ergetic) theories, these orbital following and preceding become so much the more important. These orbital following and preceding seem to have a general importance in that they should appear in every chemical phenomena including the changes in nuclear configurations. Actually, the generality can be proved directly from the Hellmann–Feynman theorem.[21b] Since the orbital following and preceding act respectively to restrain and to promote the movement of nuclear configurations, the former will occur in the movement from stable configurations[58] and the latter will occur as one of the driving forces of the movement. These points will be studied more fully in the succeeding articles.[21]

For the internal rotation about the single bond, the calculation on ethane due to Goodisman[35a] showed that the Hellmann–Feynman force cannot always give good qualitative values, if an approximate wave function is used. However, we believe that the conceptual picture is another thing and can be obtained from the ESF theory, since the basic Hellmann–Feynman theorem is exact for exact wave functions. From this standpoint, the relative importance of the three factors is very interesting and will be examined more fully in another article.

(58) For the methyl radical, the orbital following which occurs when the radical is distorted from planar structure (ref 30b, 31, and 32), causes the EC force on the proton which acts to restore the radical to planar structure. The function is parallel with that of the EC force on the carbon discussed previously.[1]

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Molecular Properties of the Triatomic Difluorides BeF_2, BF_2, CF_2, NF_2, and OF_2

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Abstract: Nonempirical self-consistent-field calculations have been carried out for the electronic ground states of BeF_2, BF_2, CF_2, NF_2, and OF_2. A contracted gaussian basis set of double ζ plus polarization quality was employed. For each molecule the following molecular properties were computed: dipole moment, quadrupole moment, octupole moment, second and third moments of the electronic charge distribution, diamagnetic susceptibility, diamagnetic shielding, and electric field gradient. In addition the electronic structures are discussed in terms of orbital energies and population analyses. For OF_2 comparison is made with experiment. The calculated and experimental values are μ = 0.45 D (0.30), $\theta_{xx} = 0.61 \times 10^{-26}$ esu cm^2 (2.1 ± 1.1), $\theta_{yy} = -0.41$ (−1.6 ± 1.4), $Q_{xx} = 7.2 \times 10^{-16}$ cm^2 (6.9), Q_{yy} = 25.1 (25.2), Q_{zz} = 3.1 (3.0), $\chi_{xx}{}^d = -119.4 \times 10^{-6}$ erg/(G^{2}mol) (−119.7), $\chi_{yy}{}^d$ = −43.5 (−42.0), and $\chi_{zz}{}^d$ = −136.9 (−136.2). The agreement is generally seen to be quite good, and it is hoped that the predicted but experimentally undetermined properties for the other molecules are equally reliable.

Perhaps the simplest and yet the most powerful intuitive device available to the chemist is the periodic table. A simple knowledge of trends expected to arise from moving up or down (or to the left or right) along the periodic table allows sensible predictions of the properties of a vast number of molecules which may be difficult to observe in the laboratory. Further, to better train his intuition, the chemist will frequently carry out experiments on a group of molecules in which a particular atom is substituted by neighboring atoms in the periodic table. Thus, ascertaining the exact nature of the differences between, for example, CH_3F, CH_3Cl, CH_3Br, and CH_3I, is a matter of enduring scientific interest.

The theoretical chemist would also like to study the electronic structure of periodically related groups of molecules. And, this can be done now if semiempirical methods are used.[2a] Furthermore, with the rapid development[2b] of new theoretical and computational methods, it seems likely that systematic *ab initio* studies of entire series of molecules will become commonplace during the next 10 years. It should be pointed out that Pople and coworkers[3] have already adopted a boldly systematic *ab initio* approach to the electronic structure of organic compounds. In the present paper we make a small step toward a systematic *ab initio* understanding of periodic properties. We report a self-consistent-field study of the first-row difluorides, BeF_2, BF_2, CF_2, NF_2, and OF_2. All five of these molecules have been observed in the laboratory[4–8]

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Table I. Geometries of AF_2 Molecules Considered[a]

	BeF_2	BF_2	CF_2	NF_2	OF_2
R(AF), Å	1.43	1.30	1.30	1.37	1.41
θ, deg	180	120	104.9	104	103.3
Coordinates of F atoms, B					
x	0.0	1.22832	1.49653	1.59390	1.65206
y	±2.702	±2.12753	±1.94820	±2.04010	±2.08812
z	0.0	0.0	0.0	0.0	0.0

[a] The coordinates (x, y, z) of the central atom A are always taken to be (0, 0, 0).

and the series should display properties related to the increased electronegativity accompanying movement from Be to O across the first row. To conclude our introduction, we note that *ab initio* calculations (using smaller basis sets) have been carried out previously for each of the molecules BeF_2,[9] BF_2,[10] CF_2,[11,12] NF_2,[10,13] and OF_2.[14-16]

Details of the Calculations

All calculations reported here were performed using the MOLE quantum chemistry system, which has been described elsewhere.[17] The ISD Univac 1108 computer was used.

The geometries chosen are seen in Table I and those for BeF_2,[18] CF_2,[6] NF_2,[19] and OF_2[20] were taken from experiment. The geometry of BF_2 was guessed on the basis of the planarity of BF_3 and several experimental B–F bond distances. Since this project was begun, Thomson[10] has completed a series of *ab initio* calculations from which he was able to predict the geometry of BF_2. Thomson's prediction, R(B–F) = 1.38 Å, θ = 118°, is in reasonable agreement with our guessed geometry, R(B–F) = 1.3 Å, θ = 120°.

The basis sets adopted were analogous to those used in our previous study[21] of NO_2 and O_3. For the B, C, N, O, and F atoms, Huzinaga's (9s 5p) primitive gaussian basis sets[22] were contracted to (4s 2p) following Dunning.[23] In addition, a set of d-like functions (xx, yy, zz, xy, xz, yz) was centered on each atom. The orbital exponents α chosen were 0.5 (Be), 0.6 (B), 0.75 (C), 0.8 (N), 0.8 (O), and 0.9 (F).

Although the 2p orbital is not occupied in the electronic ground state of the beryllium atom, p functions are expected to play a significant role in molecules containing Be. The optimum 2p Slater function for Be should have an orbital exponent ζ nearly equal to the optimum 2s value,[24] ζ = 0.956. Therefore, we made a least-squares fit of two gaussians to a 2p Slater function with ζ = 0.956. These two primitive gaussians (α = 0.509, 0.118) were then used uncontracted in the BeF_2 calculations.

Although the above choice of Be 2p functions is a reasonable one, it is clear that the Be 2p basis is not analogous to that used for B, C, N, and O. It would be quite easy to construct a set of five primitive p functions for Be. In fact, Kaufman, Sachs, and Geller[25] have obtained just such a basis by extrapolation of Huzinaga's results for the higher first-row atoms. However, Kaufman, *et al.*, used this 5p basis uncontracted, whereas in our calculations on BF_2 through OF_2 we have contracted the 5p sets to 2p following Dunning.[23] The most sensible procedure for finding the contraction coefficients would be an SCF calculation on either the ^3P or ^1P states corresponding to the $1s_2$ 2s 2p electron configuration of the Be atom. However, it is well known[26] that the 2p orbitals obtained from the ^3P and ^1P calculations are very different, the ^1P orbital being much more diffuse. Because of the ambiguities involved in the contraction of the 2p functions, we chose to employ the basis functions described in the previous paragraph.

The atomic SCF energies obtained with the above basis sets differ from the true Hartree–Fock energies by from 0.0027 hartree (boron) to 0.016 hartree (fluorine). A further barrier[2b] to obtaining the true moleculer Hartree–Fock energy is the fact that this basis contains only a single set of 3d functions on each atom and no 4f (or higher l valued) functions. We conclude that the difference between our calculated SCF energy and the Hartree–Fock energy will be greatest for OF_2 but should not be greater than ~0.08 hartree. Dunning[23,27] has made careful studies of the dependence of computed molecular properties on basis set. From his work, it would appear that molecular properties computed using the type of basis adopted herein will usually be within 10% of the Hartree–Fock properties. One of the worst experiences recorded[27] with similar basis sets was for the quadrupole moment of N_2, calculated to be 1.25 au, compared with the near Hartree–Fock value of 0.95 au.

Energetics and Population Analyses

The SCF energies and dipole moments computed with and without polarization functions[2b] (d functions in this case) are given in Table II. For BeF_2 through OF_2 the lowering of the total energy by the addition

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Table II. Total Energies (hartrees) and Dipole Moments (au) Computed in the SCF Approximation with and without d Functions

Molecule	E(4s 2p)	E(4s 2p 1d)	μ(4s 2p)	μ(4s, 2p 1d)
BeF_2	−213.6953	−213.7351	0.0	0.0
BF_2	−223.5860	−223.6744	−0.414	−0.270
CF_2	−236.6281	−236.7207	+0.021	+0.126
NF_2	−253.1484	−253.2235	−0.297	−0.222
OF_2	−273.4690	−273.5294	−0.190	−0.178

Table III. Energy Quantities (in hartrees) from SCF Calculations with a (9s 5p 1d/4s 2p 1d) Contracted Gaussian Basis

	BeF_2	BF_2	CF_2	NF_2	OF_2
Total energy	−213.7351	−223.6744	−236.7252	−253.2235	−273.5294
Potential energy	−427.2064	−447.3216	−473.3359	−506.2191	−546.7960
One-electron potential	−595.7032	−645.5970	−693.8325	−741.2198	−80.6020
Two-electron potential	126.8610	142.6041	155.7457	165.2053	180.3285
Nuclear repulsion	41.6358	55.6713	64.7509	68.5208	73.4775
Kinetic energy	213.4713	223.6472	236.6107	252.9956	273.2665
$-V/T$	2.00124	2.00012	2.00048	2.00090	2.00096
Orbital energies					
$1a_1$	−26.2657	−26.3316	−26.3743	−26.3734	−26.3993
$2a_1$	−4.7486	−7.7556	−11.4683	−15.8207	−20.8207
$3a_1$	−1.5439	−1.6678	−1.7510	−1.7291	−1.7505
$4a_1$	−0.6791	−0.8382	−0.9635	−1.0825	−1.2853
$5a_1$	−0.6392	−0.7355	−0.7996	−0.7892	−0.7999
$6a_1$		−0.4241	−0.4757	−0.5944	−0.6532
$1a_2$	−0.6205	−0.6777	−0.6995	−0.7020	−0.7218
$1b_1$	−0.6392	−0.7326	−0.7792	−0.7683	−0.8181
$2b_1$				−0.5772	−0.5821
$1b_2$	−26.2657	−26.3316	−26.3743	−26.3734	−26.3993
$2b_2$	−1.5489	−1.6365	−1.6675	−1.6388	−1.6340
$3b_2$	−0.6836	−0.7816	−0.8267	−0.8007	−0.7968
$4b_2$	−0.6206	−0.6704	−0.6856	−0.6710	−0.6783

of d functions is 0.0398, 0.0884, 0.0926, 0.0751, and 0.0604 hartree. Therefore, the d functions are most important for CF_2 by this criterion. This result is a bit surprising in light of our intuitive feeling that d functions centered on nitrogen should be somewhat more important. We note also in Table II that none of the dipole moments are changed too dramatically by the addition of polarization functions to the basis. In all cases the dipole moment becomes greater (*i.e.*, the fluorine atoms become less "negative"), the change being the largest (0.144 au = 0.37 D) for BF_2.

Various components of the total SCF energies, as well as the orbital energies, are seen in Table III. The virial ratio $-V/T$, which is exactly 2.0 for a true Hartree–Fock wave function at its equilibrium geometry, is calculated to be nearly 2 in each case. Surprisingly, the virial is best satisfied for BF_2, the only molecule for which it was necessary to guess the equilibrium geometry.

The $1a_2$ and $4b_2$ orbital energies of BeF_2 differ by 0.0001 hartree due to roundoff error. In actuality, of course, these are degenerate components of the $1\pi_g$ orbital.

For all five molecules, the order of the four highest (in terms of orbital energy) molecular orbitals is the same: $1a_2$, $4b_2$, $6a_1$, and $2b_1$. For BeF_2, BF_2, CF_2, and NF_2 the $1b_1$ orbital is the fifth highest. However, for OF_2 the $1b_1$ is seventh highest while the $3b_2$ orbital is the fifth highest lying.

Of particular interest are the inner shell orbital energies, which are accessible to X-ray photoelectron spectroscopy.[28] It is important to emphasize, however, that Koopmans' theorem, which relates orbital energy to ionization potential, is somewhat ambiguous[2b] for the open shell $^2A_1$ and $^2B_1$ ground states of BF_2 and NF_2. Note that the $1a_1$ orbital is essentially $1s(F_a) + 1s(F_b)$, the $2a_1$ orbital is the central atom (Be, B, C, N, or O) 1s orbital, while the $1b_2$ orbital is roughly $1s(F_a) + 1s(F_b)$. Of particular interest here is the relationship between inner shell orbital energies and "atomic charges." The higher a particular 1s orbital energy is, the more negative charge is thought to reside on the corresponding atom. Using this criterion, inspection of the $1a_1$ orbital energies suggests that the F atoms have the most negative charge in BeF_2. This is no surprise, of course, since the classical description of BeF_2 is $F^-\ Be^{2+}\ F^-$. BF_2 is the next most ionic, while CF_2 and NF_2 are about equally so and OF_2 is the least ionic. Note that the $1b_2$ orbital energies are identical with the $1a_1$ ϵ values.

Table IV. Population Analyses from SCF Wave Functions for AF_2 Molecules

	BeF_2	BF_2	CF_2	NF_2	OF_2
Total atomic populations					
A	2.95	4.60	5.64	6.56	7.77
F	9.53	9.20	9.18	9.22	9.12
d orbital populations					
A	0.189	0.197	0.157	0.115	0.097
F	0.019	0.070	0.057	0.037	0.033

A more direct, but necessarily arbitrary, picture of atomic charges is the Mulliken population analysis.[29] Although the results of a single population analysis should not be taken too literally, the trend over a group of related molecules should be meaningful. As Table IV shows, the calculated Mulliken populations are con-

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Table V. Calculated and Experimental (in parentheses) Molecular Properties for BeF_2 through OF_2[a]

	BeF_2	BF_2	CF_2	NF_2	OF_2
Dissociation energy, eV	10.24 (13.1[k])	9.83 (13.1[b])	6.91 (10.7[c])	1.16 (6.1[e])	−1.52 (3.97[f])
Ionization potential, eV	16.88 (14.7[k])	11.54 (9.5[b])	12.94 (11.9[d])	15.71 (12.0[e])	15.84 (13.7[g])
Dipole moment, D	0.0 (0.0)	−0.686	+0.321 (0.46[h])	−0.564	−0.452 (0.297[i])
Second moments (10^{-16} cm^2) of the electronic charge distribution					
Q_{xx}	2.57	4.88	6.37	6.74	7.19 (6.9[j])
Q_{yy}	41.57	26.54	22.53	24.34	25.08 (25.2[j])
Q_{zz}	2.57	2.85	2.88	2.99	3.07 (3.0[j])
Quadrupole moment tensor, 10^{-26} esu					
θ_{xx}	5.29	0.31	−1.94	0.10	0.61 (2.1 ± 1.1[j])
θ_{yy}	−10.58	−3.30	−0.89	−1.38	−0.41 (−1.6 ± 1.4[j])
θ_{zz}	5.29	2.99	2.83	1.28	−0.19 (−0.5 ± 1.9[j])
Third moments (10^{-24} cm^3) of the electronic charge distribution					
R_{zzz}	0.0	2.24	3.02	2.26	0.34
R_{zyy}	0.0	−2.49	−3.32	−4.63	0.13
R_{zzz}	0.0	0.31	0.29	0.20	0.16
Octupole moment tensor, 10^{-34} esu					
Ω_{zzz}	0.0	2.65	4.41	1.59	−0.50
Ω_{zyy}	0.0	−1.08	−2.06	−1.18	0.04
Ω_{zzz}	0.0	−1.57	−2.35	−0.51	0.46
Diamagnetic susceptibility tensor, 10^{-6} erg/(G^2 mol)					
$\chi_{xx}{}^{d}$	187.27	124.68	107.83	115.94	119.40 (119.7[j])
$\chi_{yy}{}^{d}$	21.81	32.81	39.27	41.29	43.53 (42.0[j])
$\chi_{zz}{}^{d}$	187.27	133.30	122.62	131.86	136.90 (136.2[j])
$\chi_{av}{}^{d}$	132.12	96.93	89.91	96.36	99.95 (99.3[j])
Potential at nucleus, au					
ϕ(A)	−8.350	−11.271	−14.522	−18.132	−22.099
ϕ(F)	−26.613	−26.550	−26.511	−26.514	−26.492
Electric field at nucleus, au					
E_z(A)	0.0 (0.0)	−0.010 (0.0)	−0.105 (0.0)	−0.126 (0.0)	−0.131 (0.0)
E_z(F)	0.0 (0.0)	0.048 (0.0)	0.061 (0.0)	0.061 (0.0)	0.058 (0.0)
E_y(F)	0.069 (0.0)	0.087 (0.0)	0.089 (0.0)	0.082 (0.0)	0.076 (0.0)
Force at nucleus, au					
F_z(A)	0.0	−0.09	−0.63	−0.88	−1.05
F_z(F)	0.0	0.43	0.55	0.55	0.53
F_y(F)	0.28	0.78	0.80	0.74	0.69
Diamagnetic shielding tensor ppm					
$\sigma_{xx}{}^{d}$ (A)	−159.2	−305.8	−408.6	−462.0	−522.8
$\sigma_{yy}{}^{d}$(A)	−481.1	−469.8	−483.9	−530.0	−586.0
$\sigma_{zz}{}^{d}$(A)	−159.2	−214.7	−270.9	−343.8	−427.9
$\sigma_{av}{}^{d}$(A)	−266.5	−330.1	−387.8	−445.3	−512.3
$\sigma_{xx}{}^{d}$(F)	−483.0	−505.3	−523.1	−526.8	−531.7
$\sigma_{yy}{}^{d}$(F)	−618.6	−643.5	−654.7	−656.5	−661.8
$\sigma_{zz}{}^{d}$(F)	−483.0	−485.9	−486.9	−490.0	−491.9
$\sigma_{zy}{}^{d}$(F)	0.0	−27.1	−37.9	−44.4	−51.8
σ_{av}(F)	−528.2	−544.9	−554.9	−557.8	−561.8
Electric field gradient at nucleus, au					
q_{xx}(A)	−0.081	0.238	0.993	0.240	−1.548
q_{yy}(A)	0.162	0.120	−0.116	−1.258	−3.447
q_{zz}(A)	−0.081	−0.358	−0.877	1.018	4.995
q_{xx}(F)	0.340	0.433	0.455	−0.004	−0.351
q_{yy}(F)	−0.678	−0.678	−0.785	−1.820	−2.645
q_{zz}(F)	0.339	0.246	0.329	1.824	2.997
q_{zy}(F)	0.000	−1.109	−2.024	−2.897	−3.897
Other expectation values in atomic units					
$\langle 1/r_A \rangle$	15.01	18.60	21.85	25.08	28.86
$\langle 1/r_F \rangle$	29.76	30.70	31.26	31.42	31.65
$\langle r^2 \rangle$, cm	166.82	122.39	113.52	121.67	126.20
δ ($r - r_A$)	32.99	67.26	120.54	195.67	296.57
δ ($r - r_F$)	425.61	425.66	425.93	426.21	426.55

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sistent with the $1a_1$ orbital energies except for BF_2. The population analysis predicts the F atoms in BF_2 to have about the same charge (−0.2 electron) as in CF_2 and NF_2. On the contrary the 1s orbital energies predict BF_2 to be significantly more ionic than either CF_2 or NF_2. In such cases of conflict, we are inclined[30] to favor the orbital energies as being a more faithful indicator of the electronic structure.

Also given in Table IV are the d orbital populations for each molecule. Here the populations give a somewhat different picture than the energy differences of Table II. We see that the d functions on boron are predicted to be the most important, followed surprisingly by Be, and then by C. Note the small d function population on fluorine in all cases. This should not, in itself, be taken to indicate that d functions on F atoms are unimportant. A large factor is simply the terminal position of the F atoms in all five molecules. For example, in ozone (O_3) we found[21] the central O atom to have a d function population of 0.150 electron, while the terminal atoms each had a corresponding population of only 0.047 electron.

Finally we note that the Be 2p functions, unoccupied in the electronic ground state of the atom, take on a population of 0.542 electron in BeF_2. The referee has suggested that the surprisingly large d orbital population on Be may be due to the use of the smaller set of primitive Be 2p functions. It is true of course that the use of a larger 2p basis on Be would tend to diminish the importance of the Be 3d functions. In this regard, we point out the referee's feeling that the Be 2p population of 0.542 electron is smaller than would be the case using a more complete basis. It may be helpful to note that the σ and π contributions to the Be p function population are 0.297 and 0.245. Finally, the Be d function population in BeF_2 breaks down into σ and π contributions of 0.128 and 0.062.

Molecular Properties

The remainder of the calculated molecular properties are seen in Table V. The calculated dissociation (to A + F + F) energies are all less than experiment, as is the case with SCF calculations.[2b] The differences between calculated and experimental dissociation energies increase monotonically from 2.9 eV for BeF_2 to 5.5 eV for OF_2. The SCF ionization potentials obtained using Koopmans' theorem are all too large, the errors ranging from 1.0 eV (CF_2) to 3.7 eV (NF_2).

The absolute values of the dipole moments of CF_2 and OF_2 have been determined experimentally. If we assume that the signs computed here are correct ($^-CF^+$ for CF_2 and $^+OF^-$ for OF_2) then the calculated dipole moment of CF_2 is 0.14 D too small and that of OF_2 is 0.155 D too small. The similarity of these differences is striking. However, the biggest surprise concerning the dipole moments is the polarity of that for CF_2, which does not appear consistent with the simple notion that F is far more electronegative than C. However, there are known exceptions (for example, CO[31] and CH_3SiH_3[32]) to this simple notion, and it is clear that the sign of a dipole moment cannot always be established using electronegativity arguments.

Most of the other calculated properties are true predictions; *i.e.*, they have not been measured experimentally. The only exceptions are those properties of OF_2 determined by Pochan, Stone, and Flygare[33] using the molecular Zeeman effect. The calculated and experimental second moments, quadrupole moments, and diamagnetic susceptibilities agree well. In fact, for the second moments and diamagnetic susceptibility the agreement is striking. For the quadrupole moment, only the *xx* component falls outside the experimental error bars. The main conclusion drawn from both the theoretical and experimental values is that the quadrupole moment is small. Parenthetically, of the five molecules only BeF_2 has a large quadrupole moment.

One property particularly worthy of discussion is the potential at each fluorine nucleus. Basch[34] and Schwartz[35] have argued that the calculated potential is directly related to inner shell ionization potentials and hence to "atomic charges." And in fact, the calculated potentials in Table V are completely consistent with the $1a_1$ and $1b_2$ orbital energies of Table III. In fact, both yardsticks suggest that the F atom in CF_2 is very slightly *less* negatively charged than in NF_2. The simplest arguments assume that C is less electronegative than N and hence the F in CF_2 should be the more negatively charged. Nevertheless, we should emphasize that calculated orbital energies and potentials are much more consistent with electronegativity arguments than are dipole moments.

Almost all the calculated properties in Table V show some periodic trend. The simplest and perhaps expected trend is a monotonic increase or decrease in calculated property from BeF_2 through OF_2. The following properties reflect this type of uniformity: Q_{xx}, Q_{zz}, θ_{zz}, R_{zzz}, χ_{yy}^d, $\phi(A)$, $E_z(A)$, $F_z(A)$, $\sigma_{xx}^d(A)$, $\sigma_{zz}^d(A)$, $\sigma_{av}^d(A)$, the entire tensor $\sigma^d(F)$, $q_{yy}(A)$, $q_{yy}(F)$, and $q_{zy}(F)$. For $E_z(A)$ and $F_z(A)$, both of which should be identically zero for true Hartree–Fock wave functions at equilibrium, this monotonic behavior is probably due to our basis set being progressively somewhat less complete as we go from Be to O.

Another type of periodic behavior seen almost as frequently in Table V is characterized by the calculated property reaching a maximum or minimum value for CF_2. That is, if the property is plotted *vs.* the atomic number, a near parabola is found. Properties displaying this behavior are: Q_{yy}, θ_{xx}, R_{zzz}, all elements of the octupole moment tensor, χ_{xx}^d, χ_{zz}^d, χ_{av}^d, $E_z(F)$, $E_y(F)$, $F_y(F)$, $q_{xx}(A)$, $q_{zz}(A)$, and $q_{xx}(F)$. These properties suggest that BeF_2, BF_2, and CF_2 are smoothly related, and that OF_2, NF_2, and CF_2 provide another monotonic series, but that the two progressions collide in some sense at CF_2. Except for BeF_2, the calculated dipole moments show this same behavior.

R_{zyy} decreases in a very orderly manner from BeF_2 to NF_2, but then lurches upward at OF_2. $\sigma_{yy}^d(A)$ has a maximum for BF_2, and $q_{zz}(F)$ a minimum for BF_2.

Only θ_{yy} and $\phi(F)$ fail to show a clearcut periodic

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behavior. However, $\phi(F)$ almost has a monotonic behavior, the calculated value for NF_2 being 0.003 au too small. The same problem occurs for θ_{yy}, with only the calculated NF_2 value preventing a monotonic increase across the series.

In summary, then, most of the theoretical properties follow one of two patterns: (a) a monotonic increase or decrease across the series or (b) a potential curve-like behavior with maximum or minimum at CF_2. The simplest understanding of these two patterns may be in the fact that the electron distribution may appear to behave differently, depending on the expectation value through which we observe it. For example, inspection of the $\langle 1/r_A \rangle$ values in Table V implies that the average distance of electrons from nucleus A decreases monotonically across the series. This behavior might be interpreted to imply that the "size" of the molecules decreases monotonically from BeF_2 to OF_2. Thus, the $\langle 1/r_A \rangle$ description of the electron distribution is consistent with properties of type a above. However, the calculated values of $\langle r^2 \rangle$ with respect to the center of mass show a different pattern, in which the molecular "size" decreases from BeF_2 to CF_2, but then *increases* at NF_2 and again at OF_2. We see that this picture of the electron distribution is harmonious with those properties following pattern b described above. We conclude that a major factor in determining the two patterns of periodic behavior for BeF_2 through OF_2 is the ambiguity involved in the concept of molecular size.

Electronic Structure of SiH_5^- and Model Studies of Inter- and Intramolecular Exchange in Pentacoordinate Silicon Species. An *ab Initio* Investigation[1]

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Abstract: The reaction $SiH_4 + H^- \rightarrow SiH_5^-$ is investigated by employing *ab initio* quantum chemical techniques. With respect to silane and a hydride ion, a trigonal-bipyramidal form of SiH_5^- is found to be stable by 16.9 kcal/mol and a tetragonal-pyramidal form by 14.0 kcal/mol. The attack of hydride ion on silane is found to proceed with the hydride ion approaching a face of the tetrahedron of silane with an activation energy of 8.6 kcal/mol. In addition, a model derived from SiH_5^- is employed to discuss conformational equilibria in $SiH_{5-n}X_n$ species, where X corresponds to a strongly electronegative substituent. It is found that the axial positions of the trigonal bipyramid are energetically preferred sites for the electronegative substituents and that the preferred mechanism for Berry pseudorotation proceeds *via* a tetragonal-pyramidal intermediate with an electropositive substituent in the apical position.

Pentacoordinate silicon intermediates have been postulated for nucleophilic displacement reactions occurring at silicon and conformational changes in the intermediate have been invoked to explain the stereochemistry of such reactions.[3] Stable pentacoordinate silicon species have been observed in the vapor[4] and solution phases[5] and the conformational changes have been studied in the latter case.[6]

In order to investigate further these processes, there was performed a series of both semiempirical CNDO[7] and *ab initio* LCBF-MO-SCF (Hartree–Fock) calculations on the model system SiH_5^-, considering both the formation of the intermediate, *i.e.*, the reaction

$$SiH_4 + H^- \longrightarrow SiH_5^-$$

as well as intramolecular rearrangement processes in the intermediate itself. In addition, similar calculations were performed on a series of model compounds derived from SiH_5^- in order to investigate the energetics of inter- and intramolecular exchange processes in pentacoordinate silicon species.

Computational Techniques

The CNDO technique was utilized to determine the geometry of the various conformers of the intermediate as well as that of the SiH_5^- systems at various positions along the reaction paths considered. This was done for reasons of economy, but it is expected that the resulting geometries are reasonable.[8] In order to investigate the energetics of the system, a series of *ab initio* calculations utilizing a fairly large basis of gaussian lobe functions,[9] including functions of d symmetry on silicon, was performed. The Si basis employed is the 12s, 9p set of Veillard,[10] using the (6 3 1 1 1 1/6 1 1 1) contraction of Rothenberg, *et al.*,[11] to which d functions of exponent

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