Mg-Si Bond in D of CaBe$_2$Ge$_2$ type

Figure 5. COOP curve for the Mg–Si bond in layer D of the CaBe$_2$Ge$_2$ structure.

Table II. Extended-Hückel Parameters

	orbital	H_{ii} (eV)	ζ
Ba	6s	−7.0	1.2
	6p	−4.0	1.2
Mg	3s	−9.0	1.2
	3p	−4.5	1.2
Si	3s	−17.3	1.38
	3p	−9.2	1.38

difference more accurately in order to predict the transition temperature.

Finally, one reason that the CaBe$_2$Ge$_2$ structure has higher average energy than the ThCr$_2$Si$_2$ type at higher temperatures is that its band gap is much smaller. Because of the larger band dispersion (see **5**) in the CaBe$_2$Ge$_2$ structure, it is easier to for the electrons to be excited to the states above the Fermi level. This

may lead to an additional contribution from vibronic excitations, as one referee pointed out. Figures 4 and 5 are the crystal orbital overlap population[13] (COOP) plots for the Mg–Si bonds in these two structures. These are really density of states weighted overlap populations, plotted in increasing energy, positive value indicating states contributing to bonding, and negative to antibonding. The magnitude shows how many states contribute to a bond, and how strong is the bond.

In Figures 4 and 5, one can see that the band gap is much larger for the ThCr$_2$Si$_2$ structure. Above the band gap, the states are all antibonding states. Thus if these states are occupied, the Mg–Si bond will be significantly weakened. This is the primary reason that at high temperatures, when these states are populated, the atomic fluctuation becomes greater. Because the band gap is larger, the antibonding states are populated at much higher temperatures for the ThCr$_2$Si$_2$ type structure.

Appendix

The extended-Hückel parameters used in the simulations are listed in Table II. The Lennard-Jones radii for atoms are taken from the BaMg$_2$Si$_2$ structure (a = 4.65 Å, c = 11.09 Å). The corresponding parameters for the atom pairs are: (A) Ba–Mg, 3.5114 × 10^6 eV Å^{12}; Ba–Si, 1.8092 × 10^6 eV Å^{12}; Mg–Si, 1.0654 × 10^5 eV Å^{12}; (B) Ba–Mg, 1.3250 × 10^3 eV Å^6; Ba–Si, 9.5110 × 10^2 eV Å^6; Mg–Si, 2.3080 × 10^2 eV Å^6. A set of 8K points generated using the method of Pack and Monkhorst[14] for tetragonal cell with lowest symmetry was used for the Monte Carlo simulations, and 64K points for the COOP calculations.

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The Role of d Functions in Correlated Wave Functions: Main Group Molecules

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Abstract: Large d function contributions to Hartree–Fock wave functions of sulfur- and phosphorus-containing molecules are often cited as evidence for hypervalent spd hybridization and for violations of the octet rule. Recent work on hypercoordinate molecules invalidates this interpretation, but the possibility remains that hypervalent bonding may be facilitated by d orbital involvement in correlated wave functions. A large sample of molecules of the first- and second-row elements has been studied by electronic structure theory at correlated levels and the d function contributions compared with results obtained at the Hartree–Fock level. Whether molecules are hypercoordinate or not, d functions added to the basis set provide a fairly constant 52 kJ m^{-1} of the MP4 correlation extra energy per valence shell electron pair. d functions in the MP4 correction to Hartree–Fock wave functions neither polarize the wave function nor act as valence d "orbitals". They are correlating functions, their effects are largely atom-centered, and their major role is to provide angular correlation. By contrast, supplementary d functions in the Hartree–Fock part of the wave function are polarizing functions, the effects of which are concentrated in the overlap regions. d functions in these two roles provide a computationally convenient way to remove the restrictions of the small-basis Hartree–Fock model, but neither is consistent with the idea of a valence role for d orbitals in main group molecules or of an expanded octet.

Supplementary d functions are indispensable in electronic structure calculations of main group molecules for reproducing

experimental quantities such as geometries, reaction energies, stretching frequencies, and deformation densities.[1] For example,

Table I. Optimized Exponents, d Function Energy Contributions, and Energies (hartrees) for Molecules Containing First-Row Elements; MP4 Level Calculations[a,b]

molecule AB_n	RHF level		MP4 level					
	optimized exponents ζ_A, ζ_B	d function energy contribution ΔE_d	optimized exponents ζ_A, ζ_B	molecular energy E_{MP4}	mean correlation energy CE/p	d function energy contributions		mean d function contribution to correlation energy $\Delta CE_d/p$
						ΔE_d	ΔCE_d	
H_2	1.08	0.005	0.74	−1.163 03	0.034	0.016	0.012	0.012
BF_3	0.53, 1.10	0.122	0.52, 1.55	−323.908 18	0.052	0.352	0.229	0.019
BCl_3	0.47, 0.71	0.090	0.41, 0.61	−1403.783 16	0.046	0.428	0.338	0.028
CH_4	0.96, 0.89	0.046	0.71, 0.73	−40.383 74	0.040	0.099	0.053	0.013
C_2	0.68	0.032	0.67	−75.732 75	0.092	0.092	0.060	0.015
CO	0.71, 1.13	0.077	0.68, 1.21	−113.059 93	0.060	0.165	0.088	0.018
CS	0.51, 0.70	0.068	0.56, 0.56	−435.588 53	0.056	0.172	0.104	0.021
CO_2	0.76, 0.80	0.124	0.68, 1.05	−188.168 76	0.062	0.267	0.143	0.018
CH_2O	0.73, 1.1*, 0.95	0.066	0.63, 1.1*, 0.97	−114.218 39	0.055	0.174	0.108	0.018
CH_3F	0.67, 1.1*, 1.14	0.049	0.60, 1.1*, 1.52	−139.422 65	0.050	0.187	0.139	0.020
HCN	1.1*, 0.81, 0.91	0.053	1.1*, 0.72, 0.93	−93.189 28	0.060	0.141	0.088	0.018
N_2	0.94	0.081	0.96	−109.274 43	0.063	0.171	0.090	0.018
NH_3	1.00, 0.74	0.037	0.95, 0.69	−56.406 42	0.052	0.117	0.080	0.020
NF_3	0.84, 0.87	0.114	0.87, 1.4*	−353.343 94	0.054	0.340	0.226	0.017
NCl_3	0.50, 0.62	0.104	0.50, 0.60	−1433.378 16	0.050	0.462	0.358	0.028
NOH_3	0.85, 0.76, 1.1*	0.059	0.86, 1.00, 1.1*	−131.354 07	0.055	0.196	0.137	0.020
NO_2F	0.71, 0.96, 0.9*	0.151	0.83, 1.19, 1.4*	−304.248 39	0.064	0.387	0.235	0.020
NOF_3	0.76, 1.0*, 0.85	0.162	0.81, 1.0*, 1.50	−428.393 97	0.060	0.473	0.365	0.023
H_2O	0.61, 1.18	0.041	0.64, 1.29	−76.251 42	0.053	0.120	0.079	0.020
O_2	0.95	0.064	1.04	−149.948 27	0.063	0.185	0.121	0.020
O_3	0.88	0.099	1.04	−224.941 58	0.070	0.277	0.183	0.020
OF_2	0.90, 0.74	0.057	1.08, 1.46	−274.111 61	0.059	0.252	0.195	0.020
OCl_2	0.56, 0.72	0.080	0.91, 0.63	−994.177 14	0.051	0.334	0.254	0.025
HF	0.68, 1.37	0.028	0.67, 1.64	−100.245 04	0.050	0.050	0.076	0.019
F_2	0.88	0.026	1.49	−199.125 24	0.056	0.160	0.134	0.019

[a] Exponents are listed in the order in which they appear in the molecular formula. The asterisk indicates an exponent which was set at the value indicated and not optimized. [b] CE signifies "correlation energy" and p is the number of valence shell electron pairs in the molecule; for meanings of other symbols, see text.

Hartree–Fock calculations of SF_6 without d functions do not even predict the molecule to exist; it is easy to conclude that d functions reproduce d orbital contributions to the wave function, thereby facilitating hypervalent bonding and violation of the octet rule. Although the apparent evidence for d orbital contributions to bonding is most dramatic in the so-called "hypervalent" molecules, higher order functions play the same role in the Hartree–Fock wave functions of numerous other first- and second-row compounds where the idea of exceeding the octet never arises.[2] Moreover, in SF_6 and PF_5, which are typical, d functions are just as important on the peripheral fluorine atoms as on the central atoms.[2] These and other criticisms have removed the apparent theoretical support for the idea of spd hybridization in hypercoordinate compounds of second and later main group elements.[3,4] In its place, d functions are ascribed the role of adding flexibility to the sp basis which by itself responds too sluggishly to the molecular potential field, especially in the region between nuclei[2] and in compounds containing bonds with strong ionic character.[4]

The energy attributable to d function supplementation of the basis set is much greater in configuration interaction calculations than at the single determinant level,[1,5] so it is now important to see how these larger energy increments can be related to the role of the added functions in correlated wave functions. The possibility remains that "hypervalent bonding", although difficult to substantiate within the MO model,[2] may find support from an analysis of multiconfiguration wave functions, as suggested recently.[6]

This paper extends two earlier studies of d function contributions to molecular energies by subjecting the sample of first- and

second-row main group molecules to configuration interaction calculations.[2,7] To make the comparisons valid, the energies were obtained with the same basis set, the same supplementation, and at the same geometries. What is sought is a qualitative description of the d function role in strongly bound molecules; there is no attempt to account for the effect of electron correlation on weakly interacting systems where multiple sets of d functions and high levels of configuration interaction, including multiple reference state calculations, are likely to be required.[8] Accordingly, supplementation was generally restricted to a single set of d functions on each atom (p functions on hydrogens). The virtue of using one set of functions is that the optimum values of the d function exponent provide clues to the d function role in each of the wave functions at which the optimization was carried out.

Method of Calculation

Restricted Hartree–Fock energy calculations at supplemented and unsupplemented basis set levels have already been reported on most of the compounds included in Tables I and II.[2,7] Electron correlation was introduced by performing second- and fourth-order Moller–Plesset calculations (including single, double, triple, and quadruple substitutions) and configuration interaction methods (including double substitutions [CID] and single and double substitutions [CISD]) using the Gaussian 86 suite of programs.[9] CASSCF methods, implemented in the GAMESS programs, were also used.[10]

The Dunning–Hay standard double-zeta (ζ) basis (11s7p/6s2p) was used throughout for second-row elements and the Huzina-

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Table II. Optimized Exponents, Energies, and d Function Energy Contributions for Molecules Containing Second-Row Elements; Supplemented MP4 Level Calculations[a,b]

| molecule AB_n | RHF level | | MP4 level | | | | | | |
| | optimized exponents ζ_A, ζ_B | d function energy contribution ΔE_d | optimized exponents ζ_A, ζ_B | molecular energy E_{MP4} | mean correlation energy CE/p | d function energy contributions | | mean d function contribution to correlation energy $\Delta CE_d/p$ |
						ΔE_d	ΔCE_d	
SiH_4	0.53, 0.58	0.051	0.41, 0.56	−291.385 65	0.039	0.113	0.067	0.017
SiH_3F	0.51, 0.5*, 0.69	0.093	0.50, 0.5*, 1.32	−390.497 63	0.044	0.209	0.116	0.017
SiH_4F^-	0.56, 0.4*, 0.70	0.082	0.50, 0.4*, 1.42	−391.078 83	0.044	0.223	0.141	0.018
SiH_2F_2	0.55, 0.4*, 0.70	0.136	0.52, 0.4*, 1.32	−489.624 53	0.047	0.309	0.172	0.017
$SiH_3F_2^-$	0.55, 0.4*, 0.71	0.162	0.49, 0.4*, 1.42	−490.221 63	0.047	0.292	0.197	0.018
SiF_4	0.53, 0.56	0.230	0.52, 1.45	−687.886 77	0.051	0.518	0.288	0.018
SiO_2	0.49, 0.61	0.156	0.43, 0.98	−439.142 49	0.059	0.276	0.120	0.015
PH_3	0.65, 0.54	0.052	0.46, 0.52	−342.615 85	0.041	0.134	0.077	0.019
P_2	0.44	0.073	0.43	−681.686 65	0.052	0.182	0.109	0.022
HCP	1.1*, 0.39, 0.65	0.052	1.1*, 0.48, 0.48	−379.388 73	0.055	0.146	0.094	0.019
PH_2F	0.62, 0.5*, 0.62	0.089	0.48, 0.5*, 1.35	−441.687 21	0.047	0.222	0.133	0.019
PHF_2	0.61, 0.5*, 0.67	0.136	0.54, 0.5*, 1.35	−540.774 70	0.049	0.321	0.185	0.019
PH_2OH	0.61, 0.5*, 0.70	0.099	0.48, 0.5*, 1.12	−417.684 93	0.049	0.239	0.140	0.020
PH_2NH_2	0.61, 0.5*, 1.09	0.083	0.60, 0.5*, 0.92	−397.832 01	0.047	0.213	0.130	0.019
PF_3	0.43, 0.62	0.188	0.41, 1.38	−639.887 68	0.051	0.423	0.235	0.018
PF_5	0.65, 0.68	0.364	0.57, 1.41	−839.221 41	0.051	0.723	0.359	0.018
POH_3	0.61, 0.8*, 1.1*	0.166	0.53, 0.8*, 1.1*	−417.668 02	0.048	0.282	0.116	0.017
POF_3	0.59, 1.1*, 0.73	0.343	0.57, 1.1*, 1.42	−714.981 31	0.052	0.633	0.290	0.018
PO_2F	0.62, 0.8*, 0.9*	0.298	0.59, 0.8*, 0.9*	−590.645 40	0.054	0.492	0.195	0.016
PCl_3	0.44, 0.43	0.166	0.50, 0.57	−1719.781 91	0.045	0.515	0.349	0.027
H_2S	0.58, 0.84	0.047	0.56, 0.55	−398.847 29	0.044	0.144	0.097	0.024
SCH_2	0.66, 0.6*, 1.1*	0.053	0.51, 0.6*, 1.1*	−436.809 20	0.050	0.184	0.131	0.021
SHOH	0.66, 0.5*, 0.66	0.085	0.56, 0.5*, 1.13	−473.866 30	0.050	0.241	0.156	0.022
$SHNH_2$	0.67, 0.5*, 1.02	0.074	0.57, 0.5*, 0.91	−473.026 34	0.049	0.231	0.157	0.022
SHF	0.53, 0.57, 0.53	0.072	0.56, 0.56, 1.35	−497.853 08	0.048	0.221	0.149	0.021
SF_2	0.70, 0.66	0.115	0.58, 1.24	−596.879 79	0.051	0.313	0.198	0.020
$SO_2{}^c$	0.76, 0.57	0.260	0.72, 0.98	−547.741 81	0.059	0.415	0.157	0.017
	2.3, 0.55, 0.67	0.277	2.3, 0.55, 1.04	−547.769 45	0.060	0.442	0.165	0.018
SNF	0.69, 0.7*, 0.9*	0.161	0.63, 0.7*, 0.9*	−551.842 17	0.057	0.333	0.172	0.019
SOF_2	0.71, 0.8*, 0.9*	0.270	0.67, 0.8*, 0.9*	−671.950 91	0.053	0.499	0.229	0.018
SF_4	0.65, 0.62	0.287	0.62, 1.36	−796.146 58	0.053	0.600	0.313	0.018
$SF_6{}^d$	0.64, 0.75	0.513	0.63, 1.40	−995.368 65	0.050	0.930	0.417	0.017
SO_3	0.68, 0.64	0.406	0.67, 1.01	−622.749 72	0.058	0.615	0.219	0.017
SCl_2	0.43, 0.46	0.175	0.47, 0.53	−1316.879 87	0.040	0.393	0.218	0.022
$SOCl_2$	0.91, 1.0*, 1.03	0.573	0.75, 1.0*, 0.83	−1389.591 67	0.068	0.886	0.313	0.024
HCl	0.62, 0.98	0.030	0.56, 0.68	−460.229 39	0.042	0.136	0.106	0.027
ClF	0.76, 0.61	0.048	0.63, 1.40	−559.186 54	0.049	0.208	0.160	0.023
ClF_3	0.71, 0.34	0.175	0.69, 1.35	−758.319 67	0.054	0.455	0.276	0.020
ClO_2	0.77, 0.57	0.227	0.75, 0.89	−609.516 23	0.057	0.434	0.207	0.020
Cl_2	0.54	0.055	0.59	−919.211 40	0.045	0.251	0.196	0.028

[a] The basis set of each atom was supplemented with a single set of 5 d functions (p functions for H atoms); d function exponents (p functions for H atoms) are listed in the order in which they appear in the molecular formula. The asterisk indicates an exponent which was set at the value indicated and not optimized. [b] CE signifies "correlation energy" and p is the number of valence shell electron pairs in the molecule; for meanings of other symbols, see text. [c] The second entry for SO_2 is for a [2D/1D] calculation. [d] Post Hartree-Fock data for SF_6 were obtained at MP2 level.

ga–Dunning double-ζ basis, for first-row elements (9s5p/3s2p) and for hydrogen (4s/2s).[11,12] Except where specifically noted, the molecules were calculated at the experimental geometries. The conclusions are not sensitive to changes in geometry.

Supplementary d functions were added to the sp basis sets and the exponents optimized by locating the minimum in a net of energy values. The nomenclature is that of Magnusson and Schaefer[7] in which the number of sets of supplementary functions is indicated for the atoms of the molecule in the order in which they appear in the molecular formula. Hence, for SO_2, (2D/1D) indicates that the sp basis described above has been supplemented by two sets of d functions on sulfur and one set on each oxygen atom. To eliminate the unwanted effect of an extra s function, the five orthogonal d functions only were used.

To investigate optimum d function sizes in molecular wave functions, it is essential to use only one supplementary function per center. The addition of further d functions or f functions to basis sets prior to CI calculations has further effects on the energies, of course, but there is no change in the pattern of values

of correlation energy or of the d function contributions to it. The results for SO_2 are typical. Adding two, rather than one optimized set of d functions to the sulfur lowers the energy by 0.538 hartree, a 2% increase over the value of 0.527 hartree for the singly supplemented calculation. The effect on the final mean correlation correction is an increase from 0.017 to 0.018 hartree only.

Interaction occurs between d and f functions in wave functions, but the degree is small and the effect of ignoring f functions has no effect on the conclusions drawn here. At the basis set level adopted in this study, the addition of a set of exponent-optimized f functions to already-optimized d functions in the SO_2 wave function lowers the energy by 0.079 hartree (15% of the d function lowering, ΔE_d). The d function exponents require re-optimizing, and in the process the energy drops a further 0.004 hartree. Detailed results of calculations on this point are being published elsewhere.[5]

Computational Results

For the purposes of this paper, the d function contribution to correlation energy (ΔCE_d) is of crucial importance. The correlation energy (CE) is taken as the difference between the MP4 and Hartree–Fock energies, each computed at optimum exponent values for the added functions. For the ordinary main group compounds studied here, the CI wave function contains the HF

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Table III. Calculations with d Function Supplementation of STO-3G Wave Functions (Energies in Hartrees)[a,b]

	RHF level			MP4 level			
molecule AB$_n$	optimized exponents ζ_A, ζ_B	d function energy contribution ΔE_d	optimized exponents ζ_A, ζ_B	molecular energy E_{MP4}	d function energy contribution		d function contribution to correlation energy $\Delta CE_d/p$
					ΔE_d	ΔCE_d	
SO$_2$	0.25, 0.68	0.376	0.53, 1.05	−541.360 02	0.537	0.161	0.018
SO$_3$	0.31, 0.60	0.604	0.37, 1.03	−615.359 53	0.868	0.264	0.022
SF$_4$	0.14, 0.42	0.543	0.18, 1.44	−786.080 00	0.969	0.426	0.025
PF$_3$	0.10, 0.82	0.372	0.15, 1.45	−631.816 95	0.699	0.328	0.025

[a] The d function contribution to the correlation energy ΔCE_d is taken as the difference between the contributions at correlated and Hartree–Fock levels. The final column holds average ΔCE_d values per valence-shell electron pair. [b] CE signifies "correlation energy" and p is the number of valence shell electron pairs in the molecule; for meanings of other symbols, see text.

wave function as its largest component by far, so the d function contributions to the HF and CI level energies must be disentangled before ΔCE_d can be obtained. It is sufficient for our purposes to estimate it simply by subtracting the HF contribution from the d contribution to the energy of the CI wave function:

$$\Delta CE_d \approx \Delta E_d(CI) - \Delta E_d(HF)^{13}$$

The values of ΔCE_d obtained by this procedure are probably slight underestimates of the true value of the d function contribution to correlation energy. Subtracting the full value of $\Delta E_d(HF)$ from $\Delta E_d(MP4)$ ignores the fact that the weight of the HF wave function in the CI wave function is less than 1.0. It also overestimates the size of the Hartree–Fock d function contribution by taking a value calculated for the optimum d function exponents at HF level, not the optimum exponents used for the CI calculation. In the case of SO$_2$, the ΔE_d is 0.260 when the d function exponents are at HF optimum values ($\zeta_S = 0.76$, $\zeta_O = 0.57$); at the MP4 optimized values, ΔE_d drops to 0.250.

Supplementary Function Contributions to Correlation Energies. Tables I and II list d function contributions to the energy (ΔE_d) and optimum exponents (ζ_{Si}, etc.) obtained from calculations of normal valency and hypercoordinate compounds at the MP4 level. For ease of comparison, values obtained at the Hartree–Fock (HF) level[2] for these quantities have been listed along with the contributions calculated at the MP4 level.

Tables I and II invite a number of generalizations. In most cases, the larger the contribution to the Hartree–Fock energy from d functions, the smaller the effect of d functions on correlation energy (ΔCE_d). The ratio of these two quantities ($\Delta CE_d:\Delta E_d$) is small for compounds of second-row elements and declines still further as extra atoms are attached (see values for PF$_3$/PF$_5$, SO$_2$/SO$_3$, and SF$_2$/SF$_4$/SF$_6$ in Table II). Among the 64 compounds sampled in Tables I and II, ΔCE_d is less than ΔE_d in only 11; 10 of these are hypercoordinate compounds and the other is SiO$_2$.

Mean values of the correlation energy CE and the d function contribution to it (ΔCE_d) are also included in Tables I and II. Both were averaged over the total number of valence shell electron pairs (VSEP) and are included in Tables I and II under the headings CE/p and $\Delta CE_d/p$. Most compounds in the sample contain a first- or second-row central atom with several oxygen or fluorine or other first-row atoms arranged around it, and for most of these compounds in the VSEP-averaged values for both the correlation energy and the d function contribution to it are unexpectedly constant.

	CE/p	$\Delta CE_d/p$
mean values ($n = 62$)	0.0525	0.0198
standard deviations	0.0083	0.0032

Most of the variance is due to a number of H-rich compounds ($\Delta CE_d/p$ values rather lower than the mean of 0.020 hartree) and

compounds with peripheral chlorine atoms ($\Delta CE_d/p$ values close to 0.027 hartree, some 30% higher than the mean).[14] The value of $\Delta CE_d/p$ calculated for the C$_2$ molecule is much lower than the mean, a fact to be related to its open-shell character. Interestingly, ΔCE_d for C$_2$ is almost independent of whether the d function is calculated for the $^1\Sigma$ or $^3\Pi$ states (0.057 and 0.058 hartree, respectively) which contrasts with the total correlation energy values (CE is almost 50% greater for the state with all valence electrons paired, as expected). The d function contributions to correlation energy are also the same for the different spin states of CS[5] and Si$_2$.

Supplementation of Minimal Basis Sets. Calculations were carried out on SO$_2$, SO$_3$, SF$_4$, and PF$_3$ using optimized d functions added to the STO-3G functions; the results appear in Table III. As reported earlier,[2] adding d functions to a minimal sp basis leads to a much bigger ΔE_d value than adding them to an extended basis, a result explained by the way in which d functions compensate for the lack of flexibility in the unsupplemented small basis. The d function contribution to correlation wave functions is quite different; either the STO-3G values of ΔCE_d show only a very small increase from the DZ values or, as in the case of SO$_2$, there is no increase at all.

Optimum d Function Exponent Values. As the results in Tables I and II make clear for both HF and MP4 calculations, d function optimum exponent values for any particular element vary in a complicated way between molecules, but it is probably true that there is more variation at the CI level. However, explaining the changes must be done cautiously because the dependence of the energy on exponent is often weak.[2] In addition, using the CI energy to determine the d function exponent variationally will not in general yield the value which is optimum for the correlation correction to the wave function because of the simultaneous d function contribution to the large RHF configuration in the CI wave function. Nevertheless, the changes in optimum d function exponent brought about by introducing correlation are large enough, and occur in sufficiently many molecules to make it clear that the polarizing role of the supplementary functions within the HF wave function is quite different from the correlating role in the CI wave function.

The claim that optimum d function exponent values for CI calculations are lower than exponents optimized in single determinant calculations is hard to substantiate; the behavior is complex and there are important exceptions. The minimum energy exponents for fluorine and oxygen, in particular, are much higher in MP2 and MP4 calculations than at HF level. For these elements the optimum molecular values are close to the values determined at the same level of calculation for the F⁻ and O²⁻ ions:

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(13) ΔCE_d, the d function contribution to the correlation energy, is equally well described as the difference between the extra correlation energy at supplemented and unsupplemented levels: $\Delta CE_d \approx CE(1D/1D) - CE(0D/0D)$ and the two formulas yield the same values.

(14) An attempt to model ΔCE_d for the molecules in the sample as the sum of contributions characteristic of the atoms (X_O, X_F, X_S, etc.) yielded the regression:

$$\Delta CE_d{}^{MP4} = -0.0050 + n_O X_O + n_F X_F + n_S X_S ...$$

($n = 53$; $R^2 = 0.942$; std error in ΔE_d, 0.0191). The atomic contributions obtained from this regression are as follows, with standard errors in parentheses: $X_H = 0.0077$ (0.0023); $X_C = 0.0341$ (0.0059); $X_N = 0.0530$ (0.0069); $X_O = 0.0525$ (0.0040); $X_F = 0.0618$ (0.0029); $X_{Si} = 0.0480$ (0.0083); $X_P = 0.0467$ (0.0072); $X_S = 0.0081$ (0.0081); $X_{Cl} = 0.0922$ (0.0118).

	ζ_d (F)	ζ_d(O)
molecules (HF)	0.5–0.7	0.6–0.7
molecules (MP4)	1.2–1.4	0.9–1.1
ions (MP4)	1.49	0.93

The d Function Contribution to Correlated Wave Functions: H_2, CO, CS, and O_3. Configuration interaction calculations on a number of diatomic molecules are described as a prelude to the investigation of the more complex results on O_3 and SO_2. Even so simple a case as H_2 turns out to be instructive; the major features of the supplementary p function contributions to H_2 recur in all the molecules considered in this report.

(a) The H_2 Molecule. The combined effect on the H_2 energy of adding p functions to the basis set and correlating the wave function is an energy lowering of 0.038 hartree of which 0.012 hartree is the p function contribution. The changes in the wave function which produce these energy changes cannot be identified from the (perturbation theory) MP4 results, so the CID wave function (configuration interaction with all double substitutions) was examined for H_2 at r = 74.1 pm. At the optimum value of the exponent (ζ_p = 0.79), the p function contribution to the total energy is 0.0152 hartree, about two-thirds of the total CID correlation energy.

The excitations considered in the CID calculation of H_2 take place from the $\sigma_g{}^2$ configuration to excited configurations constructed from the nine virtual orbitals obtained with the (2s1p) basis. These orbitals range in energy from 1.0 to 3.8 hartrees. At the restricted Hartree–Fock (HF) level of calculation, the role of the added p functions is to polarize the almost spherical wave function along the axial direction. The axial p function contribution to the HF wave function enhances the amplitude of the $1\sigma_g$ orbital in the region between the nuclei at the expense of the part of the σ_g orbital on the remote sides of the two atoms. Although the total energy is lowered by polarizing the wave function in this way, the $1\sigma_g$ eigenvalue is higher in the supplemented calculation than when no p functions are included, implying that p functions lower the total energy by reducing interelectronic repulsion energy rather than by increasing attractive energy terms. (Although the eigenvalue is not lowered, the effect on total energy is favorable because repulsion energy contributions are counted once in the latter, not twice as in the former.)

Although various kinds of contribution from p functions to the correlated wave function may be identified, the CID wave function includes contributions from a large number of the excitations and no one type of contribution emerges as dominating. However, p functions in the basis set uniquely introduce "angular" correlation, in contrast to the "in–out" and "left–right" correlation allowed when configurations built from s functions are mixed with the ground configuration.[15] p functions are also capable of introducing "left–right" correlation, but radial ("in–out") correlation from p functions is on a very limited scale because there is only one p function set in the calculation reported here.

The size of the ΔE_p contribution to the total correlation energy is explained by the fact that so many of the excited configurations in the CID wave function involve virtual orbitals containing p functions and, in addition, that these virtual orbitals contain p functions almost exclusively. For example, 15 of the 17 excitations which appear in the CID wave function with weights greater than 0.001 terminate in one or more virtual orbitals with very high p function coefficients.

(b) The CO and CS Molecules. CO and CS are valence isoelectronic molecules on which extensive calculations have recently been performed (over a range of internuclear separations) on the contributions of supplementary d functions to the energy.[5] In addition to Moller–Plesset calculations, CID and multiconfiguration SCF calculations were carried out on these two molecules as part of the d function role investigation.

The compounds provide an interesting comparison of first- and second-row elements: the d function energy increment at HF level turns out to be slightly larger for oxygen than for its second-row

analogue, sulfur. As reported elsewhere,[2] this behavior is standard for comparable compounds of the two elements and may be attributed to the higher degree of charge transfer which occurs in the compound containing the more electronegative element. The behavior is reversed at the correlated level.

d and f functions in the Hartree–Fock wave functions of these two molecules play fairly similar roles; supplementary f functions are 10–11% as important as d functions at the HF level and 16–17% as important at MP4 level. The contributions from d functions are not due to any single mechanism, d functions being involved to about the same degree in all five valence shell MOs. One fairly important feature of the supplemented wave functions, especially in CO, is the use of d functions to transfer charge back to carbon, against the general charge drift to oxygen.

In both CO and CS, the general effect of d functions on the HF wave functions is to reduce the amplitude of the wave function in the region between the nuclei. As in H_2 the d function contribution is the result of a decrease in two-electron repulsion terms, not to any increase in a one-electron term resulting from the use of d functions in an explicit bonding role. In carbon monoxide, C–O $d\pi$–$p\pi$ overlap terms have the biggest single effect on the density distribution, returning charge to carbon against the main charge drift to the more electronegative atom. In consequence, the d functions on carbon are slightly more important than the d functions on oxygen. When electron correlation is included, this situation is reversed, the extra functions on oxygen becoming the more important of the two sets. The concentration of charge on oxygen raises the requirement for correlating contributions at this center (presumably by interaction with configurations which allow "in–out" correlation and angular correlation), not only by transferring charge in the direction of the other center ("back-bonding"). Since only one set of d functions was used, the value taken by the optimum exponent reflects the most important of the roles which d functions may adopt on any center, and the rather high optimum value for the oxygen functions (ζ_O = 1.21) suggests that angular correlation of the tightly bound electrons in the vicinity of the electron-rich oxygen is more important than radial correlation or dispersal of amplitude by back-bonding.

Optimized bond distances in CO and CS both show the usual response to the introduction of correlation, the bonds being lengthened by 3–4% in the unsupplemented case. In both molecules and at both HF and correlated levels of calculation, the inclusion of d functions leads to stronger bonding and to shorter optimum bond lengths. In CO the optimum bond length shows a 6-pm reduction at MP2 level, and for CS the reduction is 9 pm. For both molecules the bond shortenings are more than twice as big as the reductions at HF level.

In CO and CS, the CID wave function contains a large number of configurations, and it is the combined effect of all of these, not of a few dominant members, which produces the energy advantage of the correlated wave function. Contributing to the correlated wave function is a considerable number of configurations involving virtual orbitals with strong d function involvement ("d-virtuals"). For the CO case there are 10 virtual orbitals in which the d functions would contribute more than about 75% of the charge distribution. All are high-lying (1.7 $\leq \epsilon_i \leq$ 3.9 hartrees at optimum d function exponent values) and all are highly sensitive to d function exponent (e.g., ϵ_{26} shows a dependence: ϵ_{26} = 3.5 + 2.2ζ_O hartrees).

In the CID wave function of the CO molecule, some 3050 configurations mix with the ground configuration with weights $c_{ij} \geq 10^{-4}$ and 130 with weights $c_{ij} \geq 10^{-2}$. Of the latter, 23 involve excitations to d-virtuals. A high proportion of the excitations to d-virtuals arise from configurations in which the HOMO is doubly filled. There are 101 excitations in this category with weights $c_{ij} \geq 10^{-4}$ and 58 of them terminate in configurations involving at least one "d-virtual". Among these 58 configurations, the d-virtuals on carbon and oxygen are represented in a 11:9 ratio, showing a slight tendency to reduce the charge transfer to the more electronegative atom which occurs in the Hartree–Fock wave function. So far as symmetry around the molecular axis is concerned, the different d-virtuals appear in this group of excited

(15) Shull, H. *J. Chem. Phys.* **1959**, *30*, 1405–1413.

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Table IV. SO_2: Energy Increments due to Correlation (CE) and Basis Set Supplementation $(\Delta E_d)^{a,b}$

level	basis	correlation energy (ΔE_{corr})		supplementation energy (ΔE_d)		ΔCE_d
		sp basis	spd basis	RHF	correlated calcn	
GVB[c]	(1D/0D)	0.099	0.108	0.193	0.203	0.010
GVB[c]	(1D/1D)	0.099	0.110	0.245	0.253	0.008
CID	STO-3G*	0.168	0.218	0.307	0.357	0.050
CID	(1D/1D)	0.296	0.444	0.260	0.335	0.075
MP2	STO-3G*	0.193	0.230	0.307	0.345	0.038
MP2	(1D/1D)	0.359	0.499	0.260	0.399	0.139
MP4	STO-3G*	0.221	0.267	0.307	0.354	0.047
MP4	(1D/0D)	0.372	0.402	0.209	0.239	0.030
MP4	(0D/1D)	0.372	0.466	0.139	0.232	0.093
MP4	(1D/1D)	0.372	0.529	0.260	0.417	0.157
MP4	(2D/1D)	0.372	0.538	0.277	0.442	0.165
MP4	(2D1F/1D)	0.372	0.570	0.291	0.490	0.199

[a] All calculations performed at the experimental geometry. [b] CE signifies "correlation energy" and p is the number of valence shell electron pairs in the molecule; for meanings of other symbols, see text. [c] GVB results from Patterson and Messmer (ref 6).

configurations roughly in the ratio of d_π:d_σ:d_δ = 3:2:1.

Over a d function exponent interval within which the carbon and oxygen atom exponents change from their optimum values by ±15% (ζ_C = 0.7 ± 0.15 and ζ_C = 1.2 ± 0.15), the d function energy contribution, ΔE_d, varies by only about 2%. This is a very small change, given that the corresponding changes in the energies of the d-virtuals themselves are 20–30%. Clearly the energy disadvantage of raising the d exponent in excitations involving d-virtuals (rapidly rising energy) must be offset by a correlation energy advantage from more compact functions, the result being a very shallow energy trough. This behavior suggests that angular correlation replaces radial and longitudinal correlation in importance when d functions are added to the basis set. A similarly high optimum exponent value is found for CI calculations of the O^{2-} ion where angular correlation must be of major importance (see the section on SO_2).

The main conclusion to be drawn from these results is that d functions in the correlated wave functions of CO and CS tend to transfer electronic charge away from the region where it is most strongly concentrated; the substitutions responsible for introducing a "coulomb hole" around each electron achieve this result by involving all 10 d-virtuals, each in a great variety of combinations so as to cover all parts of the orbital space. Without d functions, configuration interaction lengthens the bond, but with the inclusion of d functions electron correlation is achieved with less reliance on virtuals which reduce density between the nuclei. In consequence, the optimized bond length is much lower when d functions are included.

(c) Ozone. O_3 was included in the investigation because it is valence isoelectronic with sulfur dioxide.[16] The addition of d functions to the basis set has a big effect on calculated bond lengths of O_3 for both Hartree–Fock (RHF or UHF) and CI levels of calculation. In this molecule, however, omission of polarization functions from the basis set is not the only reason for the poor agreement between experiment and low level calculations. The correct involvement of the b_1 virtual orbital is mainly what is required in order to model the biradical character of the molecule and reproduce the calculated bond length and other properties. The d functions in the basis set make only a very small contribution to this orbital, so the two effects are easily distinguished.

The inclusion of supplementary d functions in the oxygen basis set decreases the energy of the ground-state configuration by 0.102 hartree, about 15% more than the effect of supplementation on the energy of the ...$a_1{}^2b_1{}^2$ configuration. The optimum d function exponent is 0.88 for the ground configuration (...$a_1{}^2a_2{}^2$) and 0.92 for the configuration with the $a_2{}^2$ to $b_1{}^2$ excitation; the energies

of both are rather insensitive to variation of this parameter, with a rise in energy of only 0.003 hartree for a 10% change in exponent from the optimum value.

Because of the smaller d function contribution to the b_1 molecular orbital, ΔE_d drops by 0.01 hartree when the ...$a_1{}^2b_1{}^2$ configuration is mixed with the ground configuration in a MCSCF calculation. ΔE_d drops a little further when the next higher level of excitation is included, recovering to the level of the ground configuration when excitations from the first three virtual orbitals are included. As for CO and CS, it is only by means of excitations to the higher lying d-virtuals that the d function contribution to the energy is able to rise substantially above the value it takes for the RHF level of calculation.

Analysis of the CID wave function shows again that the major part of the d function contribution results from the large number of excitations involving the high-lying d-virtuals. The weights of these excitations in the CI wave function are small, but they possess high d character and are responsible for the 3-fold increase in ΔE_d from the RHF calculation to MP4 level.

(d) Sulfur Dioxide. (i) Energy Contributions. To judge a hypothesis about the d function role in correlated wave functions it is necessary to know how well the electrons are correlated. Correlation energies, calculated with and without d functions in the basis set, are reported in Table IV for several procedures (MCSCF, CID, MP2, MP4) at minimal and extended basis set levels. Some GVB[17] valence bond results obtained for SO_2 by Patterson and Messmer[18] are also listed.

Supplementation of the Dunning–Hay basis set in SO_2 calculations produces an energy lowering at HF level of ΔE_d = 0.260 hartree. At the MP4 level, ΔE_d = 0.417 hartree, the size of the increase being only a small fraction of the HF value as is typical of hypercoordinate molecules. The effects of correlation (changing the level from RHF to MP4) and supplementation (changing the basis set from [0D/0D] to [1D/1D]), for calculations all conducted at the experimental SO_2 geometry, are:

ΔE_{corr}		ΔE_d	
0D/0D	1D/1D	RHF	MP4
0.370	0.527	0.260	0.417

d functions contribute to the HF wave function in SO_2 in all the valence MOs, but the contribution is large enough in the two upper occupied MOs (a_1, a_2) to depress the orbital energies below the values they take when the basis set is unsupplemented, which is unusual.[2] The d function on sulfur adds a small $d\pi$:$p\pi$ bonding contribution to the generally nonbonding a_2 orbital (the HOMO), but it is large enough to lower the MO energy by almost 0.02 hartree.

(16) In ozone nondynamical correlation is much more important than in most other molecules considered here. It is necessary in consequence of the low-lying ...($b_1{}^2$)($b_1{}^2$) configuration which results from a double excitation to the lowest virtual orbital from the ground configuration ...($b_1{}^2$)($a_2{}^2$). Correlation treatments involving multiple reference states are necessary to deal with the big effect of the ...($b_1{}^2$)($a_1{}^2$) configuration on calculated bond length, vibrational frequencies, and other experimental properties (see: Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Replogle, E. *Chem. Phys. Lett.* **1989**, *158*, 207–212 and references therein).

(17) Bobrowicz, F. W.; Goddard, W. A., III *Methods of Electronic Structure Theory*; Schaefer, H. F., III, Ed.; Plenum: New York, 1977; pp 79–126.

(18) Patterson, C. H.; Messmer, R. P. *J. Am. Chem. Soc.* **1990**, *112*, 4138–4150.
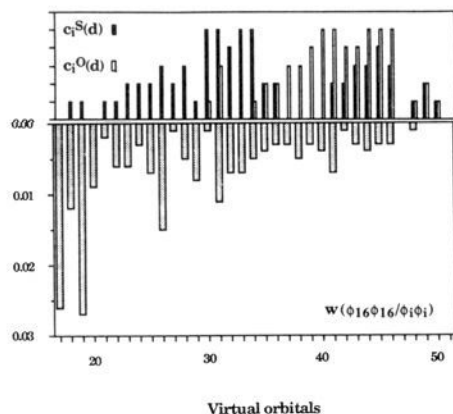
Figure 1. d function contributions [$c_i^S(d)$ and $c_i^O(d)$] from the S and O centers to the virtual orbitals of SO_2 (ϕ_{17} to ϕ_{51}) in contrast to the weights of the ($\alpha\beta/\alpha\beta$)-type ($\phi_{16},\phi_{16}/\phi_i,\phi_i$)] excitations in the CID wave function. The size of the d function contributions to the virtual orbitals (upper diagram) is indicated on an arbitrary 6-point scale.

*Calculation of the energy of SO_2 at correlated levels of cal-*culation shows the molecule to conform to the same pattern as the molecules just considered. In MCSCF calculations in which excitation to one, two, or three virtual orbitals is allowed, the d function contributions to the energy are slightly lower than in the HF case, a result of the fact that there is less d function involvement in the first three virtual orbitals than in the upper occupied MOs from which the excitations chiefly occur. The large d function contribution to correlation energy calculated at MP2 or MP4 level is, once again, a result of excitations to the very high-lying d-virtuals. The pattern of contributions from these configurations is illustrated in Figures 1-3.

(ii) d Function Exponents. The optimum value of the sulfur d function exponent is practically unchanged between HF and correlated levels of calculation (0.76 for HF; 0.72 for MP4), but the oxygen d function exponent changes from 0.57 (HF) to 0.98 (MP4). Similar values for optimum d function exponents were found by Wong et al. for supplementation of other sp basis sets.[19]

As in the previous cases, post-Hartree–Fock calculations are sensitive to the d function exponent because of the presence in the wave function of a large number of excitations involving virtual orbitals with large d function coefficients. The role of d functions in these orbitals (ϕ_{30}–ϕ_{34} for S, ϕ_{37}–ϕ_{46} for O) is quite different from their role as supplementary functions in the occupied HF orbitals (ϕ_{12}–ϕ_{16}) or the lowest virtual orbitals (ϕ_{17}–ϕ_{20}).

(iii) The Correlated Wave Function. Sampling for a rough survey of the importance of sulfur and oxygen d functions in the correlated wave function was carried out by taking the 228 excitations which appear in the CID wave function with coefficients with numerical values of 0.01 or more (mean value, 0.0142 ± 0.007). Of these, 27% involved ϕ_{17}, the lowest virtual, and a further 28% involve one or more of the virtuals ϕ_{18}, ϕ_{19}, and ϕ_{21}; d functions of sulfur and oxygen make no significant contribution to any of these virtual orbitals. The "d-virtuals" (sulfur d function coefficients in the range 0.4–0.9) are involved in 23% of the excitations. So far as excitations to virtual orbitals with major *contributions from oxygen d functions are concerned, only one* appears in the sample but, of course, there are many contributions of this kind for excitations with coefficients below the arbitrary 0.01 level.

The nature of the excitations in the sample is as follows. The lowest virtual ϕ_{17}, the most heavily represented virtual orbital in the CID wave function, is of b_1 symmetry and contains nodes between $p\pi$ orbitals on sulfur and the two oxygen atoms. As such it provides the single most important type of correlation for the $p\pi$ electrons in the molecule; $d\pi$ functions are only involved to a very small extent. The next few virtual orbitals (ϕ_{18}–ϕ_{20}) contain

(19) Wong, M. W.; Gill, P. M. W.; Nobes, R. W.; Radom, L. *J. Phys. Chem.* **1988**, *92*, 4875–4880.

nodes between in-plane s and p orbitals of oxygen and sulfur and their use in the wave function provides longitudinal correlation in the s system of the molecule; d functions are again almost absent. The virtual orbitals from ϕ_{21} to ϕ_{29} also contain nodes *between the inner and outer components of the s and p functions* in the sulfur and oxygen atom basis sets, and their use would lead to a certain amount of radial ("in–out") correlation together with the minor degree of correlation which the small d function contributions to these orbitals make possible.

The d-virtuals ϕ_{30} to ϕ_{34}, to all of which the sulfur d functions make large contributions, are the counterparts of the sulfur d function appearances in the occupied valence shell orbitals. Bonding interactions involving d functions in the canonical orbitals are small, however, because the coefficients are small. As a result, the d functions make correspondingly large contributions to the d-virtuals; they consist almost entirely of d functions on sulfur. The d-virtuals are "atomic" in nature with hardly any antibonding character at all.

The absence of destabilizing interactions in the d-virtuals provides an immediate explanation for the severe shortening of the optimum bond length in SO_2 at correlated levels of calculation produced by adding d functions to the basis set. Although cor-*related calculations invariably lead to the longer bond distances* than in the Hartree–Fock case, and even though d functions account for a major part of the correlation when the basis is supplemented, shorter bond distances are obtained from optimization of MP2, MP4, CID calculations just as they are in RHF optimizations. Results for SO_2 are:

level of calculation	supplementation	optimized r(S–O), pm
RHF	0D/0D	153.4
	1D/1D	141.2
MP2	0D/0D	162.2
	1D/1D	146.8
exptl		143.1

Comparison of CID wave functions calculated with and without d functions in the basis shows that the heavy utilization of the almost purely "atomic" d virtuals greatly reduces the weights of the virtual orbitals in the range ϕ_{17}–ϕ_{30}, thereby reducing the bond lengthening effect of antibonding interactions between s and p functions on the sulfur and oxygen atoms.

(iv) Sensitivity of the Energy to Changes in Geometry. Further clues to the role of the supplementary functions in the correlated wave function of SO_2 were obtained by observing the effects of changing the S–O bond distance and the OSO bond angle; CID level calculations were chosen for this maneuver to facilitate comparison with the readily available CID wave function.

To summarize the results in Table V, consider supplementation of the basis and inclusion of electron correlation (CID level) as two procedures for improving the wave function. At the optimum geometry [r(S–O) = 146.8 pm], the total improvement in energy from the two procedures is: $\Delta E_d + CE(1D/1D) = 0.68$ hartree. This quantity is highly sensitive to changes in the bond length but not bond angle. Shortening the bond length to 125 pm raises the combined energy contributions to 0.81 hartree; increasing the length to 175 pm lowers them by about the same amount, to 0.58 hartree. On the other hand, the arbitrary alteration of the bond angle by $\pm10°$ alters the combined energy contributions by less than 1%.

Inspection of the figures in Table V shows that most of the change in ΔE_d at CID level (or any other level which includes correlation) produced by stretching the bond between 125 and 175 pm is due to the severe drop in ΔE_d^{HF}. The d function contribution to the HF wave function, the biggest term in the CI wave function, is highly sensitive to overlap between d functions on the central atom and s and p functions on the peripheral atoms.

The bond angle variation study on SO_2 (Table V) shows no significant changes in any of the quantities investigated, whether ΔE_d values, d-virtual energies, or coefficients in the correlated wave function for configurations involving d-virtuals. Clearly,

Table V. The Sensitivity of d Supplementation Energies (ΔE_d) and CID Correlation Energies (CE) to Bond Length and Bond Angle Variation: CO, CS, and SO_2 (Energies in Hartrees)[a,b]

			r(C–O) (pm) =		
			100	111.47	125
CO	ΔE_d	RHF	0.092	0.075	0.061
		CID	0.168	0.157	0.143
	CE	(0D/0D)	0.168	0.182	0.197
		(1D/1D)	0.253	0.264	0.279

			r(C–S) (pm) =		
			125	153.4	175
CS	ΔE_d	RHF	0.102	0.066	0.049
		CID	0.195	0.162	0.143
	CE	(0D/0D)	0.131	0.143	0.152
		(1D/1D)	0.224	0.238	0.246

			r(S–O) (pm) =		
			125	146.8	175
SO_2	ΔE_d	RHF	0.426	0.245	0.111
		CID	0.540	0.374	0.252
	CE	(0D/0D)	0.266	0.302	0.330
		(1D/1D)	0.380	0.431	0.472

			∠OSO (deg) =		
			110	119.3	130
SO_2	ΔE_d	RHF	0.222	0.245	0.231
		CID	0.370	0.374	0.379
	ΔE_{corr}	(0D/0D)	0.301	0.302	0.303
		(1D/1D)	0.449	0.431	0.451

[a] Separately optimized d functions were used in the (1D/1D) calculations. For CO, ζ_C = 0.75, 0.0.69, 0.65, ζ_O = 1.31, 1.06, 1.18 at r-(C–O) = 100, 111.47, and 125 pm, respectively; for CS, ζ_C = 0.66, 0.56, 0.55, ζ_S = 0.72, 0.56, 0.50 at r(C–S) = 125, 153.4, and 175 pm, respectively; for SO_2, ζ_S = 0.88, 0.72, 0.58, ζ_O = 0.93, 0.98, 0.82 at r(S–O) = 125, 146.8, and 175 pm, respectively. [b] Bond distances in pm: 1 pm = 10^{-9} m = 10^{-2} Å.

d function contributions are not sensitive to bond angle change in either the HF or correlated wave functions.

(v) d Functions on the Peripheral Atoms. Calculations on SO_2 were extended to include supplementation of sulfur and oxygen atoms separately, viz. the (1D/0D) and (0D/1D) cases. As in the case of RHF energies, d functions from both central and peripheral atoms both make important contributions to MP4 level correlation energies. For SO_2 the contributions to correlation energy from d functions on oxygen appear to be greater than those centered on sulfur (energies in hartrees):

basis	ΔE_d^{HF}	ΔE_d^{MP4}	ΔCE_d
1D/0D	0.209	0.356	0.147
0D/1D	0.139	0.349	0.210
1D/1D	0.260	0.527	0.267

(vi) d Function Contributions to the Density. Conclusions drawn about d function roles may be tested by inspecting electron density distributions calculated with (and without) d function supplementation and with (and without) electron correlation. The d function contributions to the SO_2 electron density distribution arse difficult to visualize in total density maps such as Figure 2a but not in difference density plots. The major features of the molecular electron distribution are well illustrated in sections perpendicular to the OSO plane, and Figures 2 and 3 are confined to this view of the SO_2 electron density calculated at MP2 level.

The contribution from d functions to correlation of the SO_2 wave function cannot be determined from a map of the difference between the supplemented and unsupplemented MP2 density distributions (Figure 2c) because of the large Hartree–Fock component of the MP2 wave function. Nor can it be obtained from the difference between the MP2 and HF densities (calculated from supplemented basis sets as in Figure 3a) because the correlation process affects the sp basis functions as well as the d functions. However, the problem may be solved by applying a correction for the effect of correlation on the unsupplemented wave
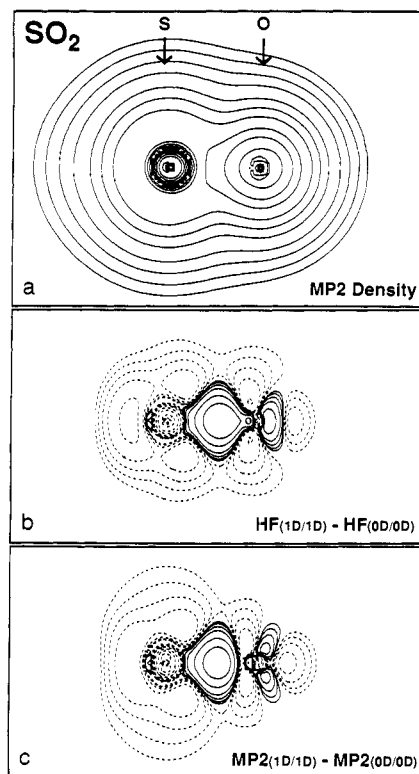
Figure 2. Electron density maps for SO_2 drawn perpendicular to the OSO plane: (a) contour diagram of the density distribution around one SO bond (correlated wave function); (b) density difference diagram, showing the d function contribution to the Hartree–Fock electron density, electronic charge being transferred to the internuclear region at the expense of charge density further out. The effect of d function supplementation on the density calculated from the correlated wave function (MP2) is shown in (c). The similarity of (b) and (c), due to the strong contribution from the HF configuration in the MP2 wave function, obscures the d function contribution to correlation.
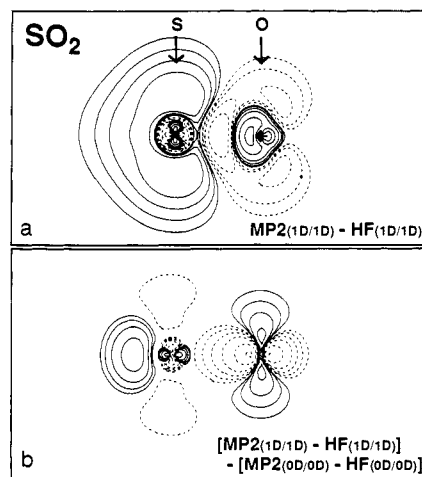
Figure 3. Density difference maps (perpendicular to the OSO plane as in Figure 2) showing the effect of correlation (MP2 level) on the SO_2 wave function. Map (a) displays the transfer of charge from inner to outer areas on S, and in the opposite direction on the O atom, due to correlation (basis sets supplemented by d functions). The d function contribution to correlation is made visible in (b) where the sp correlation contribution is subtracted from overall effect of correlation in (a).

function (Figure 3b) by exactly the same procedure used to obtain the d function contribution to correlation energy (ΔCE_d).[14]

The information in the density difference maps parallels the information contained in population figures. As is well known, calculations with d functions tend to correct for the excessive charge transfer predicted for polar bonds (like the S–O bonds)

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by unsupplemented calculations. For SO_2, the negative charge on the oxygen atoms is still further reduced by correlation. This is shown by the gross atomic charge figures calculated for sulfur and oxygen atoms from (1D/1D) calculations:

level		Hartree–Fock	MP2
q_S	(sp)	14.260	14.635
	(d)	0.376	0.358
q_O	(sp)	8.636	8.456
	(d)	0.046	0.048

The d function role in correlation is not achieved by changing the Hartree–Fock d function density, but by redistributing it—the densities of the individual d functions all change drastically as part of the angular correlation process even though the total d function density is largely unchanged.

(vii) The "Shape" of the d Functions and the Size of the d Set. It is commonly remarked, in connection with calculations of hypercoordinate second-row molecules, that "treatments which include effects of electron correlation require large basis sets, (2d1f) or even larger, to converge equilibrium distances to 1 pm".[20]

Siegbahn and co-workers referred in 1984 to the importance of obtaining the "correct shape" in the d functions added to the sulfur basis as a condition for reproducing experimental quantities in SO_2, SO_3^{2-}, and other similar sulfur compounds.[21] The same question was raised again in a paper on ClF and CCl.[22] "Shape" referred to the profile of a three-member contraction of three sets of d functions optimized for the ^3D state of Cl+ and then reduced to a <3,1,1> contraction by using the "natural orbital" coefficients. Petterson and Siegbahn found that quantitative results presupposed a basis containing at least four d sets, but, ultimately, shape was found to be of only secondary importance.[22] Results from calculations on ClF (a second study[23]), ClO_2,[24] and Cl_2[25] are consistent with this result.

If the conclusion about different d function roles in the single configuration and multiconfiguration wave functions is correct, exponent optimization of a single set of added d functions set on each center for post-Hartree–Fock calculations must produce an exponent value which is a compromise. This is confirmed for MP2 level calculations with two independent sets of d functions on each center (ζ_d^S = 2.3, 0.55; ζ_d^O = 2.0, 0.5). Inspection of the natural orbitals calculated from the MP2 density shows that the coefficients of the two independent d functions on sulfur and on each oxygen in the HF-like orbitals correspond closely to a single d function with the same exponent values as were obtained by optimization at the Hartree–Fock level (ζ_d^S = 0.76; ζ_d^O = 0.57). On the other hand, the sulfur and oxygen d function coefficients in the "d-virtuals", from which the main contribution of d functions to the correlation correction of the wave function are obtained, correspond to a wide range of sizes from ζ_d = 0.5–2.3. Few values of the effective d function exponent at the high end of this range are found for sulfur, but high exponent values (ζ_d^O = 1.0–2.0) dominate the oxygen d function contribution to the non-Hartree–Fock part of the correlated wave function. This observation confirms the contention that d functions play a different role in correlation from the polarizing role in the HF wave function and explain the change in the oxygen atom d exponent optimum from ζ_d^{HF} = 0.57 to ζ_d^{MP2} = 0.98. As for oxygen, a high value for the optimum d function exponent is also found for fluorine in correlated calculations of SF_2, SF_4, and other fluorides (ζ_d^F = 1.35–1.40).

One further result of increasing the number of independent sets of d functions on each center from one to two (to ensure appro-

priate d function shape in each part of the wave function) is a substantial increase in d function populations on all atoms: the values rise from 0.358 to 0.502 (S) and from 0.048 to 0.079 (O).

Discussion

Including electron correlation in a calculation consists of providing each electron in a molecule with a Coulomb hole, which moves with it and which is hard for other electrons to enter, and a Fermi hole, which is completely inviolable.[26] The Fermi hole is created by antisymmetrizing the wave function, the Coulomb hole, by the laborious process of mixing high-energy configurations with the configuration corresponding to the averaged Hartree–Fock potential. Without Coulomb holes, bond distances are underestimated by electronic structure modelling. On the other hand, in the absence of sufficiently flexible basis functions to respond to the molecular potential in the bonding region, bond distances are overestimated.

Correlation of the bonding electrons in a molecule is introduced by mixing configurations obtained by excitation to nonbonding and antibonding orbitals, which readily accounts for the fact that CI methodology corrects the excessively small calculated bond lengths obtained from geometry optimization at the Hartree–Fock level.[1] For molecules with very electronegative atoms and high coordination, proper correlation of the heavy electron density in some parts of the molecule is difficult to model, and the experimental bond lengths are hard to reproduce. In dealing with the special problems of molecules like ClF, CCl, SO_2, ClO_2, etc., workers have emphasized the importance of including d functions (and higher functions) in the basis and using methods which provide angular correlation and density transfer away from regions of heavy one-center density by back-bonding.[22-25] Distinct from these types of correlation but also important are radial correlation (provided by including additional, less compact, s and p functions on each center) and longitudinal correlation, introduced when the correlated wave function includes excitations from MOs containing bonding contributions to virtual orbitals with the corresponding antibonding contributions.[27]

The bond length variation results here reflect the size of the correlation energy component due to d supplementation and how much less bond-length-dependent it is than the d function contribution to RHF energy. The CO, CS, and SO_2 results all show that d functions from all centers contribute to the correlated wave function largely through the high-lying "d-virtuals"; they do so fairly uniformly across all five functions on each center. The interaction between d functions and functions on other centers in the "d-virtuals" is extremely limited; they act mainly as single-center functions. Because of this, the response of the SO_2 d function correlation energy contribution to severe bond length changes (e.g., 125–175 pm) is very mild; there is hardly any change in the coefficients for excitations involving sulfur d-virtuals (energy range 0.8–1.0 hartree). By contrast, the same changes in bond length produce profound changes in the coefficients for excitations involving the lower-lying virtual orbitals (0.0–0.8 hartree) which are characterized by antibonding interactions between s and p functions across the S–O bonds. The coefficients for excitations involving oxygen "d-virtuals" (which lie at still higher energies: 2.4–3.3 hartrees) are smaller than those for the sulfur d-virtuals, but their response to bond length variation is similarly small. Similar conclusions follow from the bond length variation results on CO and CS.

Analysis of the d function energy contributions is pertinent to the generalization about d function role in the correlated wave function. Regression on the ΔCE_d values calculated for the sample yields d function contributions characteristic of each atom. The values[14] for second- and third-row atoms rise strongly from left to right of the periodic table, a result readily explained in terms of increasing demand for electron correlation around increasingly

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(27) Radial and longitudinal correlations lie in the "dynamical" category. "Non-dynamical" correlation refers to the mixing of low-lying configurations with the ground configuration in molecules like ozone.

dense electron clouds. (The observation that supplementation of peripheral O or F atoms has a bigger effect on correlation energy than adding d functions to the central atoms corroborates this conclusion.) The apparent "atom-centered" character of the d function contribution to correlated wave functions is very difficult to harmonize with any suggestion of hypervalent bonding in compounds like SO_3 or PF_5 and is in marked contrast to the "overlap" contribution at the Hartree–Fock level.[28]

Interestingly, there is a similarity in the behavior of added d functions in F, Cl, O, and S atoms in the 64 molecules of the sample and in the individual ions F^-, Cl^-, O^2, and S^{2-}. These are the elements with electronic environments in molecules most closely resembling the closed-shell ions, and the optimum d function exponents for the anions are almost the same in MP4 wave functions calculated for the ions as in the F-, Cl-, and O-containing molecules. By contrast, the other elements represented in the sample approach the closed-shell anion distribution far less closely when bound in molecules, and it is not surprising that the optimum d function exponent values for S, P, N, Si, C, etc., in molecules differ more strongly from the values for the anions P^{3-}, N^{3-}, etc.[29] The d function energy contributions for these atoms obtained from the molecular data by regression (X_i) are lower than those calculated for the ions (ΔCE_d), presumably because the charge attributable to them in the molecules is less than it is in the ions, but the trend is similar.

ion	ΔCE_d	ζ_d	X_i
H^-	0.019	0.19	0.008
F^-	0.072	1.49	0.062
O^{2-}	0.064	0.93	0.053
Cl^-	0.104	0.58	0.092
S^{2-}	0.089	0.31	0.066

Strong support for the conclusions about the dual role for d functions in the correlated wave function is provided by the density calculations and exhibited in the difference maps and the population figures. Figures 2 and 3 show how well the Hartree–Fock d function contribution is retained in the MP2 wave function. They also show the contrast between the bonding role at Hartree–Fock level and the correlating role, the latter visualized only after a correction is made in the MP2 difference map for the effect of the former. The resulting d function contribution to the correlation correction is also seen to be strongest in the inner parts of the valence shell. As expected, angular correlation is most important in that part of the molecule where the density is greatest and around atoms with the largest charges. Combined with the population data, the density difference maps show that the effect of correlating the wave function is a redistribution of electron density among the different d functions rather than a transfer between the d and sp parts of the density. Figure 3b shows that the use of Hartree–Fock d function density to enhance S–O bonding is somewhat reduced at MP2 level, other d functions being populated in the angular correlation process.

Angular correlation has recently been invoked to explain the results of valence bond calculations of hypercoordinate molecules.[6] Patterson and Messmer (PM) suggest that d functions provide for a type of hybridization which enables additional electron pairs

to be pointed separately away from that center and form "additional bonds beyond that permitted by the octet rule". The feature is not found in H_2S where, they say, there is no requirement for accommodating additional electron pairs.

Patterson and Messmer's GVB conclusions on SO_2 are hard to reconcile with the results from the calculations reported here. As Table IV shows, the GVB approach recovers only 7% of the d function contributions to the SO_2 correlation energy obtained by MP4 calculation at the same basis set level so there is a risk that the results, although conveniently referred to a single VB wave function, are not sustainable at higher levels of calculation.[30] It is clear that d functions in the non-Hartree–Fock part of the MP4 wave function are correlating functions, not hybridizing functions as at the Hartree–Fock level; excitations involving the "d-virtuals" (where almost all of the d function contributions originate) provide no bonding. Secondly, d function correlation energy contributions, when calculated per valence shell electron pair, either remain constant or decrease with increasing degree of coordination (e.g., PF_3, PF_5; SO_2, SO_3; SF_2, SF_4, SF_6). These results are quite consistent with the idea of the separation of individual electron trajectories achievable by angular correlation using d functions, but they immediately rule out the violation of the octet rule in some cases and not in others. The "atomic" character of the d function contribution to correlation also excludes a hypervalence interpretation. A final difficulty with the idea that d functions make a major contribution to valence is the observation that, in three molecules examined (C_2, Si_2, and CS), the d function contribution to correlation energy is unaffected by whether the π electrons are paired or unpaired, whereas the total correlation energy is highly sensitive to change of spin state.

In connection with the suggestions by PM about the need to accommodate extra electron pairs around the central atom in hypercoordinate molecules, there is the strong evidence from the HF wave functions[3,4] that the bonds in such molecules are strongly ionic and that the "extra" electron pairs are arranged around the peripheral atoms, not the supposedly hypervalent central atoms; this situation is not significantly changed by the introduction of correlation.[31] It is worth noticing that the conclusion drawn from valence bond studies by Maclagan about ClF_3, also allegedly hypervalent, is that d functions have a polarization role only.[32] On the other hand, PM's conclusions about the importance of angular correlation and the transferrability of bond type between molecules are strongly supported by the MP4 results reported here.

Conclusion

The results of CI calculations on a large sample of molecules of main group elements have been interpreted to indicate that the d function polarizing role in the Hartree–Fock part of the wave function is supplemented by a correlating role, mainly angular correlation, in multiconfiguration wave functions. The former is concentrated in the overlap regions, and the latter is largely monocentric; neither corresponds to the bonding role postulated for d orbitals in supposedly hypervalent molecules. d functions thus provide angular correlation in the same way that it is provided in hydrides by supplementary p functions and for the d orbitals of transition metal compounds by f functions.[33] Unexpectedly, the correlation energy per valence shell electron pair and the d function contribution to it are both remarkably constant for molecules as different as H_2O, H_2S, HCHO, SO_3, ClF_3, and POF_3.

This conclusion is based on the following generalizations.

(a) The role of supplementary d functions at the Hartree–Fock level is preserved in the correlated wave functions, the HF con-

(28) Support for this d function role in the Hartree–Fock wave function comes from the fact that regression analysis of the Hartree–Fock d function energy contributions in Tables 1 and 1I shows that $\Delta E_d{}^{HF}$ is well represented as a sum of contributions characteristic of the bonds (X_{SO}, X_{SF}, X_{SN}, etc.) in the molecules:

$$\Delta E_d{}^{HF} = -0.0045 + n_{SO}X_{SO} + n_{SF}X_{SF} + ...$$

($n = 52$; $R^2 = 0.9914$; std error in ΔE_d, 0.0154). An attempt to model ΔE_d as a sum of contributions from atoms is not successful ($n = 53$; $R^2 = 0.7955$; std error in ΔE_d, 0.0445).

(29) The H^- ion is an example; as expected for the much more diffuse electron cloud in the anion, the optimum p function exponent is only 0.2, in contrast to values in the range 0.8 ± 0.2 for H_2 and the first- and second-row hydrides. On the other hand, the H^- localized electron pair benefits more strongly from p function supplementation (0.019 hartree) than does a pair of covalently bound H atoms (e.g., 0.012 hartree for H_2).

(30) The electron correlation missing from GVB wave functions is mainly that required in connection with the ionic terms (Goodgame, M. M.; Goddard, W. A. *Phys. Rev. Lett.* **1985**, *54*, 661–664), and it is to this component that d functions make such large contributions in correlated wave functions, particularly in the case of O and F compounds with important ionic structures.

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figuration being generally the dominant configuration. The HF contribution is concentrated between the nuclei and is bonding in nature.

(b) The optimum d function exponents are quite different at the two levels, sometimes lower and sometimes higher (especially high values for oxygen and fluorine). Because of the dual role, supplementation by a single set of d functions per center often results in a compromise between two demands. The optimum d function exponents at CI level are generally close to the values for the closed-shell ions (e.g., O in SiO_2 and F in SF_2 as in O^{2-} and F^-).

(c) The high-lying virtual orbitals ("d-virtuals") which provide the major contributions of d functions to wave functions at higher levels of correlation (MP4, CISD, etc.) do not contain the stabilizing d function contributions which characterize HF wave functions or MCSCF calculations involving the first few virtual MOs.

(d) d function contributions to correlation energy are unaffected by artificial changes in bond angle.

(e) The bond length dependence of d function energy contributions to correlation energy is quite different from the behavior at HF level.

(f) Supplementary function contributions to correlation energy (ΔCE_d) vary in inverse proportion to the size of the energy contributions at HF level; the greater the hypercoordination, the smaller the relative size of ΔCE_d.

(g) In contrast to the energy contributions of d functions at the HF level, readily modelled by regression analysis as fixed contributions from all of the bonds of each type present in the molecule, the contributions to the correlating configurations are characteristic of the atoms involved.

(h) The characteristic d function energy contributions for molecules (calculated per valence shell electron pair) are close to the values calculated for the same atoms in the closed-shell ionic state (F^-, O^{2-}, etc.).

(i) The d function role in the correlated wave function is largely independent of the sp basis set level; d functions in the correlation correction do not compensate for the inadequacy of the sp basis as in minimal basis set HF calculations.

(j) Supplementary functions on peripheral atoms (O in SO_2, F in SF_6) appear to contribute more to the correlation energy than functions on central atoms, a finding consistent with the heavier concentration of electrons on these atoms and the consequent need for effective angular correlation. The effects are strongest in the inner parts of the valence shell where damage from the independent particle approximation is most severe.

(k) d function contributions to correlation energy are insensitive to change of spin state (in C_2, Si_2, and CS, at least) which is manifestly not true of the total correlation energy in such cases.

(l) The contribution of d functions to the correlating configurations of a CI wave function is made through a large number of small contributions from many excitations in which all the members of any set of higher order functions on each center are involved; it is largely "atomic" in nature.

Ab Initio Study of Structures and Stabilities of Substituted Lead Compounds. Why Is Inorganic Lead Chemistry Dominated by Pb^{II} but Organolead Chemistry by Pb^{IV}?

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Abstract: The influence of electronegative substituents on the structures and relative stabilities of lead(IV) versus lead(II) species has been assessed by ab initio pseudopotential computations for a series of halogenated lead hydrides and methyllead compounds R_nPbX_{4-n} (R = H, CH_3; X = F, Cl; n = 0–4) and R_nPbX_{2-n} (n = 0–2). The calculated energies of various model reactions reveal the drastic degree of destabilization of tetravalent lead compounds by electronegative substituents X (X = F, Cl). The bond angles in compounds with different groups, R_nPbX_{4-n} (n = 1–3), deviate widely from 109.5°. In agreement with Bent's rule, the angles between the most electronegative substituents (F or Cl) are smaller, while those between more electropositive groups (H, CH_3, SiH_3) are considerably larger than tetrahedral. The deformations computed for R_2PbX_2 and R_3PbX are related to those observed experimentally in various organolead and organotin structures. The destabilization of the tetravalent species by relativistic effects is larger when electronegative substituents are present. There also are large relativistic effects on bond angles (up to ca. 14°). All Pb–R and Pb–X bonds shorten upon successive substitution by electronegative groups; i.e., the weakening of the bonds is accompanied by a decrease of their lengths! A simple bonding model is proposed to explain both the thermodynamic and the structural observations: The increase of the positive metal charge upon halogen substitution results in greater contraction of the 6s-orbitals than the 6p-orbitals. Hence, the 6p-orbitals are less effective in sp^n hybridization, and electronegatively substituted Pb^{IV} compounds are destabilized. While the traditional term "inert pair effect" implies the energetic unavailability of a 6s-pair of electrons for bonding, the proposed concept emphasizes the size differences between s- and p-orbitals. This supports Kutzelnigg's analysis of the bonding in compounds of the heavy main group elements. A novel type of hyperconjugation, "geminal $\sigma PbH \rightarrow \sigma^*(PbH, PbF)$ hyperconjugation" also influences the relative stabilities of substituted lead(IV) compounds.

I. Introduction

Most of inorganic lead chemistry, e.g., the halides, oxides etc., is derived from Pb^{II}. In contrast, the inorganic Pb^{IV} compounds often are either unknown, are unstable transient species, or are highly reactive. The well-characterized inorganic Pb^{IV} species are strong oxidizing agents (e.g., PbO_2, $Pb(OAc)_4$).[1,2a] On the