

analysis. The oxidation numbers of C and H atoms in each methyl group could be assigned as $-C^{-1.5}H_3^{+0.5}$ in just the same way as (O)

for the other acyclic compounds shown in Chart II(a). However, the simple rules as summarized in Chart III are not applicable to isobutane and neopentane. The $\Delta\rho_0$ values for the central carbon atoms of these two molecules are almost the same (see Table I). Further, comparison with other $\Delta\rho_0$ values suggests that the central carbon atoms are a little more reduced ($C^{-3/4}HMe_3$, $C^{-3/4}Me_4$) than what is expected from the above rules ($C^{-0.5}HMe_3$, C^0Me_4).³⁸ For the case of tetramethoxymethane ($C(OMe)_4$), the assignment based on the $\Delta\rho_0$ values is contradictory to that deduced from the electroneutrality principle.

Concluding Remarks

After a slight modification the classically assigned oxidation numbers for C, H, and O atoms in the hydrocarbons and their oxides, as long as large electronic migration and steric hindrance are not expected, give us systematic understanding of the oxidation states of the component atoms. The modified oxidation number for these molecules can be obtained by simple additivity rules as follows:

Step 1: divide the molecule into units of oxygen, oxygenated hydrogen, and/or hydrogenated carbon.

Step 2: assign -2 for the oxygen and 0 for the $-CH_n$ groups not directly bonded to oxygen.

Step 3: assign +1 or +2 to the direct neighbors of the oxygens to attain the electroneutrality around each oxygen.

(38) In the bonding region both the $\Delta\rho_0$ curves around the central carbon atoms in $CHMe_3$ and CMe_4 molecules lie just in between the $\Delta\rho_0$ curves of $C^{-1}H_2=CH_2$ and $C^{-0.5}H_3OH$.

Step 4: assign +0.5 to the hydrogens attached to carbon.

Step 5: the carbon atoms will receive all the rest of the charge so as to obey all the above rules.

For a set of nonequivalent carbon atoms in a molecule, assignment is given by the aid of the $\Delta\rho_0$ curves in the bonding region, say the $\Delta\rho_0$ value at $R = \langle r^2 \rangle^{1/2}$. The absolute values of these modified oxidation numbers are just the formal numbers as they stand, but they surely reflect not only the subtle but also the stepwise polarization of valence electrons in those carbon compounds, about which most organic chemists have been skeptical in applying the concept of the oxidation number.

For conjugated π -electronic systems a clear-cut assignment of the oxidation number becomes difficult. Study is under way along the present analysis to see if, and how far, electrons migrate in organic molecules as predicted from the conventional organic resonance theory.

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Registry No. $CH_3CH_2CH_3$, 74-98-6; $CH_3(CH_2)_2CH_3$, 106-97-8; $CH_2=C=CH_2$, 463-49-0; $CH_2=CHCH=CH_2$, 106-99-0; CH_3CH_2OH , 64-17-5; $CH_3(CH_2)_2OH$, 71-23-8; $HO(CH_2)_2OH$, 107-21-1; CH_3OCH_3 , 115-10-6; $CH_3CH_2OCH_3$, 540-67-0; CH_3OOH , 3031-73-0; CH_3OOCH_3 , 690-02-8; $\overline{CH_2CH_2CH_2CH_2}$, 287-23-0; $\overline{CH=CHCH_2CH_2}$, 822-35-5; $\overline{CH=CHCH=CH}$, 1120-53-2; $\overline{OCH_2CH_2CH_2}$, 503-30-0; $\overline{OCH_2OCH_2}$, 287-50-3; $\overline{OCH_2CH_2O}$, 6788-84-7; $\overline{CH_2CH_2CH_2}$, 75-19-4; $\overline{CH=CHCH_2}$, 2781-85-3; $\overline{OCH_2CH_2}$, 75-21-8; $\overline{OCH_2O}$, 157-26-6; $CH(CH_3)_3$, 75-28-5; $C(CH_3)_4$, 463-82-1; $C(OCH_3)_4$, 1850-14-2.

6-311G(MC)(d,p): A Second-Row Analogue of the 6-311G(d,p) Basis Set. Calculated Heats of Formation for Second-Row Hydrides

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Optimized d-function exponents have been obtained for first- and second-row atoms in various environments. The best values at Hartree-Fock and correlated levels are found to differ significantly in many cases. Optimum correlated exponents have been used in constructing the 6-311G(MC)(d,p) basis set, defined for H, He, and first- and second-row atoms, and recommended as a starting point for large-basis-set correlated calculations. The 6-31G⁺⁺ basis set has also been defined for H, He, and first- and second-row atoms and is recommended for smaller-basis-set correlated calculations. Heats of formation for second-row hydrides, calculated at the fourth-order Møller-Plesset level by using an augmented 6-311G(MC)(d,p) basis set and an isogyric correction, are generally in good agreement with experimental values. In cases where experimental information is either uncertain or lacking, the present calculated heats of formation are probably the most reliable values currently available.

Introduction

The most widely used basis sets in current electronic structure calculations are undoubtedly those that have been developed over the years by Pople and co-workers.¹ Descriptions such as STO-3G have become part of the chemical idiom and are familiar not only to practicing quantum chemists but also to many in the wider chemical community.

The simplest such basis sets are STO-3G and 3-21G.¹ At the other end of the scale, large basis sets for H, He and the first-row

atoms are based on the triple- ζ -valence 6-311G set,² supplemented by one or more sets of polarization and/or diffuse functions, as required.³ Basis sets of this type, in conjunction with a fourth-order Møller-Plesset perturbation theory treatment of electron correlation⁴ and with an isogyric correction, have been found⁵ to yield heats of formation for first-row hydrides to an accuracy of about ± 8 kJ mol⁻¹.

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TABLE I: Standard and Optimized Values of d-Function Exponents for First-Row Atoms

atom	6-31G(d,p), standard ^a	6-311G(d,p), standard ^b	6-31G(d,p), MP2, atom opt	6-31G(d,p), HF, hydride opt	6-31G(d,p), MP2, hydride opt	6-311G(d,p), MP2, atom opt	6-311G(d,p), HF, hydride opt	6-311G(d,p), MP2, hydride opt
Li	0.2	0.200	c	0.108	0.137	c	0.262	0.146
Be	0.4	0.255	0.260	0.436	0.296	0.250	0.382	0.297
B	0.6	0.401	0.390	0.511	0.479	0.388	0.791	0.550
C	0.8	0.626	0.616	0.756	0.677	0.603	0.985	0.792
N	0.8	0.913	0.918	0.857	0.898	0.877	1.016	1.016
O	0.8	1.292	1.306	0.914	1.235	1.231	1.134	1.295
F	0.8	1.750	1.737	0.882	1.663	1.657	1.325	1.645
Ne	0.8	2.304	2.298		2.298	2.169		2.169

^a From ref 7. ^b From ref 2. ^c Within the frozen-core approximation, there is no correlation energy for lithium atom.

A basis set directly analogous to 6-311G has not yet been developed for second-row atoms, and this has led to the use of extended polarization sets based on the double- ζ -valence 6-31G set.⁶⁻⁸ This clearly has the disadvantage of reduced flexibility in the sp part of the basis set. An additional shortcoming is that, whereas the d polarization functions for the 6-311G-based sets were specially chosen to be suitable for correlated calculations, those for the 6-31G-based sets were optimized for Hartree-Fock wave functions. Since correlated calculations are much more sensitive than Hartree-Fock calculations to the value of the d exponents,⁹ the former choice is more suitable for general application.

Recently, Gordon and Heitzinger¹⁰ have made the suggestion that in the absence of an explicit 6-311G basis set for second-row atoms, basis sets developed by McLean and Chandler (MC)¹¹ might be used as the underlying sp basis sets for extended calculations on systems containing such atoms. They concluded, as a result of testing on the hydrides of Si, P, S, and Cl, that use of the 6-311G basis set for first-row atoms and the MC set for second-row atoms, in each case augmented by appropriate polarization functions, provided a reasonable basis for calculations of reaction energies using correlated procedures. This is a welcome suggestion and potentially allows calculations on systems containing second-row atoms to be carried out at a level comparable to that commonly used (i.e., with an augmented 6-311G basis set) for systems with first-row atoms alone.

While recognizing the merit of the Gordon and Heitzinger proposal,¹⁰ we were concerned that their choice of d-function exponents, namely, the standard values developed for use with 6-31G,⁸ might not be ideal. As noted above, the d-function exponents for use with 6-31G were developed on the basis of Hartree-Fock optimizations and may differ substantially from the values that are optimum for correlated wave functions. Since a primary purpose of the larger basis sets is to allow reliable energy calculations using correlated procedures, it would seem preferable, therefore, to choose exponents for use with the MC basis set on the basis of correlated calculations. We explore this point in the present study.

As a result of the calculations reported in this paper, we recommend a set of "standard" exponents for second-row atoms leading, in conjunction with the 6-311G(d,p) set already available for H and first-row atoms² and a modified 6-311G(d,p) basis for He,¹² to the triple- ζ -valence plus dp-polarization 6-311G(MC)(d,p) basis set, defined for H, He, and first- and second-row atoms. The same set of exponents are recommended as standard values for correlated calculations with the (smaller) double- ζ -valence plus

TABLE II: Sensitivity (ΔE , kJ mol⁻¹) of Calculated Total Energies for First-Row Hydrides to a Variation ($\Delta\zeta$) in the d-Function Exponent (MP2/6-311G(d,p))

molecule	optimized d exponent	ΔE	
		$\Delta\zeta = -0.100$	$\Delta\zeta = +0.100$
LiH	0.146	4.43	1.10
BeH ₂	0.297	2.49	1.32
BH ₃	0.550	1.26	0.80
CH ₄	0.792	0.95	0.68
NH ₃	1.016	0.85	0.70
OH ₂	1.295	0.69	0.60
FH	1.645	0.50	0.44
Ne	2.169	0.30	0.28

dp-polarization 6-31G⁺⁺ basis set.

Method

Standard ab initio molecular orbital calculations¹ were carried out with a modified version¹³ of the GAUSSIAN 82 system of programs.¹⁴ Optimization of exponents for atoms, normal-valent hydrides (AH_n, taken to have the same valencies for second-row as for first-row hydrides), and, in some cases, protonated (AH_{n+1}⁺) and deprotonated (AH_{n-1}⁻) forms of the hydrides was carried out by using, as the underlying sp basis set, 6-31G and 6-311G for first-row elements and 6-31G and the (12s 9p) → [6s 5p] McLean-Chandler (MC) basis set¹¹ for second-row elements. Optimizations were performed at the second (MP2)-, third (MP3)-, and fourth (MP4)-order Møller-Plesset levels^{4,15} and (for hydrides) at the Hartree-Fock level. The frozen-core approximation was used throughout.

The exponent-optimization studies led to the establishment of the 6-311G(MC)(d,p) basis set, consisting of the 6-311G sp set for H, He, and first-row atoms and the MC sp set for second-row atoms, supplemented by polarization functions with standard exponents for H and first-row atoms and with new, optimized values for He and second-row atoms. The 6-311G(MC)(d,p) basis set, augmented by additional diffuse functions and d polarization and f polarization functions, was then used in conjunction with MP4 calculations to obtain heats of formation for the complete set of second-row hydrides, by using a procedure described by Pople et al.⁵ HF/6-31G(d)-optimized structures, also taken from ref 5, were used unless otherwise specified.

Results and Discussion

Polarization-Function Exponents for First-Row Atoms. Although it is not the main purpose of this paper to discuss in detail basis sets for first-row atoms, it is nevertheless instructive to examine briefly the variation in polarization-function exponents for first-row atoms at various levels and in various environments, as shown in Table I. The first two columns list the standard exponents for the 6-31G(d,p) and 6-311G(d,p) basis sets. The

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TABLE III: Standard and Optimized Values of d-Function Exponents for Second-Row Atoms

atom	Huzinaga standard ^a	6-311G(MC)(d,p) MP2, atom opt	6-31G(d,p) MP2, atom opt	6-31G(d,p) MP2, hydride opt	6-311G(MC)(d,p) MP2, hydride opt	AT, standard ^b	6-31G(d,p) HF, hydride opt	6-31G(d,p), standard	6-311G(MC)(d,p) HF, hydride opt
Na	0.061	<i>d</i>	<i>d</i>	0.207	0.146	0.157	0.481	0.175	0.420
Mg	0.101	0.171	0.181	0.200	0.200	0.234	0.238	0.175	0.258
Al	0.198	0.205	0.211	0.273	0.301	0.311	0.311	0.325	0.356
Si	0.262	0.281	0.287	0.370	0.413	0.388	0.418	0.450	0.540
P	0.340	0.373	0.379	0.422	0.445	0.465	0.505	0.550	0.664
S	0.421	0.474	0.480	0.496	0.515	0.542	0.605	0.650	0.805
Cl	0.514	0.590	0.595	0.594	0.604	0.619	0.721	0.750	0.931
Ar	0.617	0.719	0.724	0.724	0.719	0.696		0.850	

^a From ref 17. ^b Ahlrichs and Taylor.¹⁸ ^c From ref 8. ^d Within the frozen-core approximation, there is no correlation energy for the sodium atom.

former were selected⁷ on the basis of optimizations of polarization-function exponents for a variety of molecules at the HF/6-31G(d) level, while the latter were chosen² on the basis of optimizations for the individual atoms at the MP2 level with a large basis set.

It is clear from Table I that the standard exponents for 6-31G(d,p) and 6-311G(d,p) differ substantially in some instances, particularly for O, F, and Ne. The standard 6-311G(d,p) exponents are smaller than the standard 6-31G(d,p) values for atoms on the left of the period but are larger than the 6-31G(d,p) values for atoms on the right of the period. The same trend is evident, although to a diminished extent, in comparisons of optimized exponents obtained for the normal-valent hydrides at the HF/6-31G(d,p) and MP2/6-31G(d,p) levels and at the HF/6-311G(d,p) and MP2/6-311G(d,p) levels.

Differences between exponent values as optimized for atoms and for hydrides are less important. The differences are greatest for atoms in the center of the period, i.e., for those atoms whose hydrides contain the largest number of hydrogen atoms.

Table II shows the sensitivity of the calculated total energies of the first-row hydrides to deviations of the d-function exponents from optimum (MP2/6-311G(d,p)) values. For the deviations $\Delta\zeta = \pm 0.1$ examined in the table, which are typical of the differences between standard 6-311G(d,p) exponents and MP2/6-311G(d,p) optimized values for the hydrides, the associated energy changes are generally quite small. On the other hand, if the standard 6-31G(d,p) exponents (0.8) are used for O, F, and Ne in MP2/6-311G(d,p) calculations on OH₂, FH, and Ne, the resultant errors in the calculated total energies are substantial: 23, 55, and 97 kJ mol⁻¹, respectively.

The main conclusion to be drawn from the above results is that caution should be exercised in the use of the standard 6-31G(d,p) d-function exponents for correlated calculations involving atoms such as O, F, and Ne.

In a previous study,¹⁶ we introduced and examined the performance of the 6-31G⁺⁺ basis set, which differs from 6-31G(d,p) in that (1) the polarization-function exponents are assigned the standard 6-311G(d,p) values (and are therefore suitable for correlated calculations) and (2) five "pure" d functions (as in 6-311G(d,p)) rather than the six second-order Cartesian functions (as in 6-31G(d,p)) are used (leading to computational savings). For the small set of simple molecules examined in that study, we found that the 6-31G⁺⁺ basis set did not offer a significant improvement over 6-31G(d,p) in predicting equilibrium structures and atomization energies at levels of theory that include electron correlation, despite the use of exponents optimized for correlated wave functions. We believe, however, that this can only be the case for processes in which the changes in d-function exponents are very small, resulting in almost complete cancellation of error. In other cases, because the optimum correlated exponents are far from the standard 6-31G(d,p) values, the energy surface in the portion of exponent-space that is being sampled is very steep and large errors will be associated with correlated 6-31G(d,p) calculations for processes in which changes in d-function exponents are significant. Indeed, this might be expected to be the rule rather

than the exception since the flatness of the surface in the vicinity of the minimum (Table II) implies that a range of optimum exponents might be expected for different environments. In such cases, the use of basis sets with more appropriate exponents, namely, 6-31G⁺ or 6-31G⁺⁺ (in place of 6-31G(d) or 6-31G(d,p), respectively) or 6-311G(d,p) is recommended.

Polarization-Function Exponents for Second-Row Atoms. Table III lists polarization-function exponents for second-row atoms in a number of environments, including some values taken from the literature.^{8,17,18} The values of Huzinaga¹⁷ seek to maximize the radial overlap between the d functions and the underlying sp functions. Those of Ahlrichs and Taylor¹⁸ are based on an empirical fit to data obtained through correlated optimizations of some of the hydrides. Finally, the standard 6-31G(d,p) d-function exponents⁸ are average values based on HF/6-31G(d) optimizations of a selection of representative molecules. These are the values used in the MC-311G basis set of Gordon and Heitzinger.¹⁰

In addition to the literature values, Table III includes exponents optimized for the atoms or the normal-valent hydrides, at the Hartree-Fock or MP2 level, and using as underlying sp basis set 6-31G⁸ or 6-311G(MC).^{2,11} The latter basis set uses 6-311G for H (and first-row atoms, if there had been any)² and the (12s 9p) → [6s 5p] basis set of McLean and Chandler¹¹ for second-row atoms.

The columns of Table III are arranged from left to right in roughly ascending order of values of the d-function exponents. Several observations may be made.

(1) Although the variation in exponent values is less extreme than, for example, in the case of the F atom (Table I), there are significant differences between the values at different theoretical levels. For several atoms, the exponent values span a range of 0.3–0.4 units. As we shall see below, the sensitivity of the energy to the value of the exponent is considerably greater than for first-row systems.

(2) The Huzinaga approach¹⁷ consistently gives the lowest exponent values, and in several cases these differ significantly from energy-optimized values. Thus, the maximum overlap criterion does not always correspond to the most favorable situation *energetically*.

(3) MP2-optimized exponents are consistently smaller than Hartree-Fock values.

(4) As for first-row systems, the difference between atom-optimized and hydride-optimized exponents is greatest for atoms toward the center of the period.

(5) Whereas the MP2 results are not strongly dependent on the underlying sp basis set, the Hartree-Fock exponents show a significantly larger variation with basis set.

Our preferred set of exponents are the MP2/6-311G(MC)(d,p) values, as optimized for hydrides. These tend to lie toward the middle of the range of the obtained values. On the other hand, the standard 6-31G(d,p) values tend to lie at the high end of the

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TABLE IV: Variation in Optimum d-Function Exponent for S and Cl in Different Molecular Environments (6-311G(MC)(d,p) Basis Set)

species	S	Cl
deprotonated hydride atom	0.434	0.526
hydride	0.474	0.590
protonated hydride	0.515	0.604
	0.573	0.664

TABLE V: Sensitivity (ΔE , kJ mol⁻¹) of Calculated Total Energies for Second-Row Hydrides to a Variation ($\Delta\zeta$) in the d-Function Exponent (MP2/6-311G(MC)(d,p))

molecule	optimized d exponent	ΔE	
		$\Delta\zeta = -0.100$	$\Delta\zeta = +0.100$
NaH	0.146	4.16	0.74
MgH ₂	0.200	7.33	2.90
AlH ₃	0.301	7.09	3.23
SiH ₄	0.413	5.66	2.84
PH ₃	0.445	7.95	4.43
SH ₂	0.515	7.71	4.96
ClH	0.604	5.19	7.29
Ar	0.719	6.35	5.00

TABLE VI: Optimized d-Function Exponents for First- and Second-Row Atoms^a

atom	MP2	MP3	MP4	atom	MP2	MP3	MP4
Be	0.250	0.227	0.217	Mg	0.171	0.163	0.172
B	0.388	0.363	0.351	Al	0.205	0.196	0.192
C	0.603	0.570	0.556	Si	0.281	0.276	0.274
N	0.877	0.833	0.817	P	0.373	0.370	0.371
O	1.231	1.189	1.178	S	0.474	0.473	0.476
F	1.657	1.623	1.621	Cl	0.590	0.592	0.598
Ne	2.169	2.151	2.165	Ar	0.719	0.726	0.736

^aOptimized for atoms with the 6-311G(MC)(d,p) basis set.

range, particularly for P, S, Cl, and Ar, and are less suitable for correlated calculations.

To see whether the MP2/6-311G(MC)(d,p) hydride-optimized exponents are indeed suitable for general application, we have examined for S and Cl the protonated and deprotonated hydrides, representing extreme environments that we would wish to be handled adequately by the basis. Optimized d-function exponents are shown in Table IV.

Both the atom and hydride exponents lie within the range of values spanned by the protonated and deprotonated hydrides. On the other hand, the standard 6-31G(d,p) values lie outside the range for both systems. These results support the choice of the optimum exponents for the hydrides as the standard values for our basis set. The atom-optimized values are fairly similar and could also have been used, but we feel that hydrides are more representative (than atoms) of the types of systems that are normally examined.

Table V shows the sensitivity of calculated total energies of second-row hydrides to deviations in the d-function exponents from the optimized values. The sensitivity is considerably greater than for corresponding first-row systems (Table II), but this is counterbalanced by the observation (Table III) that the range of exponent values is less than for first-row systems. The errors in calculated total energies resulting from the use of standard 6-31G(d,p) exponents in MP2/6-311G(MC)(d,p) calculations on PH₃, SH₂, ClH, and Ar are respectively 4.8, 8.4, 5.1, and 8.2 kJ mol⁻¹.

Up to this stage, we have restricted our consideration of correlation-based exponents to those optimized at the MP2 level. It is important to see how the MP2 values compare with MP3- and MP4-optimized values. These are shown for the complete set of first- and second-row atoms in Table VI.

The results in Table VI indicate that the changes in going from MP2 to MP3 and MP4 are fairly small and (from Tables II and V) unlikely to have significant energetic consequences. This conclusion is reached also from an examination of a small number of the hydrides. For example, for H₂O the optimized d-function exponents at MP2, MP3, and MP4 are 1.295, 1.272, and 1.294,

TABLE VII: Standard Values of Polarization Function Exponents (ζ) for the 6-31G⁺⁺ and 6-311G(MC)(d,p) Basis Sets^{a,b}

atom	ζ_p	atom	ζ_d^c	atom	ζ_d
H	0.750 ^c	Li	0.200	Na	0.146
He	1.366 ^d	Be	0.255	Mg	0.200
		B	0.401	Al	0.301
		C	0.626	Si	0.413
		N	0.913	P	0.445
		O	1.292	S	0.515
		F	1.750	Cl	0.604
		Ne	2.304	Ar	0.719

^aThe same values apply to the 6-31G⁺ and 6-311G(MC)(d) basis sets, and to augmented versions. ^bDefined in the present paper, unless otherwise noted. ^cStandard 6-311G values, from ref 2. ^dFrom ref 12.

respectively, while for HCl the values are 0.604, 0.608, and 0.618. It would seem that the MP2-optimized exponents are reasonably representative of correlation-based exponents in general, and the values in Table VII (vide infra) are suitable for use as standard values.

Before concluding this section, we return to the 6-31G⁺ and 6-31G⁺⁺ basis sets, defined previously¹⁶ for first-row atoms. We have recommended (vide supra) the use of these basis sets for first-row atoms (in place of 6-31G(d) and 6-31G(d,p)) for correlated calculations in situations that might be expected to involve significant changes in d-function exponents. Likewise, for small-basis-set correlated calculations involving second-row atoms, we would similarly recommend the use of 6-31G⁺ and 6-31G⁺⁺ in place of 6-31G(d) and 6-31G(d,p). The d-function exponents in these basis sets for second-row atoms are now defined, for consistency, to be the same as those used in 6-311G(MC)(d,p). Thus, there is a *single set* of standard polarization-function exponents applicable to both the 6-31G⁺⁺ and 6-311G(MC)(d,p) basis sets for H, He, and first- and second-row atoms. The complete set of standard values is summarized in Table VII.

Heats of Formation for Second-Row Hydrides. As a test of the performance of the 6-311G(MC)(d,p) basis set, heats of formation for second-row hydrides were derived by using the procedure of Pople and co-workers.⁵ As a first step, total energies were obtained at the MP4 level with the 6-311G(MC)(d,p), 6-311+G(MC)(d,p), 6-311G(MC)(2d,p), and 6-311G(MC)(df,p) basis sets, and MP4/6-311+G(MC)(2df,p) total energies were estimated by assuming additivity of the basis set enhancements associated with diffuse functions, a second set of d functions, and a set of f functions. These are presented in Table VIII. The derived heats of formation are compared with literature values of Pople et al.⁵ and Gordon and Heitzinger⁸ and with experimental values, in Table IX. The experimental heats of formation have been discussed in detail by Pople et al.,⁵ and, unless otherwise noted, the values listed in Table IX are taken directly from ref 5. For the silicon hydrides, there have been several more recent experimental studies,¹⁹⁻²¹ but agreement on the heats of formation has yet to be reached.

The following observations can be made from an examination of Table IX.

(1) Without exception, the effect of basis set enhancement on the 6-31G(d,p) and 6-311G(MC)(d,p) results is to lead to lower values of the heats of formation. It would seem that a similar effect is likely to occur with the MC-311G(d,p) basis set, and this is indeed the case for the three systems (PH₃, H₂S, and HCl) for which the appropriate MC-311G(d,p)-based data are currently available (cf. point 3 below).

(2) In general, the heats of formation obtained with the non-enhanced basis sets are higher than experimental values. The MC-311G(d,p) and 6-311G(MC)(d,p) results are significantly better than those with 6-31G(d,p). Of the former pair, MC-311G(d,p) gives marginally better results, but this is likely to be

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TABLE VIII: Calculated MP4 Total Energies (hartrees)^a

species	6-311G(MC)(d,p)	6-311+G(MC)(d,p)	6-311G(MC)(2d,p)	6-311G(MC)(df,p)	6-311+G(MC)(2df,p) ^b
H	-0.499 81	-0.499 81	-0.499 81	-0.499 81	-0.499 81
H ₂	-1.167 63	-1.167 63	-1.167 63	-1.167 63	-1.167 63
Na	-161.845 93	-161.845 99	-161.845 93	-161.845 93	-161.845 99
NaH	-162.408 87	-162.408 99	-162.409 70	-162.410 85	-162.411 80
Mg	-199.638 08	-199.638 15	-199.638 13	-199.638 12	-199.638 24
MgH	-200.183 33	-200.183 44	-200.184 29	-200.185 74	-200.186 81
MgH ₂	-200.793 34	-200.793 45	-200.794 60	-200.797 69	-200.799 06
Al	-241.916 51	-241.916 73	-241.921 61	-241.918 41	-241.923 73
AlH	-242.526 88	-242.527 24	-242.531 15	-242.530 79	-242.535 42
AlH ₂	-243.103 69	-243.104 07	-243.107 83	-243.109 46	-243.113 98
AlH ₃	-243.738 85	-243.739 37	-243.742 96	-243.746 63	-243.751 26
Si	-288.910 40	-288.910 66	-288.920 34	-288.915 68	-288.925 88
SiH	-289.517 57	-289.518 21	-289.526 93	-289.525 91	-289.535 91
SiH ₂	-290.137 76	-290.138 45	-290.147 40	-290.147 75	-290.158 08
SiH ₃	-290.753 72	-290.754 16	-290.762 17	-290.764 55	-290.773 44
SiH ₄	-291.401 80	-291.402 04	-291.410 60	-291.413 49	-291.422 53
P	-340.793 82	-340.794 20	-340.802 51	-340.804 73	-340.813 80
PH	-341.395 83	-341.396 60	-341.406 23	-341.410 39	-341.421 56
PH ₂	-342.013 60	-342.014 30	-342.025 70	-342.030 86	-342.043 66
PH ₃	-342.645 04	-342.645 38	-342.658 62	-342.663 81	-342.677 73
S	-397.608 27	-397.609 83	-397.620 72	-397.631 91	-397.645 02
SH	-398.233 55	-398.234 54	-398.249 26	-398.259 46	-398.276 16
SH ₂	-398.875 86	-398.876 84	-398.894 06	-398.903 22	-398.922 40
Cl	-459.610 87	-459.611 64	-459.628 81	-459.644 17	-459.662 88
ClH	-460.268 38	-460.269 47	-460.290 09	-460.303 01	-460.325 81

^a Using HF/6-31G(d) optimized structures from ref 5. ^b Assuming additivity of basis-set enhancement effects.

TABLE IX: Calculated Heats of Formation ΔH_f° (kJ mol⁻¹)

species	6-31G(d,p) ^a	MC-311G(d,p) ^b	6-311G(MC)(d,p) ^c	6-31+G(2df,p) ^a	6-311+G(MC)(2df,p) ^c	exptl ^d
NaH	155.3	146.1	145.6	142.4	138.3	124 ± 19
MgH	258.0	250.3	250.3	244.4	241.5	232
MgH ₂	187.6	171.9	171.7	162.3	157.2	
AlH	254.8	244.6	245.1	244.6	242.0	>245
AlH ₂	285.8	270.7	272.5	267.8	264.4	
AlH ₃	156.6	142.3	136.0	127.4	123.2	
SiH	380.7	372.9	373.5	369.5	367.0	377 ± 8
SiH ₂	286.1	271.3	272.7	264.9	261.1	276, ^e 287, ^e 289 ^f
SiH ₃	218.9	200.3	204.4	197.7	193.8	194 ± 5, 203 ^f
SiH ₄	54.7	29.7	35.5	26.0	21.7	34 ± 2
PH	261.4	254.5	259.2	247.6	244.0	
PH ₂	172.4	158.1	166.2	145.7	139.8	138.5 ^g
PH ₃	53.2	31.3	42.5	16.5	9.1	7 ± 2
SH	162.8	155.6	159.9	148.1	144.5	139 ± 5, 149
SH ₂	10.9	-3.9	4.8	-14.4	-20.9	-20.5 ± 0.8
ClH	-73.6	-82.5	-78.6	-89.2	-92.8	-92.5

^a From ref 5. ^b Taken in part from ref 8. ^c Present work. Calculated by using total energies from Table VIII. ^d From ref 5, unless otherwise noted. ^e From ref 20. ^f From ref 21. ^g From ref 10.

reversed with basis set enhancement, which will result in a lowering of the MC-311G(d,p) values (cf. point 1 above).

(3) Closest agreement with the experimental heats of formation is achieved with the 6-311+G(MC)(2df,p) basis set. We have obtained heats of formation with the MC-311+G(2df,p) basis set for three systems (PH₃, H₂S, and HCl) and the results obtained (11.7, -12.6, and -90.2 kJ mol⁻¹, respectively) surprisingly do not show a significant improvement over 6-31+G(2df,p) values.

(4) For three systems for which precise experimental heats of formation are available (PH₃, SH₂, and ClH), the agreement between 6-311+G(MC)(2df,p) and experimental values is very good. In fact, the agreement is very reasonable for *all* the hydrides of P, S, and Cl.

(5) The agreement between 6-311+G(MC)(2df,p) and experimental heats of formation is less good for the silicon hydrides. One point that should be noted in this connection is that the theoretical heats of formation for the silicon hydrides are based on an experimental heat of formation for atomic silicon (450 kJ mol⁻¹)²² with an uncertainty of 8 kJ mol⁻¹, and this could account for part of the difference.

(6) For the hydrides of the more electropositive elements (Na, Mg, and Al), experimental values of the heats of formation are

more sparse and more uncertain. We believe that, for most of these systems, our MP4/6-311+G(MC)(2df,p) heats of formation are probably the most reliable values currently available.

Concluding Remarks

Several important points emerge from this study.

Optimum d-function exponents for first- and second-row atoms may differ significantly between Hartree-Fock and correlated levels of theory.

For correlated calculations, it is clearly desirable to use basis sets with d-function exponents that are appropriate for correlated wave functions.

The 6-311G(MC)(d,p) basis set, a triple- ζ -valence plus dp-polarization basis set with polarization-function exponents obtained from correlated optimizations and defined for H, He, and first- and second-row atoms, is recommended as a starting point for large basis-set correlated calculations. It may be augmented in a standard manner with additional or higher polarization functions and with diffuse functions.²³ For H and first-row atoms, it

(23) To complete the set of supplementary functions for H, He, and first- and second-row atoms given in ref 3, we recommend, on the basis of appropriate atom optimization studies, the following exponents: diffuse s functions for He, 0.0704; diffuse sp functions for Ne and Ar, 0.1362 and 0.0473, respectively; f functions for Ar, 0.880.

corresponds exactly to the standard 6-311G(d,p) basis set.

For smaller basis-set correlated calculations, it may often be advantageous to use the double- ζ -valence plus polarization 6-31G⁺ and 6-31G⁺⁺ basis sets in place of 6-31G(d) and 6-31G(d,p), particularly for processes that are likely to be accompanied by a significant change in the d-function exponent. The standard exponents for 6-31G⁺⁺ (and 6-31G⁺) are the same as those for 6-311G(MC)(d,p).

Heats of formation for second-row hydrides, calculated by using the procedure of Pople et al. at the MP4 level with an augmented

6-311G(MC)(d,p) basis set, are generally in good agreement with available experimental values and, in many cases, would represent the best estimates of the heats of formation currently available.

Registry No. H, 12385-13-6; H₂, 1333-74-0; Na, 7440-23-5; Al, 7429-90-5; Si, 7440-21-3; P, 7723-14-0; S, 7704-34-9; Cl₂, 7782-50-5; NaH, 7646-69-7; MgH, 14332-53-7; MgH₂, 7693-27-8; AlH, 13967-22-1; AlH₂, 14457-65-9; AlH₃, 7784-21-6; SiH, 13774-94-2; SiH₂, 13825-90-6; SiH₃, 13765-44-1; SiH₄, 7803-62-5; PH, 13967-14-1; PH₂, 13765-43-0; PH₃, 7803-51-2; SH, 13940-21-1; SH₂, 7783-06-4; ClH, 7647-01-0.

Optimized Two-Electron-Integral Transformation Procedures for Vector-Concurrent Computer Architectures

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Various approaches for the transformation of two-electron integrals are discussed. Using the full index symmetry (FIS) of the array to be transformed for a case with N basis functions, the N -to- N transformation yields an operation count of $(25/24)N^5$, while transformation to a small set with M orbitals yields $(1/8)N^4M$ if $N \gg M$. We discuss the vector-optimized implementation of this (FIS) procedure for concurrent architectures. Tests were carried out on an Alliant FX8/8 mini-supercomputer (eight processors sharing one memory) and compared with the performance of DEC VAX scalar machines.

I. Introduction

New computer architectures allowing multiple processors to work in parallel on a given problem are being developed. Examples include hypercubes with distributed memory (e.g., Intel, Caltech, FPS) and with shared memory (the Alliant FX8). The Alliant is especially promising for studying electronic structure problems because it has an effective, vector-concurrent optimizing Fortran compiler allowing straightforward coding, since data passing and synchronization between processors are taken care of automatically by the operating system. Furthermore, the large global memory available (currently up to 256 Mbytes) allows large systems (~ 200 basis functions) to be tackled. This, combined with use of effective core potentials, provides the capability for studying large clusters of transition metals (say, Pt₁₀).

In this paper we report progress in developing an optimized integral transformation program (FISTRN) for parallel machines. This involved restructuring the algorithms to take maximum advantage of concurrency, vectorization, and huge memory. In addition, the program must be designed specifically to take advantage of automatic vector-concurrent optimizing Fortran compilers.

II. Quantum Mechanics

For the calculation of correlated wave functions, it is essential to have an efficient procedure for transforming integrals over atomic or symmetry orbitals (AO's) into integrals over molecular orbitals (MO's). The AO two-electron integrals

$$A_{ij,kl} \equiv \left\langle \psi_i(1) \psi_k(2) \left| \frac{1}{r_{12}} \right| \psi_j(1) \psi_l(2) \right\rangle \\ \equiv \int d^3x_1 \psi_i(1) \psi_j(1) \int d^3x_2 \frac{1}{r_{12}} \psi_k(2) \psi_l(2) \quad (1)$$

are transformed into the corresponding two-electron integrals over a new set of basis functions

$$Z_{\alpha\beta,\gamma\delta} \equiv \left\langle \phi_\alpha(1) \phi_\gamma(2) \left| \frac{1}{r_{12}} \right| \phi_\beta(1) \phi_\delta(2) \right\rangle \quad (2)$$

where

$$\phi_\alpha = \sum_{n=1}^N \psi_n C_{n\alpha} \quad (3)$$

Taking the number of basis functions in each set as N , then, depending on how the Z integrals are calculated in terms of the A integrals, the number of multiplications (or the operation count, OpC) may increase as rapidly as qN^8 or as slowly as $q'N^5$. In addition, the prefactors q and q' may vary by a factor of 4. Herein we will consider in detail the techniques for such transformations.

In particular, the array of integrals A is symmetric in the indexes i and j , in the indexes k and l , and in the pairs ij and kl . In order to minimize the prefactor q , this index symmetry is exploited during the transformation.

III. Review of Two-Electron-Integral Transformation Theory¹

The two-electron integrals of eq 1 and 2 are related by

$$Z_{\alpha\beta,\gamma\delta} = \sum_{ijkl} C_{i\alpha} C_{j\beta} A_{ijkl} C_{k\gamma} C_{l\delta} \quad (4)$$

where C is the $N \times M$ transformation matrix connecting the N basis functions $\{\psi_i\}$ and the M molecular functions $\{\phi_\alpha\}$.

A. Direct Multiplication ($(1/16)N^8$). An obvious but inefficient method of accomplishing the transformation (4) would be to calculate the quantity $C_{i\alpha} C_{j\beta} A_{ijkl} C_{k\gamma} C_{l\delta}$ for each $i, j, k, l, \alpha, \beta, \gamma, \delta$. Each of these terms would then be accumulated in the appropriate $Z_{\alpha\beta,\gamma\delta}$. This technique requires the largest number of operations, $\sim (1/16)N^4M^4$, even if the full index symmetries of both A and Z are used.

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