

# Efficient Diffuse Function-Augmented Basis Sets for Anion Calculations. III.\* The 3-21+G Basis Set for First-Row Elements, Li–F

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The relatively small diffuse function-augmented basis set, 3-21+G, is shown to describe anion geometries and proton affinities adequately. The diffuse *sp* orbital exponents are recommended for general use to augment larger basis sets.

## INTRODUCTION

Difficulties known to be associated with *ab initio* calculations for anions<sup>1–4</sup> have discouraged the examination of negatively charged species by theoretical methods. While experimental geometries of anions are reproduced satisfactorily with standard split-valence basis sets,<sup>2a,3</sup> energy comparisons are unreliable even when polarization basis sets and electron correlation corrections are employed.<sup>1,4b</sup> It has long been appreciated that the addition of an extra set of diffuse functions to the basis set can dramatically improve results for anions,<sup>1a,4</sup> but no systematic evaluation of relatively small basis sets augmented with diffuse functions has been undertaken until recently.<sup>1</sup> (ref. 5 lists diffuse 2*p* B–F exponents for a 9*s*5*p* basis set; see Table I). We have shown that the addition of a set of diffuse functions to the 4-31G basis set,<sup>6</sup> giving 4-31+G,<sup>1</sup> resulted in a dramatic improvement in calculated proton affinities, especially when the MP2 correction for electron correlation<sup>7</sup> was included. With the possible exception of anions involving fluorine, results obtained with the 4-31+G basis set did not improve appreciably when a diffuse-augmented polarization basis set (6-31+G\*, based on 6-31G\*<sup>8</sup>) was used.<sup>1</sup> So encouraged, we have now developed and evaluated an even smaller

and more economical 3-21+G basis which yields results comparable to 4-31+G. Since the 3-21G basis set is available for all elements in the first<sup>9</sup> and second<sup>10</sup> rows, the 3-21+G basis has the additional advantage of being considerably more versatile than 4-31+G. A 3-21+G basis set for Na–Cl will be reported subsequently. This article reports the details of first-row basis sets and presents an evaluation of their performance in reproducing the experimental geometries of the set of anions considered by Radom<sup>3</sup> and the whole range of known first-row anion proton affinities, from NO<sub>3</sub><sup>–</sup> (324.6 kcal/mol)<sup>11</sup> to LiO<sup>–</sup> (448 ± 12 kcal/mol) (calculated from data in ref. 12).

## METHODS

All calculations employed the GAUSSIAN-76 series of programs<sup>13</sup> with suitable modifications. Geometry optimizations used analytically calculated atomic forces<sup>14</sup> in a Davidon–Fletcher–Powell multiparameter search routine.<sup>15</sup> MP2 calculations<sup>7</sup> did not include the nonvalence orbitals.

The basis sets were derived as follows. The anions H<sup>–</sup>, Li<sup>–</sup>, BeH<sup>–</sup>, BH<sub>2</sub><sup>–</sup>, CH<sub>3</sub><sup>–</sup>, NH<sub>2</sub><sup>–</sup>, OH<sup>–</sup>, and F<sup>–</sup>, in their singlet ground-state configurations were used to optimize the basis set exponents. Geometries were either 4-31G (5-21G for Li and Be),<sup>16</sup> optimized (for 4-31+G), or 3-21G optimized (for 3-21+G), and were not redetermined during optimization of the basis set. A single diffuse *sp*

\* For parts I and II, and other applications of the 4-31+G basis set, see ref. 1.

**Table I.** Diffuse orbital *sp* exponents.

Element	Dunning and Hay <sup>a</sup>	A 4-31+G <sup>b</sup>	B all other basis sets
H	-		0.0360
Li	-	0.012	0.0074
Be	-	0.026	0.0207
B	0.019	0.034	0.0315
C	0.034	0.040	0.0438
N	0.048	0.053	0.0639
O	0.059	0.068	0.0845
F	0.074	0.090	0.1076

<sup>a</sup> Exponents for *p* orbitals from ref. 5.<sup>b</sup> Basis set to be replaced by 3-21+G for general use.

shell was added to the 6-31G<sup>6</sup> and to the 6-21G<sup>9,10</sup> basis sets, and the exponents were optimized with respect to anion total energy. The core and inner two-valence shells were not altered. Two sets of diffuse exponents were thus obtained. The first, derived from the 6-31G basis set, was added to 4-31G to give 4-31+G. The second was used for 3-21+G, 6-21+G, and 6-31+G\* basis sets. A further basis set, designated 3-21++G, 6-21++G, etc., was derived by adding an extra diffuse *s* function to hydrogen. This was found to have little effect for most problems, but to be important for the calculation of H<sup>-</sup> (and hydride affinities). Table I compares the diffuse exponents thus obtained with those of Dunning and Hay.<sup>5</sup> Table II summarizes the basis sets used in this work, and Table III gives the absolute energies [for an extensive collection of 3-21G (and 6-31G)\* energies and geometries of neutral species and some anions see ref. 17].

## RESULTS

### Computer Time

The optimization of CH<sub>3</sub><sup>-</sup> (C<sub>3v</sub>) required 601 s (4-31G), 348 s (3-21G), 861 s (4-31+G), and 545 s (3-21+G) CPU time on the Erlangen CYBER 173. The optimizations all started from a standard tetrahedral-methane geometry with one hydrogen removed. The diffuse-augmented basis sets thus require ca. 60% more time, on average, than their split-valence counterparts. For CH<sub>3</sub><sup>-</sup>, 3-21+G is 37% faster than 4-31+G, but this can vary from 10% to 50%, depending on the system. The 3-21++G and 6-21++G basis sets are particularly time-consuming, as the SCF is slow to converge. In general, SCF damping is necessary when diffuse-augmented basis sets are used.

### Geometries

Optimized geometries for anions are shown in Table IV. The selection includes most of Radom's examples.<sup>2a,3</sup> As noted previously,<sup>1</sup> there generally are relatively small changes in optimized geometries between split-valence and diffuse-augmented basis sets.

Radom's conclusion,<sup>2a,3</sup> that anion geometries are reproduced reasonably well by 4-31G calculations, is confirmed. The relatively few significant changes in geometry on inclusion of diffuse functions (examples involving CH<sub>2</sub>X<sup>-</sup> anions have already been discussed in detail<sup>1b</sup>) are usually caused by the improved description of the anion lone-pair orbitals. This is expected for anions involving fluorine, oxygen, and nitrogen which are not well described by smaller basis sets. Geometries of neutral species are little affected by the inclusion of diffuse functions. In general, it appears

**Table II.** Summary of basis sets.

	Diffuse Exponents	Original Basis	Diffuse Functions Heavy Atoms	Diffuse Functions Hydrogens	D-orbitals
4-31+G	A	4-31G	yes	no	no
3-21+G	B	3-21G	yes	no	no
3-21++G	B	3-21G	yes	yes	no
6-21+G	B	6-21G	yes	no	no
6-21++G	B	6-21G	yes	yes	no
6-31+G*	B	6-31G*	yes	no	yes

**Table III.** Total 3-21+G//3-21+G energies, in atomic units.

X	X <sup>-</sup>	XH
H <sup>a</sup>	-0.48556	-1.12346
Li	-7.37691	-7.93019
BeH	-15.03897	-15.67455
BH <sub>2</sub>	-25.56422	-26.23846
CH <sub>3</sub>	-39.29075	-39.97871
NH <sub>2</sub>	-55.22658	-55.89249
OH	-74.99575	-75.61934
F	-98.93366	-99.50608
LiO	-81.77907	-82.49144
C <sub>2</sub> H	-75.79616	-76.40476
CN	-91.80801	-92.36804
CH <sub>3</sub> NH	-94.03057	-94.69921
CH <sub>3</sub> O	-113.80343	-114.42608
O <sub>2</sub>	-148.82607	-149.41083
HO <sub>2</sub>	-149.40105	-149.98373
CH <sub>2</sub> CH	-130.59483	-131.20689
CH <sub>2</sub> CHO	-151.48766	-152.07988
CH <sub>3</sub> CH <sub>2</sub> O	-152.63189	-153.25219
HCOO	-187.19184	-187.74062
N <sub>3</sub>	-162.35709	-162.90799
NO <sub>2</sub>	-202.98520	cis: -203.51572 trans: -203.51711
BF <sub>2</sub>	-222.48576	-223.10557
CH <sub>3</sub> COO	-226.01931	-226.57629
CH <sub>2</sub> NO <sub>2</sub>	-241.77186	-242.31739
NO <sub>3</sub>	-277.41201	-277.90186

<sup>a</sup> With diffuse function on hydrogen.

to be an acceptable procedure to use 4-31G or 3-21G optimized geometries for single-point calculations with diffuse-augmented basis sets, although some exceptional anions, such as CH<sub>2</sub>Li<sup>-</sup>, have different structures at the two levels.<sup>1b</sup>

### Energy Lowerings

The lowering of the calculated total energy of a molecule or ion on extension of the basis set can be used to test the adequacy of the original basis (i.e., extension of a basis set which is close to the Hartree-Fock limit does not lower the total energy significantly, but smaller basis sets can be drastically improved by the addition of extra basis functions). Table V shows the energy lowerings for the XH<sub>n</sub> and XH<sub>n-1</sub> species (X = Li-F), on addition of diffuse functions to the nonhydrogen atoms (3-21G → 3-21+G and 4-31G → 4-31+G) and on the further addition of hydrogen diffuse functions (3-21+G → 3-21++G).

As found previously,<sup>1b</sup> energy lowerings are modest for the neutral molecules where X = Li-C, but larger for NH<sub>3</sub>, H<sub>2</sub>O, and HF, which have nonbonding lone pairs. The energy lowerings for these three molecules on going from 3-21G to 3-21+G are 2-3 times larger than those for 4-31G → 4-31+G, suggesting that the larger 4-31G basis set describes electronegative elements significantly better than 3-21G. (However, results using larger basis sets, such as 6-31G\* and even 6-311G\*\*, are also improved by the addition of diffuse orbitals to N, O, and F.<sup>18</sup>)

The anions all show larger energy lowerings, the smallest being found for CH<sub>2</sub>Li<sup>-</sup> and the largest for CH<sub>2</sub>F<sup>-</sup>. As for the neutral compounds, the energy lowerings are particularly large for X = N, O, and F for 3-21G → 3-21+G, but smaller for 4-31G → 4-31+G. The two basis sets are comparable for CH<sub>3</sub>CH<sub>2</sub><sup>-</sup>, but 4-31G → 4-31+G shows very large energy lowerings for X = Li, Be, and B. This may be a manifestation of the "falling in"<sup>9</sup> of the 4-31G basis set (5-21G for Li and Be<sup>16</sup>) in the original optimization. The addition of diffuse s functions to hydrogen (3-21+G → 3-21++G) is only important for the hydride ion. Omission of the extra hydrogen functions is justified for most applications.

### Inversion Barriers

As shown in Table VI, the inversion barriers of CH<sub>3</sub><sup>-</sup> and NH<sub>3</sub> are decreased dramatically by the inclusion of diffuse functions. However, this amplifies the serious underestimation of the experimental NH<sub>3</sub> barrier already given by the unmodified split-valence basis sets (3-21G and 4-31G). The inclusion of polarization functions (6-31G\*) is necessary in order to obtain reliable NH<sub>3</sub> inversion barriers<sup>19,20</sup>; the 6-31+G\*\*//6-31+G\* value, which includes both diffuse and polarization functions, is 5.5 kcal/mol. With correlation (MP2/6-31+G\*\*//6-31+G\*), a 5.0 kcal/mol barrier is found.

While no experimental CH<sub>3</sub><sup>-</sup> inversion barrier is known, very high levels of theory give 1-2 kcal/mol.<sup>1a,1b,4b,19</sup> The value at 6-31+G\*\*//6-31+G\* is 3.1 kcal/mol. Taking the MP2/6-31+G\*\*//6-31+G\* value (2.4 kcal/mol) in Table VIII as the reference standard, it is clear that barriers given by nondiffuse orbital-augmented basis sets are too large. This is also true for the inversion barrier of the vinyl anion and the rotation barrier of the allyl anion.<sup>1a,21</sup>

**Table IV.** Optimized geometries of anions.<sup>a,b</sup>

Anion	Param.		STO-3G <sup>b</sup>	3-21G	6-31G*	3-21+G	Exper.
OH <sup>-</sup>	C <sub>∞v</sub>	r <sub>OH</sub>	1.068	1.029	0.962	0.978	0.97
NH <sub>2</sub> <sup>-</sup>	C <sub>2v</sub>	r <sub>NH</sub>	1.080	1.066	1.029	1.029	1.03
		<HNN	95.2	98.0	99.2	105.9	104
FHF <sup>-</sup>	D <sub>∞h</sub>	r <sub>FH</sub>	1.111	1.145	1.127	1.152	1.13-1.14
BH <sub>4</sub> <sup>-</sup>	T <sub>d</sub>	r <sub>BH</sub>	1.176	1.241	1.243	1.244	1.25
BF <sub>4</sub> <sup>-</sup>	T <sub>d</sub>	r <sub>BF</sub>	1.395	1.403	1.393	1.428	1.40-1.43
CN <sup>-</sup>	C <sub>∞v</sub>	r <sub>CN</sub>	1.162	1.166	1.161	1.171	1.15
N <sub>3</sub> <sup>-</sup>	D <sub>∞h</sub>	r <sub>NN</sub>	1.202	1.176	1.156	1.177	1.12-1.18
NO <sub>2</sub> <sup>-</sup>	C <sub>2v</sub>	r <sub>NO</sub>	1.294	1.286	1.228	1.285	1.24
		<ONO	114.3	116.4	116.7	116.5	115.4
NO <sub>3</sub> <sup>-</sup>	D <sub>3h</sub>	r <sub>NO</sub>	1.315	1.283	1.226	1.286	1.22-1.27
HCOO <sup>-</sup>	C <sub>2v</sub>	r <sub>CO</sub>	1.266	1.249	1.231	1.266	1.24-1.25
		r <sub>CH</sub>	1.152	1.125	1.127	1.103	-
		<OCO	130.4	130.7	131.0	129.6	126.3
CH <sub>3</sub> COO <sup>-</sup>	C <sub>s</sub>	r <sub>CC</sub>	1.631	1.576	1.543 <sup>c</sup>	1.546	1.53
		r <sub>CO</sub>	1.263	1.250	1.256 <sup>c</sup>	1.268	1.25
		r <sub>CH</sub>	1.087	1.085	1.084 <sup>c</sup>	1.085	-
		<OCO	130.5	129.8	130.4 <sup>c</sup>	127.9	125.7
		<HCC	111.4	110.5	110.0 <sup>c</sup>	110.9	-
NCN <sup>2-</sup>	D <sub>∞h</sub>	r <sub>NC</sub>	1.234	1.240 <sup>c</sup>	-	1.242	1.25
CO <sub>3</sub> <sup>2-</sup>	D <sub>3h</sub>	r <sub>CO</sub>	1.330	1.305 <sup>c</sup>	-	1.318	1.29

<sup>a</sup> All distances in Ångströms, angles in degrees.<sup>b</sup> All data, except 3-21+G, are taken from refs. 2a, 3, 17, and W. Hehre, private communication.<sup>c</sup> At 4-31G//4-31G. For other 4-31G values, see refs. 2a, 3.

## Proton Affinities

Split-valence basis sets without diffuse functions cannot describe anions adequately and overestimate proton affinities.<sup>1a,1b,4</sup> Table VII

compares 4-31G, 4-31+G, 3-21G, and 3-21+G proton affinities. The two basis sets with diffuse functions are in considerably better agreement than 3-21G or 4-31G. The estimated zero-point energy corrections, needed because theoretical

**Table V.** Energy lowerings (kcal/mol) due to addition of diffuse orbitals (geometries optimized at all levels indicated).

X	3-21G+3-21+G		3-21+G+3-21++G <sup>a</sup>		4-31G+4-31+G	
	XH	X <sup>-</sup>	XH	X <sup>-</sup>	XH	X <sup>-</sup>
H	-	-	0.3	53.4	0.1 <sup>a</sup>	40.2 <sup>a</sup>
Li	0.2	6.4	0.5	-	0.3	18.2
BeH	0.5	19.0	0.3	1.6	0.8	37.3
BH <sub>2</sub>	0.7	21.6	0.0	0.4	0.5	31.6
CH <sub>3</sub>	1.1	32.2	0.1	0.4	0.7	30.4
NH <sub>2</sub>	12.7	56.8	0.2	0.6	5.3	32.6
OH	21.0	79.8	0.3	0.9	6.6	37.9
F	28.8	101.4	0.5	-	9.8	49.2

<sup>a</sup> Diffuse functions on all hydrogen atoms are included.

**Table VI.** Inversion barriers of  $\text{CH}_3^-$  and  $\text{NH}_3$  (kcal/mol).

	3-21G// 3-21G	3-21+G// 3-21+G	4-31G// 4-31G	4-31+G// 4-31+G	6-31G*// 6-31G*	6-31+G*// 6-31+G*	Best
$\text{CH}_3^-$	9.1	0.9	8.1	0.5	13.0	3.1	2.4 <sup>a</sup>
$\text{NH}_3$	1.6	0.5	0.4	0.2	6.5	5.5	5.8 <sup>b</sup>

<sup>a</sup> MP2/6-31+G\*//6-31+G\* (see text).<sup>b</sup> Experimental value, J. D. Swalen and J. A. Ibers, *J. Chem. Phys.*, **36**, 1914 (1962). The MP2/6-31+G\*//6-31+G value is 5.0 kcal/mol.**Table VII.** Calculated and experimental proton affinities (kcal/mol).

Base	4-31G <sup>a</sup>	4-31+G <sup>a</sup>	3-21G	3-21+G	ZPE Corr. <sup>a,b</sup>	Exper. <sup>c</sup>
$\text{H}^-$	442.0	401.8	453.4	400.3	6.3	400.4
$\text{Li}^-$		347.6	353.3	347.2	1.9	355.6
$\text{BeH}^-$		400.0	417.3	398.8		(388)
$\text{BH}_2^-$		424.9	443.9	423.1		(355 <sup>±</sup> 25)
$\text{CH}_3^-$	463.1	433.5	462.8	431.7	8.0	416.6
$\text{NH}_2^-$	448.6	421.2	462.0	417.9	7.3	403.6
$\text{OH}^-$	426.0	394.6	450.1	391.3	6.2	390.8
$\text{F}^-$	401.3	361.9	431.8	359.2	4.8	371.5
$\text{LiO}^-$	457.1	450.9	456.1	447.0		(448 <sup>±</sup> 15 <sup>d</sup> )
$\text{HCC}^-$	408.3	385.6	405.4	381.9		375.4
$\text{CN}^-$	374.2	354.2	379.1	351.4		353.1
$\text{CH}_3\text{NH}^-$	441.6	422.6	-	419.6		403.2
$\text{CH}_3\text{O}^-$	409.0	393.1	-	390.7		379.2
$\text{O}_2^-$			-	366.9		350.6 <sup>±</sup> 2.2
$\text{HOO}^-$			-	365.6		367.9 <sup>d</sup>
$\text{CH}_2\text{CN}^-$	402.2	386.1	-	384.1		372.2
$\text{CH}_2\text{CHO}^-$	391.3	374.5	-	371.6		366.4
$\text{CH}_3\text{CH}_2\text{O}^-$	410.5	391.7	-	389.2		376.1
$\text{HCOO}^-$	359.9	346.9	-	344.4		345.2
$\text{N}_3^-$			-	345.7		344 <sup>±</sup> 2 <sup>e</sup>
$\text{NO}_2^-$			cis: 332.9 trans: 333.8			338.3 <sup>±</sup> 8 <sup>f</sup>
$\text{BF}_2^-$			-	388.9		(404 <sup>±</sup> 31)
$\text{CH}_3\text{COO}^-$			-	349.5		348.5
$\text{CH}_2\text{NO}_2^-$	361.1	350.5	-	342.3		358.7
$\text{NO}_3^-$			-	307.4		324.6

<sup>a</sup> From refs. 1a and 17, unless indicated otherwise.<sup>b</sup> Zero-point energy corrections to be subtracted from the calculated energies for comparison with experimental values at OK. These corrections depend on the gain in vibrational frequencies on formation of a new bond in going from an anion to the protonated neutral. Values on the order of 6–8 kcal/mol are expected for the CH, NH, and OH bonds in the cases listed.<sup>c</sup> Reference 11.<sup>d</sup> Reference 12.<sup>e</sup> M. J. Pellerite, R. L. Jackson, and J. I. Brauman, *J. Phys. Chem.*, **85**, 1624 (1981).<sup>f</sup> Values for cis and trans forms. The JANAF PAs (ref. 12) are much smaller, 298.4 ± 14 and 298.9 ± 12 kcal/mol, and appear to be in error.

**Table VIII.** Calculated and experimental fluoride affinities.

Acid	$D(M-F^-)$ , kcal/mol		Ref.
	3-21+G	Exper.	
HF	50.8	50.7 av	22
H <sub>2</sub> O	28.7	23.3	a
H <sub>3</sub> N	14.1	2 <sup>±</sup> 1	21
HCN	40.0	48 <sup>±</sup> 2	21
CO <sub>2</sub>	38.9	33 <sup>±</sup> 3	23
F <sub>2</sub> CO	62.5	35 <sup>±</sup> 3 <sup>b</sup>	23
LiF	75.5	26.5 <sup>±</sup> 15	12

<sup>a</sup> M. Arshadi, R. Yamdagni, and P. Kebarle, *J. Phys. Chem.*, **74**, 1475 (1970).

<sup>b</sup> May be up to 19 kcal/mol higher (see text).

calculations refer to the hypothetical motionless state, bring a further improvement.

The examples in Table VII were chosen to encompass the entire range of proton affinities (PAs) available from the literature. The value of LiO<sup>-</sup> from the JANAF Tables,<sup>12</sup> 448 ± 15 kcal/mol, while only approximate, is the highest known for any first-row anion. The CH<sub>3</sub><sup>-</sup> PA value, 416.6 kcal/mol, is the highest listed by Bartmess and McIver<sup>11</sup>; their lowest anion value is 324.6 kcal/mol (for NO<sub>3</sub><sup>-</sup>).

The 4-31G results in Table VII show a 30.5-kcal/mol mean deviation between theory and experiment. The more limited 3-21G results are even worse (42 kcal/mol). With only one exception (Li<sup>-</sup>), all 4-31G and 3-21G PAs are too high, indicating the systematic nature of the error. (The values in parentheses were omitted in these evaluations because of large uncertainties in the experimental values.) In contrast, the mean deviations are reduced to 5.6 kcal/mol at 4-31+G and to only 3.1 kcal/mol at 3-21+G. The slope of the 3-21+G least-squares line is 1.25 and the correlation coefficient is 0.96. The calculated values used for these analyses are uncorrected for zero-point energy changes which would lead to an average reduction of 6–8 kcal/mol (see Table VII, footnote b). While still better agreement with experiment can be achieved at higher levels of theory, the relatively small and efficient 3-21+G basis performs satisfactorily. The addition of a diffuse *s* function to the hydrogen basis set is necessary to describe H<sup>-</sup> adequately.

## Fluoride Affinities

Only a few experimental data are available for fluoride affinities,  $D(M-F^-)$ , of small first-row molecules,<sup>21</sup> and many values do not appear to be well established.<sup>22,23</sup> For example, experimental estimates of the F<sup>-</sup> affinity of HF range from 30<sup>22c</sup>–60 kcal/mol.<sup>23</sup> The “average of all reported values,” 50.7 kcal/mol,<sup>23</sup> agrees fortuitously with the 3-21+G//3-21+G estimate, 50.8 kcal/mol. Table VIII lists other comparisons between theory and experiment. (Zero-point corrections, which will reduce the calculated values, have not been included.) The values for H<sub>2</sub>O, HCN, and CO<sub>2</sub><sup>25</sup> agree moderately well, but the experimental  $D(M-F^-)$  data for H<sub>3</sub>N, F<sub>2</sub>CO, and LiF are much lower than the calculations indicate. A large uncertainty is listed for the experimental  $D(\text{FLi}-F^-)$  value<sup>12</sup> and  $D(\text{OCF}_2-F^-)$  is in doubt. The upper limit for the latter was based on  $D(\text{O}_2\text{S}-F^-) = 40$  kcal/mol,<sup>24</sup> but this value has been revised upward to 59 kcal/mol more recently.<sup>25</sup> Therefore, 3-21+G may well be suitable for the calculation of fluoride affinities including hydrogen bonding of weak acids to F<sup>-</sup>. Further examples will be published subsequently.

## OTHER APPLICATIONS

As is well known,<sup>4</sup> diffuse functions also are needed to describe Rydberg and other excited states. While the recommended exponents in Table I were not developed for this purpose and may not be ideal, they may afford some advantages. We have not yet examined such applications.

The relatively large diffuse-function energy lowerings for nitrogen, oxygen, and fluorine compounds in Table V (3-21G → 3-21+G) and (4-31G → 4-31+G), and in an earlier paper<sup>1b</sup> for higher levels (6-31+G\* and MP2/6-31+G\*), indicate that lone-pair electrons are not fully described with the standard basis sets, 3-21G, 4-31G, and 6-31G\*. Thus, results for N-, O-, and F-containing molecules can be improved by adding diffuse functions to the basis sets.<sup>18</sup> The same may be true for  $\pi$  (multiply-bonded) systems. We will report the results of such examinations in future.

Because of differences in multiplicity, it is not possible to calculate electron affinities of anions directly at lower theoretical levels which neglect corrections for electron correlation.<sup>1a,4</sup> However, electron-affinity estimates can be made indirectly in some cases by use of equations which balance

the number of lone-pair and unpaired electrons. We will present such applications subsequently.

## RECOMMENDATIONS

In order to standardize procedures as much as possible, we follow the current practice of the Pople school<sup>17</sup> to replace 4-31G and 4-31+G by the more efficient 3-21G and 3-21+G bases, respectively, which give results of similar quality. We also recommend the use of a single set of diffuse orbital exponents—the 6-21G derived values (set B in Table I)—for use with all augmented basis sets, e.g., 3-21+G, 6-31+G\*, etc.

## CONCLUSIONS

The addition of a set of diffuse *sp* functions to small split-valence basis sets improves anion energy calculations dramatically at a cost of about 50% extra computer time for geometry optimizations. Proton affinities are reproduced within about 5 kcal/mol<sup>-1</sup> for small anions with either the 4-31+G or 3-21+G basis sets when zero-point energy corrections are included. Systematic errors for anions inherent in basis sets lacking diffuse functions are eliminated.

Although some exceptions are noted, geometries do not usually change dramatically upon the addition of diffuse functions. For many applications, 3-21G geometries may be used, for e.g., 3-21+G single-point calculations.

A diffuse *s* function on hydrogen is only necessary for the calculation of energies involving the hydride ion. Such H-diffuse functions lead to considerable increases in computer time in other cases with no significant improvement of results.

We recommend replacement of the 4-31+G by the more efficient 3-21+G basis set. A single, standard set of diffuse exponents should be used to augment all basis sets.

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