potentials and hence the contribution of proton tunneling to mutation rates.

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Effect of Electron Correlation on Theoretical Equilibrium Geometries

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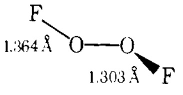
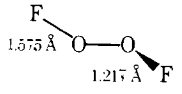
Abstract: Theoretical HF/6-31G* (Hartree–Fock, 6-31G* basis set) and MP2/6-31G* (second-order Møller–Plesset, 6-31G* basis set) equilibrium geometries have been obtained for a set of one- and two-heavy-atom molecules containing only first-row elements and for which experimental structural data are available. Geometrical parameters from the MP2/6-31G* calculations, which treat effects of electron correlation explicitly, are generally in better agreement with the experimental data than are those derived from the corresponding single-determinant wave functions. This is particularly true for bonds involving highly electronegative atoms (e.g., O and F), which generally are too short at the Hartree–Fock limit. Here the correlation corrections result in significant bond lengthening; the MP2/6-31G* values for single bond lengths are in good accord with experimental values. However, MP2/6-31G* lengths of multiple linkages are generally overestimated. The 6-31G* polarization basis set appears to be among the simplest representations suitable for use in molecular orbital calculations which take partial account of electron correlation.

Introduction

Hartree–Fock theory has proven to be remarkably successful in the calculation of the equilibrium structures of small molecules.[2a] Basis sets as simple as STO-3G generally yield bond lengths to within a few hundredths of an ångstrom of the experimental values, and bond angles to within a few degrees. The level of agreement of theoretical equilibrium geometries with experiment increases with the basis set size. Nevertheless, with very large basis sets the theoretical geometries for some very simple molecules are seriously in error. For example, the best single determinant calculations yet performed[2b] on the fluorine molecule yield a bond length 0.1 Å shorter than the experimental value. Worse yet, the near Hartree–Fock equilibrium bond lengths for the fluorine hydroperoxide molecule are very different from the experimental values. Partial consideration



Hartree–Fock



experimental

Table I. Theoretical and Experimental Structures of One- and Two-Heavy-Atom Molecules[a]

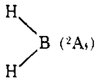
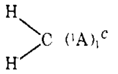
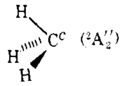
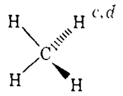
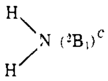
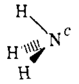
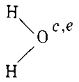
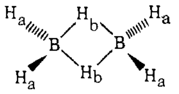
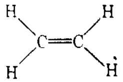
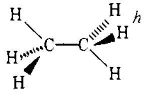
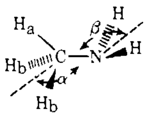
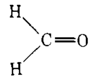
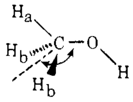
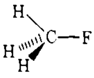
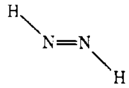
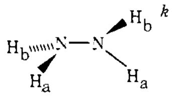
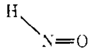
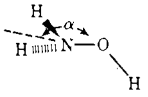
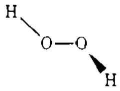
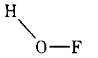
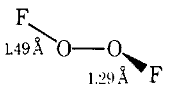
molecule	point group	geometrical parameter	HF/6-31G*	MP2/6-31G*	expt.[b]
H-H	$D_{\infty h}$	r(HH)	0.730	0.738	0.741
Li-H	$C_{\infty v}$	r(LiH)	1.636	1.640	1.595
Be-H	$C_{\infty v}$	r(BeH)	1.383	1.385	1.343
B-H	$C_{\infty v}$	r(BH)	1.225	1.233	1.230
 $(^2A_1)$	C_{2v}	r(BH)	1.185	1.188	1.181
		∠(HBH)	126.6	127.6	131
C-H[c]	$C_{\infty v}$	r(CH)	1.108	1.120	1.120
 $(^1A_1)$[c]	C_{2v}	r(CH)	1.096	1.109	1.111
		∠(HCH)	103.0	102.1	102.4
$(^3B_1)$[c]	C_{2v}	r(CH)	1.071	1.077	1.078
		∠(HCH)	130.8	131.6	136
 [c] $(^2A_2'')$	D_{3h}	r(CH)	1.073	1.079	1.079
 [c,d]	T_d	r(CH)	1.084	1.090	1.086
N-H $(^3\Sigma^-)$[c]	$C_{\infty v}$	r(NH)	1.024	1.039	1.045
 $(^2B_1)$[c]	C_{2v}	r(NH)	1.013	1.028	1.024
		∠(HNH)	104.3	103.3	103.4
$(^2A_1)$[c]	C_{2v}	r(NH)	0.988	0.999	0.976
		∠(HNH)	141.8	142.6	144
 [c]	C_{3v}	r(NH)	1.002	1.017	1.012
		∠(HNH)	107.2	106.4	106.7
O-H[c]	$C_{\infty v}$	r(OH)	0.958	0.979	0.971
 [c,e]	C_{2v}	r(OH)	0.947	0.969	0.959
		∠(HOH)	105.5	104.0	103.9
F-H[c]	$C_{\infty v}$	r(FH)	0.911	0.934	0.917
Li-Li	$D_{\infty h}$	r(LiLi)	2.807	2.772	2.67
Li-O-H[f]	$C_{\infty v}$	r(LiO)	1.592	1.594	1.582
		r(OH)	0.938	0.960	
Li-F	$C_{\infty v}$	r(LiF)	1.566	1.570	1.564
	D_{2h}	r(BB)	1.778	1.753	1.763
		r(BH$_a$)	1.185	1.191	1.201
		r(BH$_b$)	1.315	1.310	1.320
		∠(H$_a$BH$_a$)	122.1	121.8	121.0
HC≡CH	$D_{\infty h}$	r(CC)	1.185	1.217	1.203
		r(CH)	1.057	1.063	1.061
	D_{2h}	r(CC)	1.317	1.335	1.339
		r(CH)	1.076	1.085	1.085
		∠(HCH)	116.4	116.5	117.8
 [h]	D_{3d}	r(CC)	1.527	1.527	1.526
		r(CH)	1.086	1.094	1.088
		∠(HCH)	107.7	107.7	107.4
HC≡N	$C_{\infty v}$	r(CN)	1.132	1.178	1.153
		r(CH)	1.059	1.069	1.065
HN≡C[g]	$C_{\infty v}$	r(NC)	1.154	1.187	1.165
		r(NH)	0.985	1.002	0.994
	C_s	r(CN)	1.453	1.465	1.471
		r(CH$_a$)	1.091	1.101	1.099
		r(CH$_b$)	1.084	1.093	1.099
		r(NH)	1.001	1.018	1.010
		∠(NCH$_a$)	114.8	115.5	114.6
		∠(α)	123.8	123.1	123.6
		∠(H$_b$CH$_b$)	107.4	107.5	108.0
		∠(β)	126.3	123.8	125.7
		∠(HNH)	106.8	106.1	107.1
$^-$C≡O$^+$	$C_{\infty v}$	r(CO)	1.114	1.152	1.128
	C_{2v}	r(CO)	1.184	1.220	1.208
		r(CH)	1.092	1.104	1.116
		∠(HCH)	115.7	115.6	116.5
 [i]	C_s	r(CO)	1.399	1.423	1.421
		r(CH$_a$)	1.081	1.090	1.093
		r(CH$_b$)	1.087	1.097	1.093
		r(OH)	0.946	0.970	0.963
		∠(OCH$_a$)	107.2	106.4	107.0

Table I. (*Continued*)

molecule	point group	geometrical parameter	HF/6-31G*	MP2/6-31G*	expt.[b]
		$\angle(\alpha)$	130.1	130.8	129.8
		$\angle(\mathrm{H_bCH_b})$	108.6	108.9	108.5
		$\angle(\mathrm{COH})$	109.5	107.4	108.0
 [j]	C_{3v}	$r(\mathrm{CF})$	1.364	1.392	1.383
		$r(\mathrm{CH})$	1.082	1.093	1.100
		$\angle(\mathrm{HCH})$	109.8	109.7	110.6
N≡N	$D_{\infty h}$	$r(\mathrm{NN})$	1.078	1.133	1.098
	C_{2h}	$r(\mathrm{NN})$	1.215	1.267	1.252
		$r(\mathrm{NH})$	1.014	1.036	1.028
		$\angle(\mathrm{NNH})$	107.4	105.4	106.9
 [k]	C_2	$r(\mathrm{NN})$	1.414	1.440	1.447
		$r(\mathrm{NH_a})$	0.999	1.016	1.008
		$r(\mathrm{NH_b})$	1.002	1.021	1.008
		$\angle(\mathrm{NNH_a})$	107.9	106.3	109.2
		$\angle(\mathrm{NNH_b})$	112.2	111.4	109.2
		$\angle(\mathrm{H_aNH_b})$	108.2	106.9	113.3
		$\omega(\mathrm{H_aNNH_b})$	90.6	90.7	88.9
	C_s	$r(\mathrm{NO})$	1.174	1.238	1.212
		$r(\mathrm{NH})$	1.031	1.058	1.063
		$\angle(\mathrm{ONH})$	108.8	107.4	108.6
	C_s	$r(\mathrm{NO})$	1.404	1.453	1.453
		$r(\mathrm{NH})$	1.002	1.021	1.016
		$r(\mathrm{OH})$	0.946	0.971	0.962
		$\angle(\alpha)$	115.2	111.4	112.7
		$\angle(\mathrm{HNH})$	106.6	105.2	107.1
		$\angle(\mathrm{NOH})$	104.1	101.2	101.4
O=O	$D_{\infty h}$	$r(\mathrm{OO})$	1.168	1.245	1.207
	C_2	$r(\mathrm{OO})$	1.393	1.467	1.475
		$r(\mathrm{OH})$	0.949	0.976	0.950
		$\angle(\mathrm{OOH})$	102.2	98.7	94.8
		$\omega(\mathrm{HOOH})$	115.2	121.3	120.
	C_s	$r(\mathrm{OF})$	1.375	1.444	1.442
		$r(\mathrm{OH})$	0.952	0.979	0.964
		$\angle(\mathrm{HOF})$	99.8	97.2	97.2
F-F	$D_{\infty h}$	$r(\mathrm{FF})$	1.345	1.424	1.417

[a] Theoretical data from present work except where otherwise noted. [b] Except where otherwise noted experimental data for diatomic molecules from S. Boucier, "Tables of Constants and Numerical Data", Vol. 17, "Spectroscopic Data Relative to Diatomic Molecules", Pergamon Press, Elmsford, N.Y., 1970, or from G. Herzberg, "Spectra of Diatomic Molecules", Van Nostrand-Reinhold, Princeton, N.J., 1970. For polyatomic molecules: J. H. Callomon, E. Hirota, K. Kuchitsu, W. J. Lafferty, A. G. Maki, and C. S. Pote in Landolt-Bornstein, "Numerical Data and Function Relationships in Science and Technology", Vol. 7, New Series, "Structure Data on Free Polyatomic Molecules", K. H. Hellwege, Ed., Springer-Verlag, West Berlin, 1976. [c] HF/6-31G* values from ref 8. [d] Experimental r_e reported by A. G. Robiette at the Seventh Austin Symposium on Gas Phase Molecular Structure, University of Texas, Austin, Texas, 1978. [e] Experimental equilibrium structure from R. L. Cook, F. C. De Lucia, and P. Helminger, *J. Mol. Spectrosc.*, **53**, 62 (1974). [f] Estimate of LiO bond length from M. W. Chase, J. L. Curnutt, A. T. Hu, H. Prophet, A. N. Stuerud, and L. C. Walker, *J. Phys. Chem. Ref. Data*, **3**, 311 (1974). [g] Experimental equilibrium structure from G. L. Blackman, R. D. Brown, and P. D. Godfrey, and H. I. Gunn, *Nature (London)*, **261**, 395 (1976); E. F. Pearson, R. A. Creswell, M. Winnewisser, and G. Winnewisser, *Z. Naturforsch. A*, **31**, 1394 (1976). [h] L. S. Bartell, S. Fitzwater, and W. J. Hehre, *J. Chem. Phys.*, **63**, 4750 (1975). [i] Experimental structure from M. C. L. Gerry, R. M. Lees, and G. Winnewisser, *J. Mol. Spectrosc.*, **61**, 231 (1976). [j] Experimental structure from N. W. Clark and F. C. De Lucia, *J. Mol. Struct.*, **32**, 29 (1976). [k] Experimental structure from S. Tsunekawa, *J. Phys. Soc. Jpn.*, **41**, 2077 (1976).

of correlation effects via configuration interaction results in considerable improvement in the calculated geometry, although the theoretical OF bond length is still seriously in error.[3] It appears, therefore, that, while the geometrical structures of many molecules are accurately described within the Hartree-Fock framework, correlation effects may in some instances play a major role.[4]



Hartree–Fock + configuration interaction

The results of a systematic study of the role of electron correlation on molecular geometry were recently presented by Ditchfield and Seidman.[5] These authors reported theoretical equilibrium geometries for AH$_n$ molecules obtained from single determinant wave functions corrected for correlation between electrons of opposite spin by Møller-Plesset perturbation theory terminated at second order.[6] Their work employed the 6-31G* polarization basis set.[7] The results of Ditchfield and Seidman clearly show that the correlation correction lengthens AH bonds, leading in most cases to improved agreement with experiment. These authors also observed that calculated Hartree-Fock bond angles in the AH$_n$ systems changed only slightly as a result of the inclusion of electron correlation.

The theoretical results presented in this paper extend the study of Ditchfield and Seidman to molecules of known geometrical structure containing two first-row heavy (nonhydrogen) atoms. In addition we have extended their selection of AH$_n$ species to the known hydrides of lithium, beryllium, and boron. Our purpose, like theirs, has been to assess the effect of correlation on theoretical equilibrium geometries.

Theoretical Models

Two theoretical models have been employed. The first,

Table II. Mean Absolute Deviations of Theoretical Structures from Experimental Values

structural type	number of comparisons	mean deviation[b] HF/6-31G*	mean deviation[b] MP2/6-31G*
One-Heavy-Atom Systems			
AH bond lengths	17	0.013	0.011
HAH bond angles	7	2.2	1.4
Two-Heavy-Atom Systems			
AH bond lengths	23	0.011	0.008
AB bond lengths	23	0.036	0.017
HAH bond angles[a]	11	1.0	1.4
HAH bond angles[a]	13	1.8	1.4

[a] As listed in Table I. [b] Lengths in Å, angles in degrees.

termed HF/6-31G*, is standard single determinant molecular orbital theory using the 6-31G* polarization basis set.[7] Spin-restricted theory (RHF) is used for singlet states and spin-unrestricted theory (UHF) elsewhere. Previous studies on small molecules have suggested that theoretical equilibrium geometries obtained with the 6-31G* basis set are quite close to limiting Hartree-Fock values.[8] The second model, designated MP2/6-31G*, allows for partial account of electron correlation effects according to the perturbation method of Møller and Plesset terminated at second order.[6] Computational details have been presented elsewhere.[6b] This Møller-Plesset scheme requires a partial transformation of two-electron integrals to the molecular orbital basis. Although this computational step adds only a small fraction to the cost of the calculations for the smaller molecules dealt with in this paper, it becomes more significant computationally for the larger systems. Our MP2/6-31G* results for AH_n systems differ slightly from those of Ditchfield and Seidman.[5] This is because in our work the molecular orbitals which are primarily associated with inner-shell electrons have not been included in the calculation of the correlation energy. Such an approximation, termed the *frozen-core approximation*, significantly reduces the computational labor associated with the two-electron integral transformation, the time-consuming step in the post-Hartree-Fock procedure at this level. Comparison of the results presented in this work with those of Ditchfield and Seidman[5] shows that this approximation raises the total molecular energy by several millihartrees for AH_n systems. However, the comparison also shows that changes in equilibrium geometries are negligibly small. These results are consistent with the notion that correlation energy contributions associated with inner-shell electrons are practically independent of molecular environment.

Structure optimizations have been carried out using the Fletcher-Powell method.[9] Reported values represent convergence to ±0.001 Å for bond lengths and 0.1° for bond angles. All calculations have been performed using either the GAUSSIAN 77/UCI program[10] on a Harris Corp. Slash 6 digital computer or the GAUSSIAN 78/CMU program[11] on a Digital Equipment Corp. Vax 11/780 digital computer.

Results and Discussion

Theoretical HF-6-31G* and MP2/6-31G* structural data are presented in Table I. Energies corresponding to the optimized structures will be published elsewhere.[12] Table II compiles mean absolute deviations of the theoretical geometric parameters from experimental values. Hartree-Fock structures for many of the one-heavy-atom hydrides have previously been reported;[8] HF/6-31G* and MP2/6-31G* structures for only a few of the remaining systems have appeared in the literature.

As the data in Table I attest, geometrical parameters calculated within the single-determinant framework with the 6-31G* basis set are, for the most part, in good accord with the corresponding experimental quantities. In particular, AH bond lengths in the one-heavy-atom hydrides are well described at the HF/6-31G* level, the mean absolute deviation of theory from experiment being 0.013 Å for 17 comparisons. The largest deviations occur for LiH and BeH, where the theory overestimates the experimental bond distances by 0.041 and 0.040 Å, respectively. HAH bond angles in these systems are also reasonably well described at this level. All of these trends for AH_n systems have previously been noted.[8] Observe, however, that the structures of some very simple two-heavy-atom molecules are poorly described even with as flexible a representation as 6-31G*. In particular, the HF/6-31G* FF bond length in the fluorine molecule is 0.072 Å shorter than the experimental value. Similarly, the theory seriously underestimates the OO bond length in hydrogen peroxide by 0.082 Å and the NN, NO, and OF bond distances in hydrazine, hydroxylamine, and hypofluorous acid by 0.033, 0.049, and 0.067 Å, respectively. Smaller but significant errors also appear in calculated multiple bond lengths: again the theoretical bond distances are too short, the largest deviations occurring for linkages involving two strongly electronegative atoms (e.g., the double bonds in *trans*-diazene, nitroxyl, and oxygen are too short by 0.037, 0.038, and 0.039 Å, respectively). The bond length in the weakly bonded Li_2 molecule is seriously overestimated by the HF/6-31G* calculation (by 0.14 Å), although the LiO and LiF linkages in lithium hydroxide and lithium fluoride are well described at this level. Overall the mean absolute deviation between calculated and experimental AB bond distances is 0.036 Å for 23 comparisons.

HAB and HAH bond angles in the two-heavy-atom systems are generally well described at the HF/6-31G* level in contrast to the performance of the single determinant theory with smaller basis sets. This behavior parallels that previously noted for HAH bond angles in the AH_n systems.

Theoretical equilibrium structures calculated at the MP2/6-31G* level generally agree better with experiment than those obtained from the corresponding Hartree-Fock wave functions. Improvements in AH bond lengths in the one-heavy-atom systems have already been noted.[5] At the MP2/6-31G* level the mean absolute deviation of the theory from experiment is only 0.011 Å (17 comparisons). The diatomic hydrides of lithium and beryllium are poorly described at both theoretical levels. HAH bond angles in the AH_n systems are affected very little by the consideration of electron correlation. The mean absolute deviation of the calculations is reduced slightly from 2.2° (HF/6-31G*) to 1.4 (MP2/6-31G*).

It is in the two-heavy-atom systems that the correlation corrections have the greater effect. Overall the mean absolute deviation between MP2/6-31G* and experimental AB bond lengths is 0.017 Å (23 comparisons), compared with a mean standard deviation of 0.036 Å for the same set of bonds at the HF/6-31G* level. Of particular note is that bond lengths involving two electronegative atoms are now well described. For example, the linkage in F_2 is now only 0.007 Å from its experimental value compared with a deviation of 0.072 Å at the HF/6-31G* level. Both lengths in hydrogen peroxide and hypofluorous acid are also well described at the MP2/6-31G* level, deviations being 0.008 and 0.002 Å. The N-O bond length in hydroxylamine is now in exact agreement with experiment. The Hartree-Fock structures for doubly bonded systems are also systematically improved by the perturbative treatment of electron correlation. The N=N and N=O bonds in *trans*-diazene and nitroxyl, respectively, underestimated by the HF/6-31G* calculations by 0.037 and 0.038 Å, are now in better agreement with experimental values, although the bond-length deviations here are still significant. In all cases examined, the MP2/6-31G* calculations overestimate the lengths of multiple bonds. The errors are greatest for linkages containing strongly electronegative atoms and larger for triple bonds than for double bonds. The bond length in the nitrogen molecule is overestimated by 0.035 Å; the bond length in O_2 is too long by 0.038 Å. Bond-length deviations in hydrogen cyanide, hydrogen isocyanide, and carbon monoxide are 0.025, 0.024, and 0.024 Å, respectively. The MP2/6-31G* calculations do somewhat better than the corresponding Hartree-Fock method in describing the linkages in the weakly bound Li_2 molecule, although its length is still overestimated by 0.1 Å.

HAH and HAB bond angles change little in going from the HF/6-31G* to MP2/6-31G* calculations, consistent with previous observation on one-heavy-atom systems.[5]

The equilibrium structures of many of the molecules in Table 1 have earlier been obtained at the HF/STO-3G and HF/4-31G levels.[1,12] Both sets of present results are superior, insofar as the majority of systems are concerned. A limited number of structure optimizations have also been carried out at the MP2/STO-3G and MP2/4-31G levels. For both of these basis sets the Møller-Plesset correlation correction leads to an overall deterioration of the purely Hartree-Fock structural results. The worst deviations here are extreme and are for molecules with multiple bonds. For example, the HF/STO-3G and MP2/STO-3G bond lengths for N_2 are 1.134 and 1.228 Å, respectively, to be compared with an experimental value of 1.098 Å; the corresponding HF/4-31G and MP2/4-31G bond distances are 1.085 and 1.150 Å, respectively. It has been noted, however, that Møller-Plesset expansions terminated at third order, instead of to second order as described here, result in some improvement in multiple bond lengths at the 6-31G* level. Such theoretical treatments of correlation are more difficult computationally that the second-order method and at present are not yet widely applicable to molecules of moderate size.

In concluding this section, it should be noted that some of the deviation between theoretical and experimental parameters is attributable to experimental uncertainty. The theoretical equilibrium geometries refer to minima on the potential surface (r_e, θ_e values). Experimental values of r_e and θ_e have to be derived from observations on vibrating molecules using data on anharmonicities and other molecular properties which may be incompletely known. For the diatomics, these corrections should be reliable and most of the deviation between the final two columns of Table 1 is no doubt due to inadequate theory. For some of the polyatomics, however, vibrational corrections have only been applied approximately or not at all; the extent of experimental uncertainty is variable and not easy to assess. Another point to note is that some of the experimental results have been obtained under the assumption that certain bonds have equal lengths even though this is not required by symmetry. For example, the structure determination quoted for methanol made no attempt to distinguish between inequivalent CH lengths in the methyl group; theory predicts considerable differences (Table I). Such limitations of experimental analysis also contribute to calculated mean deviations.

Conclusion

The following general conclusions derive from our present work and are worthy of special mention:

1. Hartree-Fock equilibrium geometries obtained with the 6-31G* polarization basis set are generally in good accord with experimental values. The most notable exceptions occur for bonds involving two electronegative atoms where the theory significantly underestimates the experimental distances.

2. Calculations using the MP2/6-31G* model reproduce experimental structural data more accurately than the corresponding Hartree-Fock computations. For example, the mean absolute deviation between experimental and theoretical AB bond lengths for the 23 two-heavy-atom molecules dealt with in this paper is 0.017 Å at the MP2/6-31G* level compared to 0.036 Å for the corresponding HF/6-31G* calculations. Calculated AH bond lengths and HAH and HAB bond angles improve to a lesser extent.

3. Inclusion of polarization (d-type) functions in the atomic basis set appears to be required for the proper description of equilibrium geometries using the second-order Møller-Plesset method. Limited explorations suggest that the minimal STO-3G and split-valence 4-31G basis set are not suitable for use in a foundation for post-Hartree-Fock treatments of molecular geometry. Similar observations have been made for correlation treatments involving the configuration interaction method.[4] It appears, therefore, that the 6-31G* basis set is one of the simplest representations for which the introduction of correlation effects via the second-order Møller-Plesset approach leads to a net improvement in structural prediction.

The MP2/6-31G* results which we have presented suggest that the method has promise as a widely applicable scheme for the calculation of molecular geometry, yielding structures close to the range of experimental uncertainty.

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