum number to the basis, such that the added functions also transform according to the same s and p function spanned-irreducible representation. For example in  $H_2S$ , we ask for the effect of adding a set of d functions to sulfur, knowing that in the ground state only the  $A_1$ ,  $B_1$ , and  $B_2$  representations of  $C_{2v}$  are occupied, and that these are spanned by the s and p functions on sulfur and the s functions on hydrogen. In addition, however,  $d_{z^2}$  and  $d_{x^2-y^2}$  on sulfur both transform according to  $A_1$ , and  $d_{xy}$  and  $d_{yz}$  transform according to  $B_1$  and  $B_2$ , respectively. The effect of the addition of functions to representations which are already spanned will be one of increased basis set completeness, then, and the effects seen as a result of such additions should be attributable to this; d orbitals should hold no special reverence in this context compared to other methods of increasing the completeness of a basis. We use the term "completeness" in a loose sense here. A more proper treatment of the problem should use one of the

available tests for completeness<sup>55-57</sup> of a basis for a variety of different bases to clarify the distinction. The inclusion of additional functions to increase the completeness of the basis within already spanned representations (often referred to as adding polarization functions or increasing the flexibility of the basis)<sup>14</sup> results in a quantitative improvement of the calculation, but generally not in a qualitative change in the computational results. We present below some computations on simple model compounds to illustrate these points.

Take as an example ground state hydrogen. The state may be represented as  $^1\Sigma_g^+$ :  $1\sigma_g^2$ . The single occupied molecular orbital transforms according to  $\Sigma_g^+$ , which is spanned by the symmetric sum of the 1s atomic orbitals. If we restrict to a minimal basis, these two functions will not span all of the portion of space that the molecular wave function samples. In fact, any number of purely s functions centered on the two nuclei will fail to adequately span the space. There are several ways that this problem might be ameliorated. For instance, functions of higher azimuthal quantum number might be added to the computational basis—in this case p functions might be added, but not centered on the atoms, in the spirit of the floating spherical Gaussian orbital (FSGO)<sup>59</sup> scheme. Either of these schemes to increase the completeness of the basis spanning an irreducible representation aims to provide enough flexibility to adequately mock up the exact charge density of the molecule. One wishes the basis to have sufficient generality to adjust to polarization of the charge cloud; thus the origin of the idea of adding "polarization" functions to a basis.<sup>14</sup> The need for such addition depends on the problem under consideration. A certain basis may be perfectly adequate for representation of some properties of a system, such as the total energy, but completely inadequate to represent others such as quadrupole moment.<sup>60</sup>

We consider the case of the ground ( $^1\Sigma_g^+$ ) state of the hydrogen molecule at the experimental internuclear distance of 1.40 bohr.<sup>61</sup> A variety of basis sets were used, all derived from the hydrogen set used by Moskowitz et al.<sup>62</sup> The first basis, designated 1, consisted of the Moskowitz (4s,1p) set contracted as (3,1;1) augmented by a single set of hydrogenic d functions with orbital exponent 0.75. The set is designated (3,1;1;1). Here and in the following no attempt has been made to optimize the exponents of the added functions. The second basis, designated (1,1,1,1;1;1), was identical with the first, but uncontracted. It should be better than basis 1, as it has more flexibility, the linear combinations of the basis functions all being freely determined by the SCF procedure. A third basis

**Table IV.** Properties Calculated<sup>a</sup> for H<sub>2</sub> (<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) Various Basis Sets ( $R_{\text{HH}} = 1.40$  bohr)

Basis <sup>b</sup>	Deleted orbitals	Quadrupole moment		Field gradient		Diamagnetic susceptibility	
		$Q_{xx}$	$Q_{zz}$	$F_{xx}$	$F_{zz}$	$\chi_{xx}$	$\chi_{zz}$
1a	None	-0.2153	0.4305	0.1832	-0.3665	-1.4824	-1.0519
1b	p	-0.1728	0.3455	0.1963	-0.3927	-1.4741	-1.1285
1c	d	-0.2097	0.4193	0.1811	-0.3623	-1.4770	-1.0577
1d	p,d	-0.1603	0.3207	0.1923	-0.3846	-1.4628	-1.1421
1e	s'	-0.0178	0.0357	-0.0376	0.0752	-0.6257	-0.5899
1f	s',p	0.0010	-0.0020	-0.0296	0.0593	-0.6261	-0.6281
1g	s',d	-0.1430	0.2861	0.0149	-0.0299	-0.6135	-0.3274
1h	s',p,d	-0.1386	0.2772	0.0167	-0.0335	-0.6137	-0.3364
2a	None	-0.2143	0.4287	0.1828	-0.3657	-1.4840	-1.0552
2b	p	-0.1795	0.3591	0.1981	-0.3963	-1.4660	-1.1068
2c	d	-0.2101	0.4202	0.1811	-0.3623	-1.4821	-1.0618
2d	p,d	-0.1604	0.3208	0.1921	-0.3842	-1.4574	-1.1366
3		-0.2500	0.5000	0.1926	-0.3853	-1.5221	-1.0220
4a	None	-0.2937	0.5874	0.1720	-0.3441	-1.6329	-1.0455
4b	p	-0.2937	0.5874	0.1720	-0.3441	-1.6329	-1.0455
4c	d	-0.4899	0.9799	0.2012	-0.4024	-1.7866	-0.8066

<sup>a</sup> In atomic units; evaluated at nuclei in principal axis coordinates. <sup>b</sup> See text for explanation.

**Table V.** Calculated Results for Ground State (<sup>1</sup>A<sub>1</sub>) Water with Various Basis Sets<sup>a</sup>

Basis <sup>b</sup>	Deleted orbitals	$E_{\text{tot}}$	$q_{\text{O}}$	$q_{\text{H}}$	$\mu$
1a	None	-76.045 733	8.5519	0.7240	0.7955
1b	p'	-76.043 716	8.7393	0.6304	0.8158
1c	p,p'	-76.034 009	8.8660	0.5670	0.8060
1d	d'	-76.043 410	8.4833	0.7584	0.8272
1e	d,d'	-76.034 050	8.4180	0.7910	0.8731
1f	p,p',d,d'	-76.004 971	8.7651	0.6175	1.0375
4a	None	-76.046 402	8.5899	0.7051	0.7947
4b	p'	-76.044 800	8.7769	0.6115	0.8166
4c	p,p'	-76.036 923	8.9288	0.5356	0.8114
4d	d'	-76.044 405	8.4973	0.7514	0.8218
4e	d,d'	-76.035 965	8.3926	0.8037	0.8591
4f	p,p',d,d'	-76.007 073	8.7697	0.6152	1.0297
3a	None	-74.231 066	8.5958	0.7021	0.7038
3b	p	-74.208 854	8.7463	0.6269	0.7038
3c	d	-74.212 947	8.5073	0.7464	0.8489
3d	p,d	-74.175 371	8.6787	0.6607	0.9048

<sup>a</sup> All values given in atomic units. <sup>b</sup> See text for explanation of basis sets.

follows the FSGO idea, and consists of the s functions set of basis 1, augmented by three additional s functions, located at the bond center and at  $\pm 0.35$  bohr, with exponent of 0.4. Basis 4 is of one-center expansion<sup>63</sup> type, consisting of the s,p,d function set of one of the atoms of basis 1, centered at the bond center, augmented by an additional s function, with orbital exponent of 0.4. The population analysis and energetics resulting from these calculations using the previously described bases, and selectively deleting various orbitals, are presented in Table III. Here s' refers to the free Gaussian s function in basis 1. A similar tabulation for some one-electron properties is presented in Table IV.

The largest effect comes from the deletion of the 1s' function from basis 1. This change far overshadows the inclusion or exclusion of the higher azimuthal quantum number functions, and can only be due to the incompleteness of the function set being used to span the irreducible representation of the occupied molecular orbital, and not in any way to polarization or flexibility. If we make a hierarchy of bases according to increasing quality, we would group the bases as 1e-1h, 1a-1d, and 2. In going up the hierarchy, we notice that the inclusion of the polarization functions becomes less important as the s-basis improves. Thus the inclusion of the 1s' function in basis

1 is much more important energetically, for the population analysis, and for the properties (taking 2a, the variationally best calculation, as the "correct answer"), than inclusion of polarization functions. Observations of this sort have led certain people to conclude correctly that it is very important to begin a calculation with an adequate valence basis set, perhaps of double  $\zeta$  quality or better, before adding polarization functions.<sup>34</sup> Otherwise one may get an exaggerated population in the added d orbitals, and a distorted view of the quantitative necessity for inclusion of the polarization functions in the basis. Inspection of the population of the d functions in the calculations 1e and 1f (a poor s basis) and comparing these large populations to the more reasonable values obtained from the good bases 1a, 1b, 2a, and 2b, supports this idea.

A similar illustration is provided by calculations on the ground (<sup>1</sup>A<sub>1</sub>) state of the water molecule. Again a variety of bases with various deleted orbitals was used. The basis described in section II above, uncontracted, is designated basis 4. A contracted version of it, slightly better than double  $\zeta$  in quality, (2,3,2,2,1;3,1,1;1,1/3,1;1) is designated basis 1, and a highly overcontracted single  $\zeta$  version, (7,3;5;2/4;2) is referred to as basis 3. The results of these calculations are presented in Table V, and the preceding remarks concerning the

quantitative variation of the different bases apply here as well.

Further insight as to the nature of higher  $\ell$  functions in a given basis derives from the population shifts on deletion of these functions, and their relative energetic importance. From Tables II and V, the relative energetic importance of p functions and d functions is highly dependent on the system under consideration. As expected, the p functions are very much more important in molecular hydrogen than are the d's, as evidenced by the greater rise in energy when the p functions are deleted than when the d functions are. Note, however, that the effect of loss of polarization by removing p functions can be nearly completely compensated for in other ways such as by use of an FSGO-type basis. The observation holds regardless of the quality of the s basis, with the exception of the one-center calculation, where the p orbitals cannot contribute by symmetry. A similar observation holds for water. Here the d functions are centered on the oxygen while the p's are centered on hydrogen, but it appears that the d functions are slightly more important. The effects are of a quantitative nature only, and no qualitative changes are wrought by deletion of any of these functions. This conclusion is further confirmed by the charge migration attendant on basis orbital deletion. In all possible cases a large fraction of the charge from the deleted orbital ends up in s orbitals. Migration seems to be predominantly d to s and p to s, rather than d to p and p to d.

Table IV again reinforces the above conclusions. The deletion of d orbitals from basis 2 in  $H_2$  only trivially affects the quadrupole moment, field gradient or diamagnetic susceptibility, but it is necessary to include the p functions to get numerically good answers. Similarly, there is less effect on the properties due to deletion of p and d functions from basis 2 than from basis 1, while deletion of the  $1s'$  orbital from basis 1 destroys any reliance one might have in the calculated properties.

The problem of overcompleteness of the molecular basis occasionally arises, since functions centered in one place may add to the basis of functions centered in another. When the supermolecule approach is used to describe molecular interactions, the basis on one fragment may help span the portion of space sampled by the wave function of the other fragment,<sup>64</sup> and thus lower the energy of that fragment. When polarization functions are used in the bases, the danger of this occurring is especially high, particularly when the s,p basis is nearly complete.

Finally, it should be mentioned that the question of  $\pi$ -type bonds involving p and/or d orbitals<sup>16</sup> is equivalent to the same symmetry argument made here. We prefer to discuss the problem using symmetry concepts, while others<sup>16</sup> use words adapted from chemical bonding ideas. There is no fundamental difference.

#### IV. Summary

We have proposed that the distinction be drawn between the symmetry-dictated qualitative necessity of inclusion of orbitals with higher azimuthal quantum number in the computational basis set, which presumably contains an adequate number of valence functions, and the quantitative necessity of including such functions predicated on the desire for numerically accurate answers. This symmetry criterion, when used in conjunction with the idea of balanced basis sets,<sup>34</sup> or their equivalent,<sup>64</sup> and the normal overlap criteria<sup>46</sup> should allow one to determine the necessity to include higher angular momentum functions. As long as the compounds have no occupied molecular orbital which transforms according to an irreducible representation of the molecular point group which is spanned only by d functions on the central atom, the d functions are not qualitatively necessary. They may be useful if one wishes to

get numerically accurate results, as their inclusion will increase the completeness of the computational basis. Thus  $CH_2CHSiH_3$  and  $CH_2CHCH_3$  would be expected to require the same type functions in the basis for a qualitative description, although the silane, being larger, will probably need more basis functions for a quantitatively correct description of the bonding. The same remarks should hold, for example, for ethers and thioethers.<sup>66</sup>

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## The 14-Electron Isoelectronic Series. Some ab Initio Calculations on a Series of Related Molecules

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**Abstract:** Ab initio calculations on a number of related 14-electron molecules have been carried out using a 4-31G basis set and the equilibrium geometries and the electronic structure of the molecules in these geometries are presented. A primary purpose of this investigation was to detect patterns in the total energies, geometries, and ordering of the molecular orbitals for these related isoelectronic systems. Such patterns have been observed and are discussed and where possible interpreted. In addition, the results of protonation are described and a preliminary result of the study of the potential energy surface for the protonation of NO<sup>+</sup> is given. The study also provides equilibrium geometries for a number of previously uninvestigated molecular species which will hopefully be of assistance to experimentalists interested in detecting and identifying such species.

The 14-electron isoelectronic series contains a number of important and thoroughly investigated molecules such as carbon monoxide, nitrogen, hydrogen cyanide, and acetylene. It also contains a number of molecules which have recently been identified as being present in interstellar space and have more recently still been produced and studied in the laboratory. These are the molecular species HCO<sup>+</sup>, HNN<sup>+</sup>, and HNC. Individual members of this series have been studied using ab initio molecular orbital techniques and a wide variety of basis sets. Among these are CF<sup>+</sup>,<sup>1,2</sup> HBNH,<sup>3,4</sup> NO<sup>+</sup>,<sup>2</sup> CO,<sup>5</sup> HCO<sup>+</sup>,<sup>6-8</sup> N<sub>2</sub>,<sup>9</sup> NNH<sup>+</sup>,<sup>2,8,10,11</sup> CN<sup>-</sup>,<sup>12</sup> HCN,<sup>13</sup> HNC,<sup>14-16</sup> HCNH<sup>+</sup>,<sup>17</sup> HBO,<sup>18</sup> C<sub>2</sub><sup>2-</sup>,<sup>19</sup> HCCH,<sup>20</sup> BF,<sup>9</sup> HBF<sup>+</sup>,<sup>21</sup> and O<sub>2</sub><sup>2+</sup>.<sup>19</sup> While much effort has been expended, with some success, in empirical and semiempirical calculations, using a consistent methodology, to study series of related molecular systems with the hope of discovering patterns of behavior in the energies, molecular orbital order, and other electronic properties there is little or no evidence of similar studies, using a consistent basis set, in ab initio calculations. The work re-

ported here deals with such a set of calculations involving a group of isoelectronic molecules and using a 4-31G Gaussian basis set. The results obtained are analyzed with a view to observing regularities in the ordering of energies of the molecules, the molecular orbitals, and the geometry parameters.

Within the group of isoelectronic molecules studied are subgroups related by the presence or absence of one or more protons. Another purpose of this study was to investigate the effect of protonation on the orbital energies and total energies and to observe what changes in electron density distribution occur. A set of calculations on the single protonation of BF, CO, and N<sub>2</sub><sup>21</sup> discussed the systems HBF<sup>+</sup>, HCO<sup>+</sup>, COH<sup>+</sup>, and NNH<sup>+</sup> but used a smaller basis set than the one employed here and provide no information on the total energy or equilibrium geometry of COH<sup>+</sup>.

A number of the molecular systems discussed in this study have either never been previously investigated, have been studied using a smaller basis set, or have been subject to only partial optimization. It is hoped that the equilibrium geome-