

# On the Additivity of Basis Set Effects in Some Simple Fluorine Containing Systems

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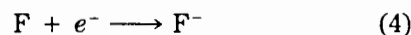
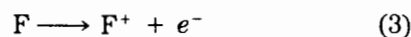
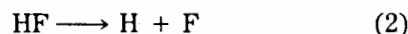
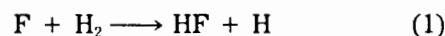
Received 5 November 1990; accepted 9 February 1991

The reactions  $F + H_2 \rightarrow HF + H$ ,  $HF \rightarrow H + F$ ,  $F \rightarrow F^+ + e^-$  and  $F + e^- \rightarrow F^-$  were used as simple test cases to assess the additivity of basis set effects on reaction energetics computed at the MP4 level. The 6-31G and 6-311G basis sets were augmented with 1, 2, and 3 sets of polarization functions, higher angular momentum polarization functions, and diffuse functions (27 basis sets from 6-31G(*d*, *p*) to 6-31++G(3*df*, 3*pd*) and likewise for the 6-311G series). For both series substantial nonadditivity was found between diffuse functions on the heavy atom and multiple polarization functions (e.g., 6-31+G(3*d*, 3*p*) vs. 6-31+G(*d*, *p*) and 6-31G(3*d*, 3*p*)). For the 6-311G series there is an extra nonadditivity between *d* functions on hydrogen and multiple polarization functions. Provided that these interactions are taken into account, the remaining basis set effects are additive to within  $\pm 0.5$  kcal/mol for the reactions considered. Large basis set MP4 calculations can also be estimated to within  $\pm 0.5$  kcal/mol using MP2 calculations, est.  $E_{MP4}(6-31++G(3df, 3pd)) \approx E_{MP4}(6-31G(d, p)) + E_{MP2}(6-31++G(3df, 3pd)) - E_{MP2}(6-31G(d, p))$  or  $E_{MP4}(6-31+G(d, p)) + E_{MP2}(6-31++G(3df, 3pd)) - E_{MP2}(6-31+G(d, p))$  and likewise for the 6-311G series.

## INTRODUCTION

Ideally one would like to carry out electronic structure calculations with basis sets large enough to assure that the properties of interest are appropriately converged. Since calculations with larger and larger basis sets quickly become prohibitively expensive, it is common to assume that the effects of various types of basis sets extensions are roughly additive (see references<sup>1-8</sup> for some examples). In the course of studying the heats of formation of  $SiH_nF_m$  and related compounds,<sup>9</sup> we became acutely aware of problems with the non-additivity of the basis set effects for fluorine containing compounds. Other atoms seem to be far less sensitive to additivity problems. Hence, simple reactions involving fluorine may be important limiting cases for studying basis set effects. The energetics for the reaction  $F + H_2 \rightarrow HF + H$  are notoriously difficult to compute accurately and basis set effects for this reaction have been studied by a number of groups (for leading references see 10 and 11). Bond dissociation energies and electron affinities are also known to be very sensitive to basis set size (for example references 1, 2, 12, 13). Since the energetics of these reactions are particularly difficult to compute accurately, they can serve as useful tests for the additivity of basis set effects in more general systems.

In this short note, we compare a number of additivity schemes for the energetics of the following reactions,



at the Hartree-Fock level and with electron correlation energy computed by Møller-Plesset perturbation theory<sup>14</sup> up to fourth order. Various schemes for basis set additivity for reaction (1) have been studied previously.<sup>1-8</sup> The present article extends this work by exploring the details of the additivity/nonadditivity of incremental enhancements of the 6-31G and 6-311G\* basis sets and examining the extent to which basis set expansion and improvements in the treatment of correlation corrections are additive. A number of new additivity schemes are suggested.

## THEORETICAL METHODS

All calculations were carried out with the Gaussian 88 system of programs<sup>15</sup> using standard, built-in basis sets.<sup>16-19</sup> The HF/6-31G(*d*) optimized geometries were used for  $H_2$  ( $R = 0.72996 \text{ \AA}$ ) and HF ( $R = 0.91096 \text{ \AA}$ ). Larger basis sets were constructed from the 6-31G split valence<sup>16</sup> and 6-311G<sup>17</sup> triple split valence basis sets by adding diffuse functions<sup>18</sup> (e.g., 6-

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311+G for a set of diffuse *sp* functions on heavy atoms and 6-311++G for diffuse *s* functions on hydrogen as well as diffuse *sp* functions on heavy atoms), several sets of first polarization functions<sup>19</sup> (e.g., three sets of *d* functions on heavy atoms and three sets of *p* functions on hydrogens, 6-311G(3*d*, 3*p*)), and higher angular momentum polarization functions<sup>19</sup> (e.g., a set of *f* functions on heavy atoms and *d* functions on hydrogens, 6-311G(3*df*, 3*pd*)). Note that 6*d* functions are used with the 6-31G series whereas 5*d* functions are used with the 6-311G series; both series use 7*f* functions. A total of 27 basis sets were used in the 6-31G series, ranging from 6-31G(*d*, *p*) to 6-31++G(3*df*, 3*pd*); likewise 27 different basis sets were used in the 6-311G series. Correlation corrections were calculated by Møller-Plesset perturbation theory to fourth order including triple substitutions (MP4SDTQ) with the 1*s* core orbital of F frozen.

## RESULTS AND DISCUSSION

The total energies for F, H, H<sub>2</sub>, and HF calculated at HF, MP2, MP3, and MP4 levels with different basis sets are collected in Tables I-III. Using these Tables, various schemes can be devised to mimic a large basis set calculation by combining smaller computations that separately probe different types of basis set extensions. One family of schemes for estimating the energy for a large basis set calculation is

$$\text{estimated } E(\text{large basis}) = E(\text{reference basis set}) + \{E(\text{extra first polarization functions})\}$$

**Table II.** Total energies for hydrogen molecule.<sup>a,b</sup>

H <sub>2</sub>	<i>d</i> , <i>p</i>	2 <i>d</i> , 2 <i>p</i>	3 <i>d</i> , 3 <i>p</i>
6-31G			
HF	-1.13133	-1.13195	-1.13213
MP2	-1.15765	-1.16112	-1.16167
MP3	-1.16314	-1.16709	-1.16763
MP4	-1.16454	-1.16859	-1.16912
6-31++G			
HF	-1.13140	-1.13204	-1.13230
MP2	-1.15776	-1.16122	-1.16184
MP3	-1.16325	-1.16719	-1.16779
MP4	-1.16466	-1.16869	-1.16927
6-311G			
HF	-1.13249	-1.13299	-1.13304
MP2	-1.16027	-1.16273	-1.16301
MP3	-1.16623	-1.16865	-1.16885
MP4	-1.16772	-1.17014	-1.17035
6-311++G			
HF	-1.13250	-1.13301	-1.13305
MP2	-1.16030	-1.16280	-1.16304
MP3	-1.16627	-1.16875	-1.16889
MP4	-1.16776	-1.17026	-1.17038

<sup>a</sup>In Hartrees, 6-31+G energies are the same as 6-31G; 6-311+G energies are the same as 6-311G; MP4SDQ energies are the same as MP4SDTQ.

<sup>b</sup>The energies of hydrogen atom are -0.49823, -0.49880, -0.49981 and -0.49982 Hartree with the 6-31G, 6-31++G, 6-311G and 6-311++G basis sets respectively.

$$\begin{aligned} & - E(\text{reference basis set}) \\ & + \{E(\text{extra second polarization functions})\} \\ & - E(\text{reference basis set}) \\ & + \{E(\text{extra diffuse functions})\} \\ & - E(\text{reference basis set}) \end{aligned} \quad (5)$$

For example, a medium size basis set such as 6-31G(*d*, *p*) can be augmented with extra polarization

**Table I.** Total energies for fluorine atom (Hartrees).<sup>a</sup>

F	<i>d</i>	<i>df</i>	2 <i>d</i>	2 <i>df</i>	3 <i>d</i>	3 <i>df</i>
6-31G						
HF	-99.36496	-99.36610	-99.36617	-99.36735	-99.36652	-99.36770
MP2	-99.48727	-99.50382	-99.51897	-99.53929	-99.52839	-99.54824
MP3	-99.49569	-99.51397	-99.52928	-99.55151	-99.53879	-99.56048
MP4SDQ	-99.49745	-99.51571	-99.53055	-99.55266	-99.53967	-99.56125
MP4SDTQ	-99.49865	-99.51715	-99.53231	-99.55488	-99.54171	-99.56375
6-31+G						
HF	-99.37165	-99.37276	-99.37340	-99.37454	-99.37303	-99.37417
MP2	-99.49882	-99.51512	-99.53085	-99.55087	-99.53946	-99.55903
MP3	-99.50669	-99.52467	-99.54055	-99.56244	-99.54922	-99.57059
MP4SDQ	-99.50913	-99.52699	-99.54243	-99.56408	-99.55064	-99.57179
MP4SDTQ	-99.51087	-99.52897	-99.54481	-99.56692	-99.55330	-99.57491
6-311G						
HF	-99.39687	-99.39801	-99.39754	-99.39870	-99.39765	-99.39882
MP2	-99.55417	-99.57469	-99.57314	-99.59321	-99.57596	-99.59666
MP3	-99.56252	-99.58470	-99.58222	-99.60406	-99.58492	-99.60737
MP4SDQ	-99.56375	-99.58569	-99.58327	-99.60488	-99.58599	-99.60816
MP4SDTQ	-99.56534	-99.58767	-99.58580	-99.60790	-99.58894	-99.61161
6-311++G						
HF	-99.39989	-99.40101	-99.40055	-99.40169	-99.40066	-99.40181
MP2	-99.55959	-99.58000	-99.57860	-99.59856	-99.58154	-99.60212
MP3	-99.56749	-99.58954	-99.58721	-99.60892	-99.58999	-99.61230
MP4SDQ	-99.56912	-99.59086	-99.58859	-99.60999	-99.59144	-99.61340
MP4SDTQ	-99.57112	-99.59325	-99.59155	-99.61344	-99.59484	-99.61731

<sup>a</sup>6-31++G energies are the same as 6-31+G; 6-311++G energies are the same as 6-311+G.

**Table III.** Total energies of hydrogen fluoride (Hartrees).

HF	<i>d, p</i>	<i>df, p</i>	<i>2d, 2p</i>	<i>2df, 2p</i>	<i>3d, 3p</i>	<i>3df, 3p</i>
6-31G						
HF	-100.01155	-100.01245	-100.01530	-100.01628	-100.02049	-100.02130
MP2	-100.19451	-100.21283	-100.23322	-100.25532	-100.25181	-100.27313
MP3	-100.19634	-100.21638	-100.23571	-100.25977	-100.25330	-100.27643
MP4SDQ	-100.19902	-100.21884	-100.23796	-100.26188	-100.25565	-100.27838
MP4SDTQ	-100.20131	-100.22147	-100.24163	-100.26593	-100.26043	-100.28375
6-31 + G						
HF	-100.02421	-100.02494	-100.02757	-100.02850	-100.02785	-100.02858
MP2	-100.21553	-100.23338	-100.25324	-100.27499	-100.26365	-100.28471
MP3	-100.21472	-100.23429	-100.25317	-100.27685	-100.26351	-100.28638
MP4SDQ	-100.21918	-100.23837	-100.25703	-100.28018	-100.26678	-100.28915
MP4SDTQ	-100.22271	-100.24223	-100.26206	-100.28579	-100.27240	-100.29536
6-31 ++ G						
HF	-100.02421	-100.02495	-100.02761	-100.02853	-100.02785	-100.02858
MP2	-100.21564	-100.23349	-100.25330	-100.27505	-100.26368	-100.28474
MP3	-100.21482	-100.23438	-100.25323	-100.27690	-100.26354	-100.28641
MP4SDQ	-100.21930	-100.23848	-100.25708	-100.28023	-100.26681	-100.28918
MP4SDTQ	-100.22283	-100.24235	-100.26114	-100.28585	-100.27242	-100.29538
6-311G						
HF	-100.04662	-100.04740	-100.04968	-100.05034	-100.05264	-100.05357
MP2	-100.26721	-100.28977	-100.29290	-100.31456	-100.30116	-100.32365
MP3	-100.26731	-100.29167	-100.29253	-100.31600	-100.29967	-100.32395
MP4SDQ	-100.27032	-100.29421	-100.29517	-100.31815	-100.30287	-100.32654
MP4SDTQ	-100.27421	-100.29861	-100.30073	-100.32433	-100.30955	-100.33386
6-311 + G						
HF	-100.05298	-100.05377	-100.05533	-100.05599	-100.05609	-100.05693
MP2	-100.27877	-100.30112	-100.30294	-100.32443	-100.30726	-100.32951
MP3	-100.27685	-100.30101	-100.30078	-100.32406	-100.30469	-100.32874
MP4SDQ	-100.28114	-100.30468	-100.30443	-100.32711	-100.30847	-100.33184
MP4SDTQ	-100.28610	-100.31016	-100.31098	-100.33428	-100.31571	-100.33972
6-311 ++ G						
HF	-100.05302	-100.05776	-100.05532	-100.05598	-100.05616	-100.05700
MP2	-100.27887	-100.30123	-100.30303	-100.32452	-100.30738	-100.32963
MP3	-100.27696	-100.30111	-100.30085	-100.32413	-100.30481	-100.32885
MP4SDQ	-100.28124	-100.30479	-100.30451	-100.32719	-100.30859	-100.33196
MP4SDTQ	-100.28621	-100.31027	-100.31107	-100.33437	-100.31583	-100.33984

functions, higher angular momentum polarization functions and diffuse functions to form the 6-31 ++ G(3df, 3pd) basis set and the energy could be estimated by

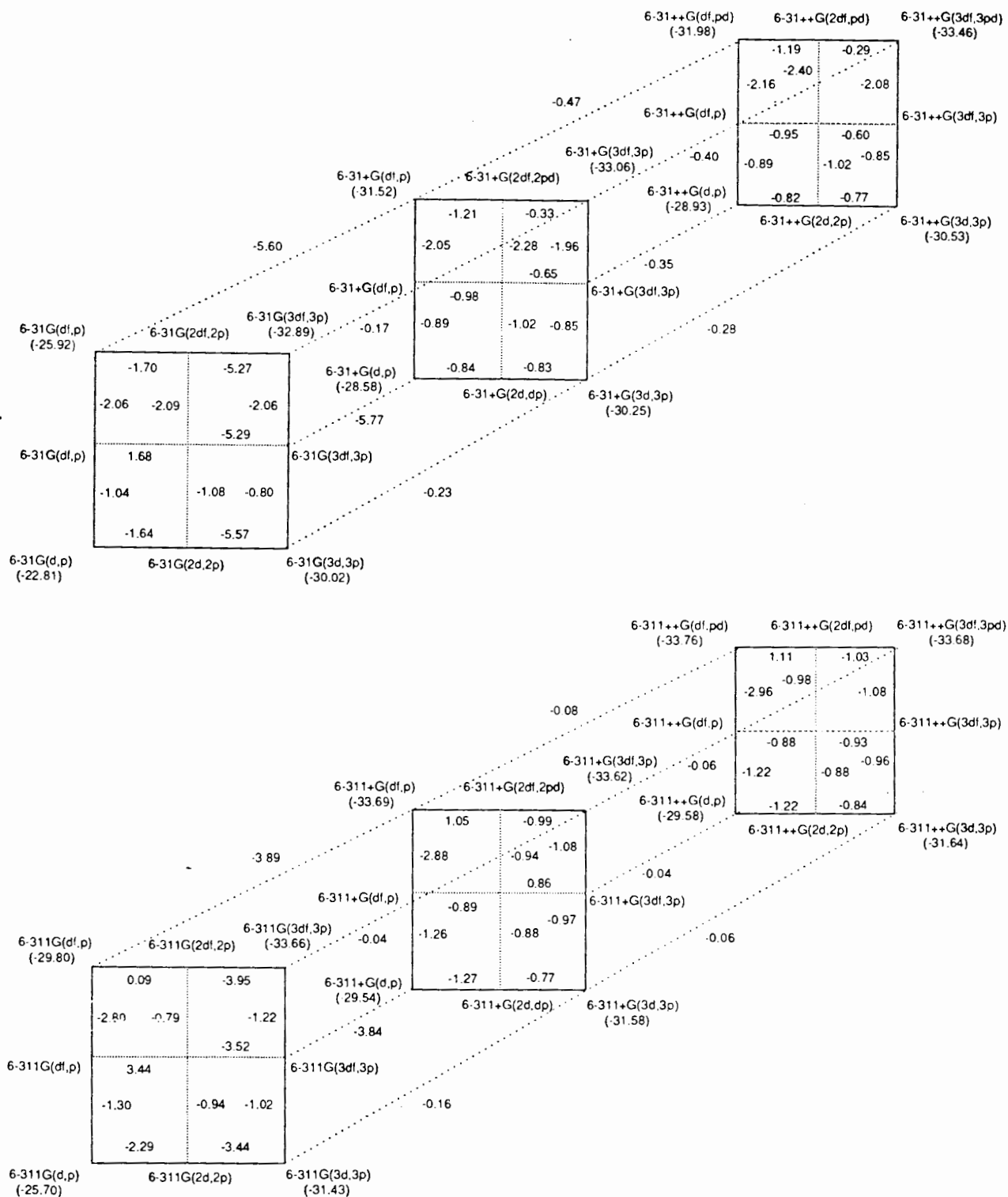
$$\begin{aligned}
 & \text{estimated } E(6-31 ++ G(3df, 3pd)) \\
 &= E(6-31G(d, p)) \\
 &+ \{E(6-31G(3d, 3p)) - E(6-31G(d, p))\} \\
 &+ \{E(6-31G(df, pd)) - E(6-31G(d, p))\} \\
 &+ \{E(6-31 ++ G(d, p)) - E(6-31G(d, p))\}
 \end{aligned} \quad (6)$$

A total of 20 different estimates of this type can be written for the 6-31G series and likewise for the 6-311G series. The accuracy of the estimates is judged by comparison with the full 6-31 ++ G(3df, 3pd) or 6-311 ++ G(3df, 3pd) calculations (it is not the purpose of this paper to test whether these basis sets are large enough to compute the energetics of the reaction to experimental accuracy).

Basis set effects on the energetics for reactions (1) through (4) are shown in Figures 1 to 4 for both the 6-31G series (top) and the 6-311G series (bottom) using the MP4 energies. Similar trends in the additivity/nonadditivity of basis set effects are found at the Hartree-Fock and MP2 levels. The three

types of basis set extensions considered are arranged in the form of rectangular box: multiple first polarization functions ((*d, p*), (*2d, 2p*) and (*3d, 3p*)—horizontal axis), higher angular momentum polarization functions (*f* on heavy atoms, *d* on hydrogen—vertical axis) and diffuse functions (*sp* on heavy atoms (+) and also *s* on hydrogens (++) — front to back in Figures 1–4). In addition to the computed reaction energy (in parentheses at selected vertices), Figures 1–4 also give the changes in the reaction energy as the basis sets are incremented.

The additivity or nonadditivity of basis set effects can be read directly from Figures 1–4. If the change in energy for a particular type of basis set increment does not depend on the other supplementary basis functions, then that increment is additive. For example, in reaction (1) with the 6-31G series, the effect of *f* functions on the heavy atom is relatively constant (–1.04, –1.08, –0.80, –0.89, –1.02, –0.85, –0.89, –1.02, –0.85 kcal/mol, i.e., the lower vertical segments in Figure 1(a)). Thus the effect of *f* functions on the reaction energy in a 6-31 ++ G(3df, 3pd) calculation could be computed as  $E(6-31G(df, p)) - E(6-31G(d, p))$  with little loss in accuracy.



**Figure 1.** MP4 energies for the reaction  $F + H_2 \rightarrow HF + H$  showing the effects of adding multiple first polarization functions (horizontal axis), higher angular momentum polarization functions (vertical axis), and diffuse functions (front to back). Energy differences for the reaction (in kcal/mol) are given in parentheses; values between the vertices indicate changes in the reaction energy as basis functions are added.

Likewise, the changes in energy due to *d* functions on hydrogen and diffuse functions on hydrogen are also additive.

For some basis set increments, the change in energy may depend dramatically on which other supplementary basis functions are present. For example,

in Figure 1(a) the effect of adding a third set of polarization functions depends strongly on whether or not diffuse functions are included for the heavy atom ( $-5.57$ ,  $-5.29$ ,  $-5.27$  kcal/mol without diffuse functions on F and  $-0.83$ ,  $-0.66$ ,  $-0.33$ ,  $-0.77$ ,  $-0.61$ ,  $-0.29$  kcal/mol with diffuse functions on F,

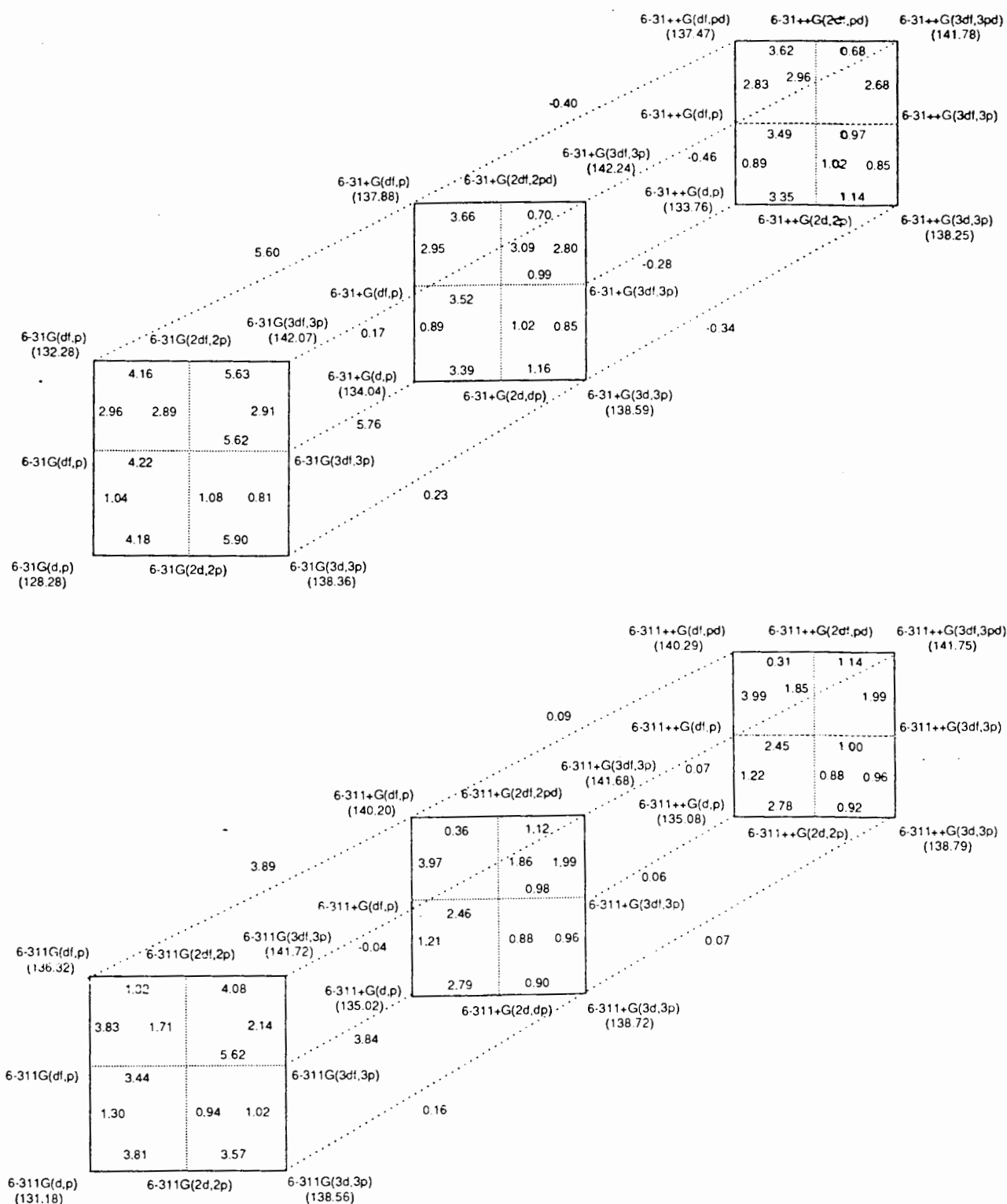


Figure 2. MP4 bond dissociation energies for HF (see caption of Figure 1 for details).

i.e. the rightmost horizontal segments in Figure 1(a). Hence,  $E(6-31G(3d, 3p)) - E(6-31G(2d, 2p)) = -5.57$  kcal/mol would be a very poor estimate of the importance of the third set of polarization functions in a  $6-31++G(3df, 3pd)$  calculation ( $-0.29$  kcal/mol when computed at the highest level). The nonadditivity in this case can be traced to the fact

that the third set of polarization functions is rather diffuse and spans part of the same space as the diffuse  $sp$  shell on the heavy atom. Similarly, the changes in energy due to the second set of polarization functions is not additive.

Reactions (1) and (2) show the same behavior for the 6-31G series: the energy changes due to diffuse

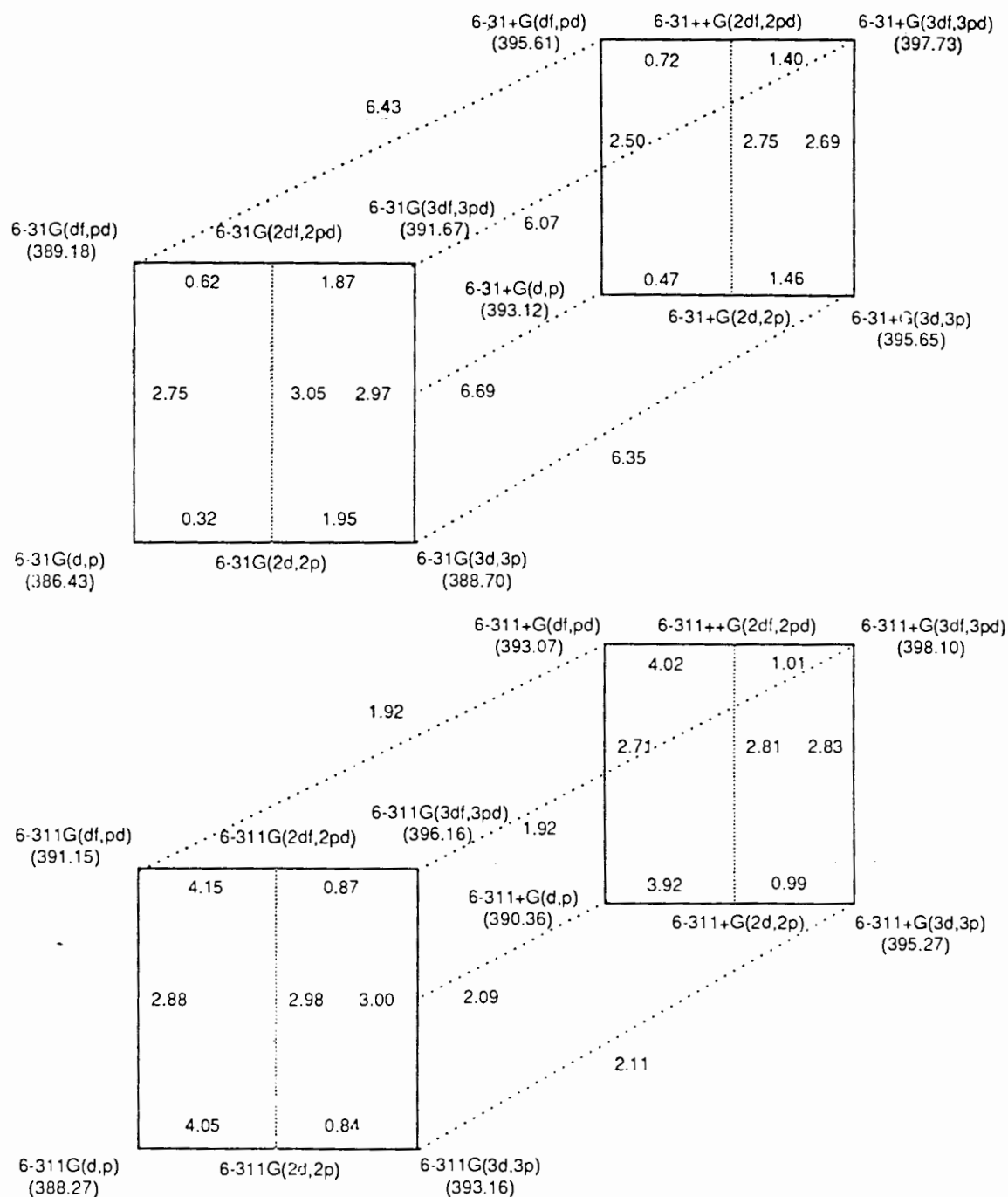


Figure 3. MP4 ionization potential for F (see caption of Figure 1 for details).

functions and multiple polarization functions are not additive and eq. (6) leads to an error of ca. 6 kcal/mol. The minimum additivity relationship must include heavy atom diffuse functions in the reference basis set; an error of 0.1 – 0.5 kcal/mol is obtained with eq. (7).

$$\begin{aligned} & \text{estimated } E(6-31++G(3df, 3pd)) \\ &= E(6-31+G(d, p)) \\ &+ \{E(6-31+G(3d, 3p)) \\ &- E(6-31+G(d, p))\} \\ &+ \{E(6-31+G(df, pd)) \end{aligned}$$

$$\begin{aligned} & - E(6-31+G(d, p))\} \\ &+ \{E(6-31++G(d, p)) \\ &- E(6-31+G(d, p))\} \end{aligned} \quad (7)$$

The effects of higher angular momentum polarization functions could also be estimated from  $E(6-31G(df, pd)) - E(6-31G(d, p))$  with very little loss in accuracy. Omission of the diffuse functions on hydrogen increases the error to 0.5 – 1.0 kcal/mol.

The trends with the 6-311G series are similar, but with one extra nonadditivity between multiple polarization functions and *d* functions on hydrogen.

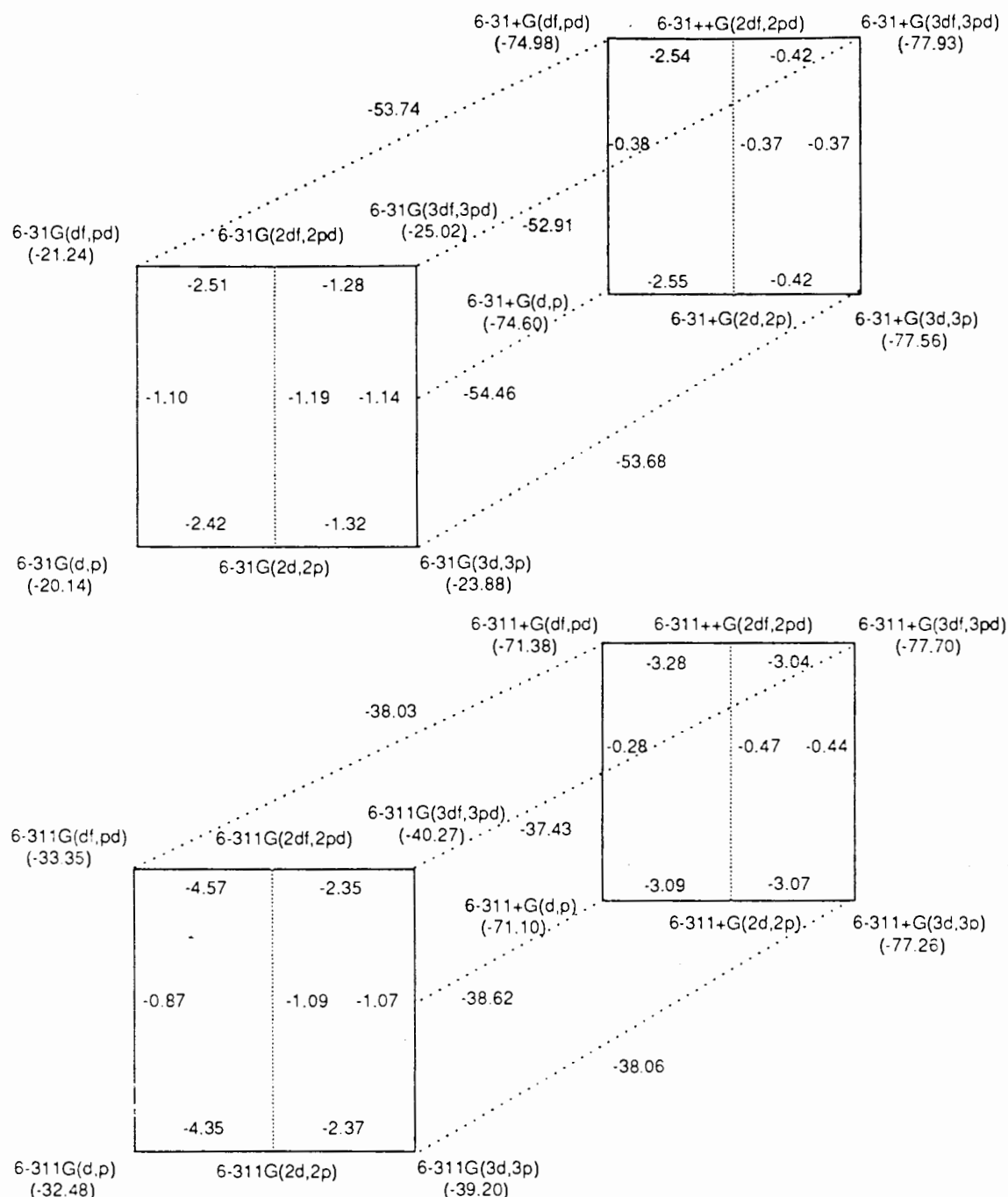


Figure 4. MP4 electron affinity for F (see caption of Figure 1 for details).

The simplest useful additivity relation in the spirit of eq. (5) is

$$\begin{aligned}
 & \text{estimated } E(6-311++G(3df, 3pd)) \\
 &= E(6-311+G(2d, 2p)) \\
 &+ \{E(6-311+G(3d, 3p)) \\
 &\quad - E(6-311+G(2d, 2p))\} \\
 &+ \{E(6-311+G(2df, 2pd)) \\
 &\quad - E(6-311+G(2d, 2p))\} \\
 &+ \{E(6-311++G(2d, 2p)) \\
 &\quad - E(6-311+G(2d, 2p))\}
 \end{aligned} \quad (8)$$

with an average error of 0.3 kcal/mol for reactions (1) and (2). Diffuse functions on hydrogen can be

omitted with almost no loss in accuracy. If the effects of higher angular momentum polarization functions are computed from  $E(6-311G(2df, 2pd)) - E(6-311G(2d, 2p))$ , the error increases only slightly.

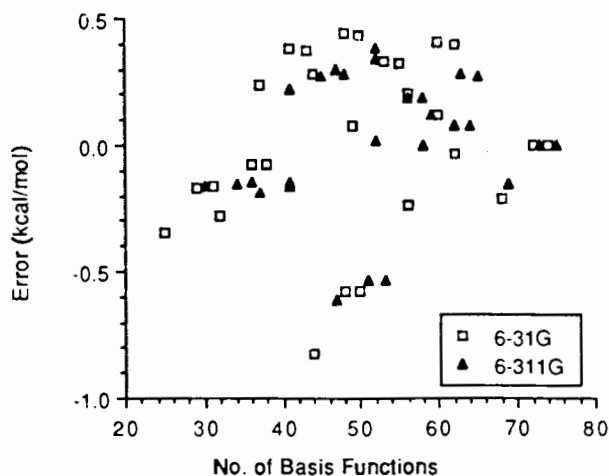
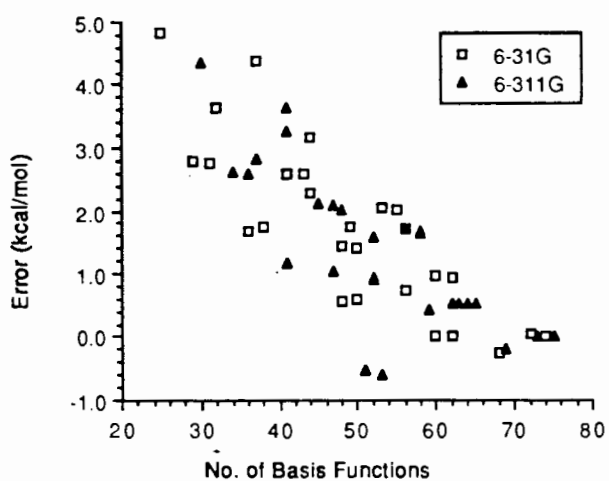
Fewer problems with the additivity of basis set effects are encountered for the IP and EA of fluorine, reactions (3) and (4). This is largely because these are one center problems and functions of different angular momentum are orthogonal. The average error with eq. (6) is 0.5 – 1.5 kcal/mol whereas with eq. (7) the error is 0.2 kcal/mol. For the 6-311G analogues, the errors are 0.8 and 0.1 kcal/mol, respectively.

Although eq. (6)–(8) provide useful estimates with

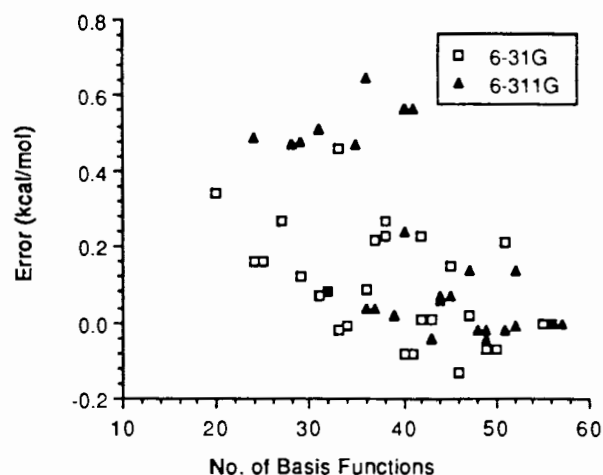
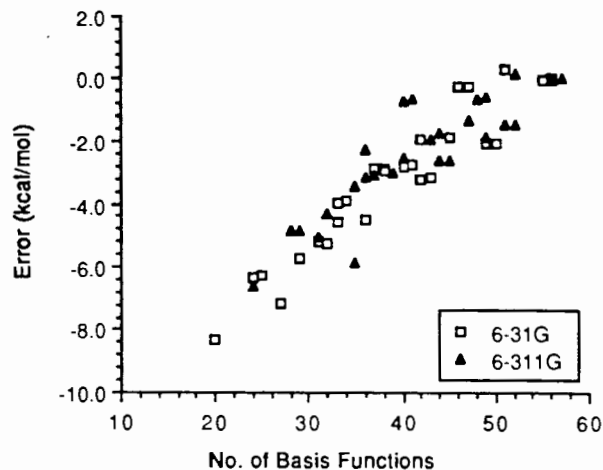
acceptably small errors, some of the calculations needed to make the estimates involve relatively large basis sets. This is a significant drawback at the MP4 level, since these scale with the seventh power of the basis set size. An alternative to eq. (5) at the MP4 level is to make use of basis set effects computed at the Hartree-Fock level or the MP2 level (which formally scale with the fourth and fifth power of the basis set size). The MP4 energy can be estimated by

$$\begin{aligned} & \text{estimated } E_{\text{MP4}}(\text{large basis}) \\ &= E_{\text{MP4}}(\text{reference basis set}) \\ &+ \{E_{\text{HF}}(\text{large basis}) \\ &- E_{\text{HF}}(\text{reference basis set})\} \quad (9) \end{aligned}$$

$$\begin{aligned} & \text{estimated } E_{\text{MP4}}(\text{large basis}) \\ &= E_{\text{MP4}}(\text{reference basis set}) \\ &+ \{E_{\text{MP2}}(\text{large basis}) \\ &- E_{\text{MP2}}(\text{reference basis set})\} \quad (10) \end{aligned}$$



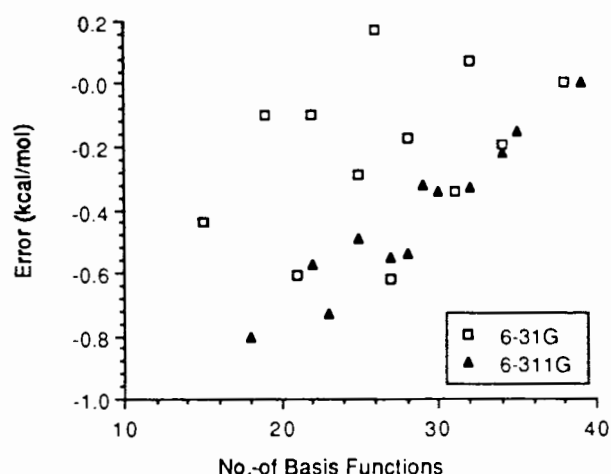
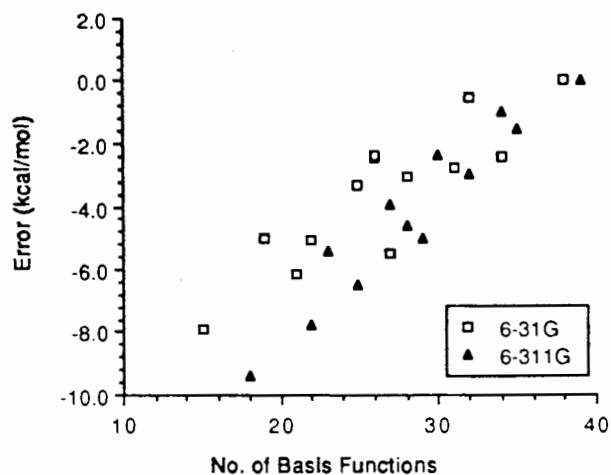
**Figure 5.** Error in the estimated MP4 energy for the reaction  $\text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H}$  using: (a) eq. (9) (effect of basis set expansion calculated at the Hartree-Fock level) and (b) eq. (10) (effect of basis set expansion calculated at the MP2 level) plotted versus the number of functions in the reference basis set.



**Figure 6.** Error in the estimated MP4 bond dissociation energies for HF using: (a) eq. (9) and (b) eq. (10) plotted versus the number of functions in the reference basis set.

A similar scheme has been used previously in the study of basis set effects on reaction (1).<sup>10</sup> The results obtained by using eq. (9) and (10) for reactions (1)–(4) are presented in Figures 5–8. One important feature readily apparent in these figures is that the range of errors is 10 times larger when the basis set effects are computed at the Hartree-Fock level as when they are computed at the MP2 level. This indicates that the Hartree-Fock level provides a poor estimate of the effect basis set expansion on MP4 calculations, but the MP2 level provides a reasonably good estimate. A second important feature is that when the Hartree-Fock level is used to estimate the basis set effects, the errors in the estimated energies decline steadily as the reference basis set is increased, whereas the errors are relatively constant when the MP2 level is used. This indicates that for these reactions the most important consequence of basis set expansion is not the improvement of the one electron orbitals, but the increase in the number





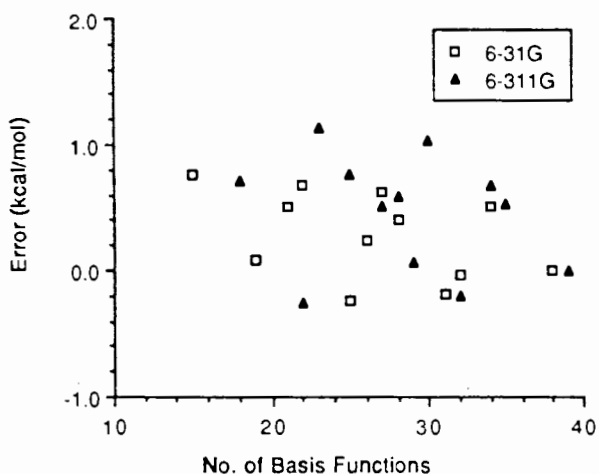
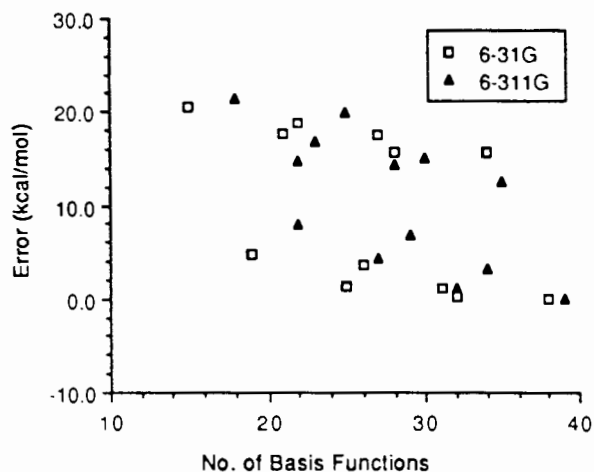
**Figure 7.** Error in the estimated MP4 ionization potential for F using: (a) eq. (9) and (b) eq. (10) plotted versus the number of functions in the reference basis set.

of configurations used to compute electron correlation. Apparently, the MP2 level is sufficient to pick up the bulk of this effect. Stated another way, large basis sets do not seem to be needed to pick up the important higher excitations in the MP4 calculation for these reactions. For eq. (11) and (12), i.e. eq. (10) with a 6-31G(*d, p*) or 6-311G(*d, p*) reference basis set, the error is less than 0.5 kcal/mol for reactions (1) and (2), and less than 1 kcal/mol for (3) and (4).

$$\begin{aligned} & \text{estimated } E_{\text{MP4}}(6-31++G(3df, 3pd)) \\ &= E_{\text{MP4}}(6-31G(d, p)) \\ &+ E_{\text{MP2}}(6-31++G(3df, 3pd)) \\ &- E_{\text{MP2}}(6-31G(d, p)) \end{aligned} \quad (11)$$

$$\begin{aligned} & \text{estimated } E_{\text{MP4}}(6-311++G(3df, 3pd)) \\ &= E_{\text{MP4}}(6-311G(d, p)) \\ &+ E_{\text{MP2}}(6-311++G(3df, 3pd)) \\ &- E_{\text{MP2}}(6-311G(d, p)) \end{aligned} \quad (12)$$

Inclusion of diffuse function in the reference basis reduces the error to 0.5 kcal/mol or less for all four



**Figure 8.** Error in the estimated MP4 electron affinity for F using: (a) eq. (9) and (b) eq. (10) plotted versus the number of functions in the reference basis set.

reactions. A larger reference basis may be necessary if the same accuracy is needed when bonds between heavy atoms are broken.<sup>20</sup>

A number of assumptions about the additivity of incremental basis set improvements are made by the G1 level of theory.<sup>2a</sup> Nevertheless, very respectable atomization energies and heats of formation are calculated for most of the compounds considered. Significant improvements in the energetics are obtained at the G2 level of theory,<sup>2b</sup> which drops most of the additivity of incremental basis set enhancements but retains the additivity between basis set improvement at the MP2 level and higher order treatments of electron correlation.

## CONCLUSIONS

Both the 6-31G and 6-311G series of basis sets show a substantial nonadditivity between diffuse functions on heavy atoms and multiple polarization func-

tions. For the 6-311G series, there is an additional nonadditivity between the *d* functions on hydrogen and multiple polarization functions. Once three sets of polarization functions, diffuse functions and higher angular momentum polarization functions are added to both basis sets (e.g., 6-31++G(3*df*, 3*pd*) and 6-311++G(3*df*, 3*pd*)), the two give the same energetics to within  $\pm 0.4$  kcal/mol for the four reactions. Equations (6) and (7) (with or without the variations discussed above) are additivity schemes that provide acceptable errors (ca.  $\pm 0.5$  kcal/mol) relative to the full 6-31++G(3*df*, 3*pd*) and 6-311++G(3*df*, 3*pd*) calculated energies.

As an alternative, the additivity between basis set expansion and improvements in the level of theory was examined. The effects of basis set expansion can be estimated at the MP2 level (but not at the HF level) and combined with a medium size MP4 calculation, as in eq. (11) or (12) (with or without the variations discussed above). As the number of basis functions increase, this approach becomes computationally less expensive than eq. (6) or (7). Furthermore, direct MP2 methods<sup>21</sup> make it feasible to apply this approach to larger molecules.

Only the *additivity* of basis set effects is considered in this article. Larger basis sets and higher levels of correlation may be necessary for chemical accuracy in the energetics; barrier heights can even be more demanding than heats of reaction.

We would like to thank the Computer Services Center at Wayne State University and the Pittsburgh Supercomputing Center for generous allocation of computer time. This work was supported by a grant from the National Science Foundation (CHE-87-11901).

## References

1. J.A. Pople, B.T. Luke, M.J. Frisch, and J.S. Binkley, *J. Phys. Chem.*, **89**, 2198 (1985).
2. J.A. Pople, M. Head-Gordon, D.J. Fox, K. Raghavachari, and L. Curtiss, *J. Chem. Phys.*, **90**, 5622 (1989). L. Curtiss, K. Raghavachari, G.W. Trucks, and J.A. Pople, *J. Chem. Phys.*, submitted.
3. M.J.S. Dewar and A.J. Holder, *J. Comp. Chem.*, **11**, 312 (1990).
4. R.H. Nobes, W.J. Bouma, and L. Radom, *Chem. Phys. Lett.*, **89**, 497 (1982).
5. M.L. McKee and W.N. Lipscomb, *J. Am. Chem. Soc.*, **103**, 4673 (1981).
6. J.V. Ortiz and W.N. Lipscomb, *Chem. Phys. Lett.*, **103**, 59 (1983).
7. P. Pulay, J.-G. Lee, and J.E. Boggs, *J. Chem. Phys.*, **79**, 3382 (1983).
8. M.L. McKee and W.N. Lipscomb, *Inorg. Chem.*, **24**, 762 (1985).
9. E.W. Ignacio and H.B. Schlegel, *J. Chem. Phys.*, **92**, 5404 (1990).
10. M.J. Frisch, J.S. Binkley, and H.F. Schaefer III, *J. Chem. Phys.*, **81**, 1882 (1984).
11. C.W. Bauschlicher, Jr., S.P. Walch, S.R. Langhoff, P.R. Taylor, and R.L. Jaffe, *J. Chem. Phys.*, **88**, 1743 (1988).
12. J.M.L. Martin, J.P. François, and R. Gijbels, *J. Comp. Chem.*, **10**, 875 (1989).
13. K. Raghavachari, *J. Chem. Phys.*, **82**, 4142 (1985).
14. C. Möller and M.S. Plesset, *Phys. Rev.*, **46**, 618 (1934).
15. Gaussian 88, M.J. Frisch, M. Head-Gordon, H.B. Schlegel, K. Raghavachari, J.S. Binkley, C. Gonzalez, D.J. DeFrees, D.J. Fox, R.A. Whiteside, R. Seeger, C.F. Melius, J. Baker, L.R. Martin, L.R. Kahn, J.J.P. Stewart, E.M. Fluder, S. Topiol, and J.A. Pople, Gaussian, Inc., Pittsburgh PA, 1988.
16. P.C. Hariharan and J.A. Pople, *Theor. Chim. Acta*, **28**, 213 (1973) and references cited.
17. R. Krishnan, J.S. Binkley, R. Seeger, and J.A. Pople, *J. Chem. Phys.*, **72**, 650 (1980).
18. T. Clark, J. Chandrasekhar, G.W. Spitznagel, and P.v.R. Schleyer, *J. Comp. Chem.*, **4**, 294 (1983).
19. M.J. Frisch, J.A. Pople, and J.S. Binkley, *J. Chem. Phys.*, **80**, 3265 (1984) and references cited.
20. J.A. Pople, private communication.
21. M. Head-Gordon, J.A. Pople, and M.J. Frisch, *Chem. Phys. Lett.*, **153**, 503 (1988).