Theoret. chim. Acta (Berl.) 28, 213—222 (1973)

Commentationes

The Influence of Polarization Functions on Molecular Orbital Hydrogenation Energies

P. C. Hariharan and J. A. Pople
Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

Received September 25, 1972

Polarization functions are added in two steps to a split-valence extended gaussian basis set: *d*-type gaussians on the first row atoms C, N, O and F and *p*-type gaussians on hydrogen. The same *d*-exponent of 0.8 is found to be satisfactory for these four atoms and the hydrogen *p*-exponent of 1.1 is adequate in their hydrides. The energy lowering due to *d* functions is found to depend on the local symmetry around the heavy atom. For the particular basis used, the energy lowerings due to *d* functions for various environments around the heavy atom are tabulated. These bases are then applied to a set of molecules containing up to two heavy atoms to obtain their LCAO-MO-SCF energies. The mean absolute deviation between theory and experiment (where available) for heats of hydrogenation of closed shell species with two non-hydrogen atoms is 4 kcal/mole for the basis set with full polarization. Estimates of hydrogenation energy errors at the Hartree-Fock limit, based on available calculations, are given.

Polarisationsfunktionen werden in zwei Schritten einer Basis von Gauß-Orbitalen hinzugefügt: *d*-Gauß-Funktionen für die Atome C, N, O und F und *p*-Gaußfunktionen für H. In allen Fällen ist ein *d*-Exponent von 0.8 bzw. ein *p*-Exponent von 1.1 bei den Hydriden befriedigend. Dabei hängt die Energieerniedrigung, die tabelliert wiedergegeben wird, von der lokalen Symmetrie am schweren Kern ab. Mit dieser Basis wird dann die LCAO-MO-SCF-Energie für Moleküle mit 2 schweren Atomen berechnet. Die mittlere absolute Abweichung zwischen Theorie und Experiment für Hydrierungswärmen von solchen Molekülen (mit abgeschlossener Schale) ist 4 kcal/Mol bei Einschluß aller Polarisationsfunktionen. Der Schätzwert für Hydrierungswärmen in der Hartree-Fock-Grenze wird ebenfalls angegeben.

1. Introduction

Although it has long been recognized that single-determinant molecular orbital theory does not give good bond dissociation energies because of neglect of electron correlation, there remains the possibility that it is more effective in predicting the energies of reactions involving only closed shell species, where correlation corrections may largely cancel. This hypothesis was put forward by Snyder [1]. One important class of reactions of this type is hydrogenations of organic molecules to products containing only one non-hydrogen atom (methane, ammonia, water, etc.). The energies of such reactions relate the strength of bonds between heavy atoms to bonds involving hydrogen. The validity of such a hypothesis is important since an adequate theory of hydrogenation energies would permit evaluation of the total energy of larger molecules, the energies of the hydrogenation products being well known.

Ideally, molecular orbital calculations should be carried out with a large enough basis for the Hartree-Fock limit to be reached. In practice, however, this is only possible for a number of rather small systems. Consequently, attention has been devoted to reaction energies using a more limited basis set, requiring that the same basis be used for reactants and products. Here it is hoped that some of the errors due to the limitation of basis set will also cancel to some extent. An extensive study of this sort was first carried out by Snyder and Basch [2], who examined a number of reactions using a contracted gaussian basis of the "split-shell" or "double zeta" type – that is with two basis functions per atomic orbital (ten functions for carbon, nitrogen etc. and two for hydrogen). They found moderate agreement with experiment for heats of hydrogenation, the theoretical values being mostly too negative. Further work with a rather simpler "split valence shell" basis (4-31*G*) gave similar results [3, 4].

All the systematic molecular orbital studies of hydrogenation energies to date have used only *s*- and *p*-type atomic functions in the basis. For a limited number of the molecules involved, more extensive basis sets including polarization functions (*d*-type on heavy atoms and *p*-type on hydrogen) have been used in individual calculations so that Snyder and Basch [2] were able to make some observations about the difference between errors with their "double-zeta" basis and errors at the Hartree-Fock limit. However, nobody has yet attempted a systematic study of hydrogenation energies at a uniform level with a basis including polarization functions. Such a study is presented here for a set of molecules involving atoms H, C, O, N and F with two non-hydrogen atoms. The aims are (1) to find whether addition of polarization functions gives overall improved agreement with experimental hydrogenation energies, and (2) to make a comparative study of the consequent total energy lowering as a function of atom and type of chemical environment.

2. Method and Procedure

The molecules considered in this paper are those containing H, C, N, O and F which can be represented by a classical valence structure without formal charges and which contain up to two heavy atoms. Standard model geometry [4, 5] is used throughout (see footnote [a] to Table 2). Carbon monoxide is added to the list with a bondlength of 1.13 Å. The standard model is used partly because experimental geometries are incompletely known and partly so that the results can be fitted in with a systematic study of larger molecules. Various studies not reported in detail here indicate that hydrogenation energies calculated at experimental geometries are generally within 1 kcal/mole of the standard geometry values.

Molecular orbital methods are standard using the Roothaan equations [6] (with the appropriate unrestricted generalization [7] for the triplet ground state of O_2). We begin with already published results using the 4-31*G* basis set [4, 8]. This has an *s* inner shell function which is a linear combination of four *s*-type gaussians and a valence shell (*s* and *p*) represented by inner (three-gaussian) and outer (one-gaussian) parts. For hydrogen, similar (31) *s*-type functions are used. This basis has the special feature that gaussian *s* and *p* exponents are shared in the valence shell for computational efficiency.

The 4-31*G* basis is improved in three successive steps. To begin with, it is replaced by 6-31*G* which differs by improvement of the inner shell function [9]. This is found to lower total energies substantially, but should not lead to large changes in chemical properties such as reaction energies. Nevertheless, it is desirable to test this before adding polarization functions.

The next step is the addition of a set of single (uncontracted) *d*-gaussian functions to the 6-31*G* set for heavy atoms, the hydrogen functions being unmodified. The additional six (unnormalized) functions are

$$(x^2, y^2, z^2, xy, yz, zx) \exp(-\alpha_d r^2).$$

These are equivalent to the five pure *d*-type functions

$$(3z^2 - r^2, xz, yz, xy, x^2 - y^2) \exp(-\alpha_d r^2)$$

together with the further *s*-type function $r^2 \exp(-\alpha_d r^2)$. We have retained all six functions rather than just the five pure-*d* functions, since the appropriate integrals can be evaluated more directly.

The addition of the *d*-functions would be most economically carried out if the exponent α_d were chosen to be identical to that in the outer *s* and *p* functions of 6-31*G*. This is because the integral evaluation program actually treats all ten functions *s*, *p* and *d* together. However, this turns out to be somewhat ineffective since the outer *s* and *p* functions are very diffuse and the *d*-type polarization functions do not interact strongly with the inner valence shell functions.

It is next necessary to select some standard values for the *d*-gaussian exponent α_d. To do this, energy-optimized values were first obtained for the six molecules listed in Table 1 by minimizing the total energy. The results are reasonably consistent with some comparable previous studies. For methane, Rothenberg and Schaefer [10] found $\alpha_d = 0.74$ for *d*-functions added to a double-zeta type basis. For ammonia, Kari and Csizmadia [11] obtain 0.75. Dunning [12] has given values of 0.75 for water and 0.98 for the nitrogen molecule. Diercksen [13] obtained 1.0 for water. Hankins, Moskowitz and Stillinger [16] found an optimum exponent of 0.897 for water. These results suggest that the optimum value of α_d does not depend strongly on the underlying *sp* basis provided extended basis sets are used.

The results of Table 1 suggest that α_d has some dependence on chemical environment (as with pairs NH_3, N_2 and CH_4, C_2H_2) but, on the other hand,

Table 1. Total energies (hartrees) and optimum *d*-type exponents α_d

Molecule	Optimum α_d	Energy 6-31 *G*	 6-31 *G* + *d* functions
CH_4	0.73	− 40.18038	− 40.19518
NH_3	0.75	− 56.16320	− 56.18381
H_2O	0.74	− 75.98508	− 76.00994
HF	0.84	− 99.98348	−100.00287
N_2	0.92	−108.86762	−108.94336
C_2H_2	0.83	− 76.79261	− 76.81737

there is little evidence of significant change along the atomic series C, N, O, F. On the basis of the optimum values given here, we select $\alpha_d = 0.8$ as the standard value for all the heavy atoms C, N, O and F. We adopt this value in all subsequent calculations.

The next step is to extend the basis further by adding *p*-polarization functions

$$(x, y, z) \times \exp(-\alpha_p r^2)$$

on the hydrogen atoms and find optimum values for α_p. This has been done by first fixing $\alpha_d = 0.8$ and minimizing the energy for α_p. No attempt has been made to find the minimum by varying both parameters. This procedure has been carried out only for CH_4 and HF. For CH_4, the optimum value of α_p is found to be 1.2, leading to a total energy of -40.20162 hartrees. Rothenberg and Schaefer [10] found $\alpha_p = 1.08$ in a comparable study. For HF, the optimum value is 1.0 giving an energy of -100.01124 hartrees. On the basis of these results, a choice of an average value of $\alpha_p = 1.1$ seems appropriate. This will be adopted as standard in subsequent calculations.

3. Results and Discussion

We have now introduced two extensions of the 6-31*G* basis. In the first (which we refer to as 6-31*G**), there are six extra uncontracted *d*-type gaussian functions on heavy atoms. The second, more elaborate, set (6-31*G***) also has three *p*-type gaussian functions on each hydrogen atom. All three of these bases have been applied to the complete set of molecules under investigation. The total energies are listed in Table 2.

In the following discussion, we shall attempt to make some comparisons with results at the Hartree-Fock limit even though these are not well established for many molecules. The final column of Table 2 gives a set of estimates of the energy at this limit for molecules which have been studied with more extensive bases than any used here. These figures are slightly below the best calculated energies in most cases and necessarily rather tentative.

Energies of hydrogenation reactions (ΔE) are easily derived from the results in Table 2. The theoretical values of ΔE for the 4-31*G*, 6-31*G* and the full polarization set 6-31*G*** are listed in Table 3. The corresponding estimates at the Hartree-Fock limit are also given for C_2H_2, HCN, CO, N_2 and F_2. Again, these values are subject to considerable uncertainty and may have an error of ± 5 kcal/mole. The final column of Table 3 lists experimental values corrected for temperature effects and zero-point motion. For some of the molecules these may also be subject to an uncertainty of several kilocalories.

The theoretical results are clearly poorest for O_2 which is reasonable, since this molecule has a triplet ground state and hydrogenation involves a change in the number of unpaired electrons. If O_2 is omitted from the list, we may test the relative success of the basis sets by evaluating the mean absolute deviation between theory and experiment when the latter is available. This gives 6.8, 7.1 and 4.0 kcal/mole for 4-31*G*, 6-31*G* and 6-31*G*** respectively. We deduce that improvement of inner shell orbitals causes little change in theoretical hydrogenation energies but that addition of polarization functions leads to a marked overall improvement. If we consider the available results for single hydrogenations (addition of only one molecule of hydrogen), the mean deviation is reduced to 3.1 kcal/mole for the basis with full polarization functions.

Before analyzing these results in more detail, it is useful to present the energy lowerings due to *d*-function inclusion (6-31*G*→6-31*G**) for various valence environments of the heavy atoms. These are given for symmetrical molecules in Table 4 and show a number of interesting features. The energy lowerings are

Table 2

Total energies (hartrees) with standard polarization functions and estimated Hartree-Fock limits

Molecule[a]	6-31 *G*	6-31 *G**	6-31 *G***	Limit[c]
H_2	− 1.12676	− 1.12676	− 1.13129	− 1.1336
CH_4	− 40.18038	− 40.19506	− 40.20159	− 40.225
NH_3	− 56.16320	− 56.18374	− 56.19499	− 56.225
OH_2	− 75.98508	− 76.00987	− 76.02255	− 76.065
FH	− 99.98343	−100.00281	−100.01122	−100.071
$HC{\equiv}CH$	− 76.79261	− 76.81732	− 76.82138	− 76.860
$H_2C{=}CH_2$	− 78.00317	− 78.03037	− 78.03754	
$H_3C{-}CH_3$	− 79.19651	− 79.22774	− 79.23724	
$HC{\equiv}N$	− 92.82763	− 92.87317	− 92.87515	− 92.920
$H_2C{=}NH$	− 93.97527	− 94.02105	− 94.02824	
$H_3C{-}NH_2$	− 95.16717	− 95.20819	− 95.22200	
$C^-{\equiv}O^+$	−112.66722	−112.73718	−112.73718	−112.791
$H_2C{=}O$	−113.80789	−113.86370	−113.86711	
$H_3C{-}OH$	−114.98682	−115.03387	−115.04501	
$H_3C{-}F$	−138.99200	−139.03445	−139.03961	
$N{\equiv}N$	−108.86762	−108.94234	−108.94234	−108.997
$HN{=}NH$	−109.92792	−109.99123	−109.99768	
$H_2N{-}NH_2$	−111.11852	−111.16733	−111.18147	
$HN{=}O$	−129.71179	−129.78123	−129.78426	
$H_2N{-}OH$	−130.92160	−130.97505	−130.98818	
$H_2N{-}F$	−154.90449	−154.95130	−154.95897	
$O{=}O$[b]	−149.54546	−149.61440	−149.61440	
$HO{-}OH$	−150.70287	−150.75299	−150.76540	
$HO{-}F$	−174.68169	−174.72327	−174.72980	
$F{-}F$	−198.64605	−198.67290	−198.67290	−198.770

[a] Bond lengths and angles as specified in Ref. [5]. $r(C^-{\equiv}O^+) = 1.13$ Å. Other conformational information: Staggered bonds for single bonds to carbon, $HN{=}NH$ *trans*, $H_2N{-}NH_2$ with 90° dihedral angle between nitrogen lone pair directions, $H_2N{-}OH$ with nitrogen lone pair *cis* to OH, $HO{-}OH$ with 90° dihedral angle.

[b] Lowest triplet state energies.

[c] Estimated Hartree-Fock limits based on the following references or calculations reported therein: H_2, Kolos, W., Roothaan, C. C. J.: Rev. mod. Physics **32**, 219 (1960); CH_4, Ref. [10]; NH_3, Ref. [14]; OH_2, Neumann, D., Moskowitz, J. W.: J. chem. Physics **49**, 2056 (1968); FH, Cade, P. E., Huo, W. M.: J. chem. Physics **47**, 614 (1967); $HC{\equiv}CH$ and $HC{\equiv}N$, McLean, A. D., Yoshimine, M.: Tables of linear molecule wave functions (IBM Corporation, 1967); $C^-{\equiv}O^+$, Huo, W. M.: J. chem. Physics **43**, 624 (1965); $N{\equiv}N$, Cade, P. E., Sales, K. D., Wahl, A. C.: J. chem. Physics **44**, 1973 (1966); $F{-}F$, Ref. [15].

Table 3. Complete hydrogenation energies ΔE (kcal/mole)

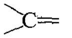
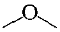
Reaction	Calculated				
	4-31 G[a]	6-31 G	6-31G**	Limit[b]	Exp.[c]
$HC{\equiv}CH + 3H_2 \rightarrow 2CH_4$	−117.8	−117.9	−117.9	−119	−105.4
$H_2C{=}CH_2 + 2H_2 \rightarrow 2CH_4$	− 65.9	− 65.3	− 64.7		− 57.2
$H_3C{-}CH_3 + H_2 \rightarrow 2CH_4$	− 23.5	− 23.5	− 21.7		− 18.1
$HC{\equiv}N + 3H_2 \rightarrow CH_4 + NH_3$	− 83.4	− 85.1	− 80.0	− 81	− 76.8
$H_2C{=}NH + 2H_2 \rightarrow CH_4 + NH_3$	− 72.1	− 72.0	− 66.4		
$H_3C{-}NH_2 + H_2 \rightarrow CH_4 + NH_3$	− 30.9	− 31.2	− 27.2		− 25.7
$C^-{\equiv}O^+ + 3H_2 \rightarrow CH_4 + H_2O$	− 72.4	− 74.0	− 58.4	− 64	− 63.9
$H_2C{=}O + 2H_2 \rightarrow CH_4 + H_2O$	− 64.3	− 65.3	− 59.3		− 57.3
$H_3C{-}OH + H_2 \rightarrow CH_4 + H_2O$	− 32.0	− 32.6	− 30.0		− 30.3
$H_3C{-}F + H_2 \rightarrow CH_4 + HF$	− 27.4	− 28.3	− 26.3		− 29.5
$N{\equiv}N + 3H_2 \rightarrow 2NH_3$	− 47,3	− 49.3	− 33.7	− 33	− 37.7
$HN{=}NH + 2H_2 \rightarrow 2NH_3$	− 90.7	− 91.0	− 81.4		− 83.5
$H_2N{-}NH_2 + H_2 \rightarrow 2NH_3$	− 50.4	− 50.9	− 48.5		− 50.0
$HN{=}O + 2H_2 \rightarrow NH_3 + H_2O$	−114.2	−114.8	−107.1		−102.9
$H_2N{-}OH + H_2 \rightarrow NH_3 + H_2O$	− 62.0	− 62.7	− 61.5		
$H_2N{-}F + H_2 \rightarrow NH_3 + HF$	− 71.2	− 72.4	− 72.8		
$O{=}O + 2H_2 \rightarrow 2H_2O$	−107.1	−107.4	−105.5		−125.1
$HO{-}OH + H_2 \rightarrow 2H_2O$	− 86.3	− 88.2	− 93.1		− 86.8
$HO{-}F + H_2 \rightarrow H_2O + HF$	− 98.2	−100.4	−108.4		
$F{-}F + H_2 \rightarrow 2HF$	−118.9	−121.8	−137.0	−149	−133.8

[a] From Ref. [5] except for carbon monoxide which is based on E(4-31 G) = − 112.55234 hartrees for a bondlength of 1.13 Å.

[b] Based on estimated Hartree-Fock limiting energies listed in Tab. 2.

[c] Heats of hydrogenation at 0 °K corrected for zero-point vibrations. See Ref. [4] for details.

Table 4. Energy lowerings per atom (kcal/mole) due to addition of d-functions

Atom	Molecule	Energy lowering
	CH_4	9.2
	C_2H_6	9.8
	C_2H_4	8.5
—C≡	C_2H_2	7.8
	NH_3	12.9
	N_2H_4	15.3
	N_2H_2	19.9
N≡	N_2	23.4
	H_2O	15.6
	H_2O_2	15.7
O=	O_2	22.1
F—	HF	12.2
	F_2	8.4

generally smallest for carbon. Comparing various types of carbon, it is found that the lowering is greatest for saturated tetrahedral carbon. This is a slightly surprising result in view of the high symmetry involved. It may perhaps be rationalized by noting that tetrahedral symmetry does not include an inversion operation and does, therefore, permit mixing of d-functions into those molecular orbitals which already include the valence *p*-functions. The carbon atoms in acetylene, on the other hand, have an approximate local center of inversion, in the sense that there are bonds in opposite directions. Mixing between *d* and *p* functions may well be reduced under these circumstances. $s-d$ mixing may occur, but this may be less effective because the *s*-type orbitals are more tightly bound. The trigonal carbon in ethylene is apparently intermediate between acetylene and ethane.

For nitrogen and oxygen atoms, the energy lowerings are larger. This can perhaps be attributed to greater anisotropy and non-uniformity of the charge distribution within the atom, leading to stronger polarization effects. Unlike the carbon series, the effect is greatest for the atom with unsaturated valency. Triply-bonded nitrogen and doubly-bonded oxygen have no pseudo-center of symmetry and *d*-polarization is large. The doubly-bonded oxygen value obtained from O_2 is not, of course, a suitable general model, but the strong *d*-lowering in formaldehyde (35.0 kcal/mole) suggests that the carbonyl oxygen contribution is of the order of 26 kcal/mole.

Table 5 gives a corresponding set of energy lowerings due to the addition of *p*-functions on hydrogen subsequent to *d*-function inclusion ($6\text{-}31G^* \rightarrow 6\text{-}31G^{**}$). These are smallest for H—H and C—H bonds but increase sharply in going to more polar bonds. This can be attributed partly to additional polarization effects in the σ-bond, but another contributing factor in a molecule such as HF is delocalization of π-electron onto hydrogen if $p\pi$ functions are available there.

We now return to the discussion of the hydrogenation energies shown in Table 3. The results for the hydrocarbons show little change due to the addition of polarization functions, all hydrogenation energies being too negative. Using the $6\text{-}31G^{**}$ basis, the results for acetylene give $\Delta E_{\text{th}} - \Delta E_{\text{exp}} = -12.5$ kcal/mole which is the poorest result for all the singlet-state molecules. The fact that no improvement is achieved by addition of polarization functions suggests that an error of this order may remain at the Hartree-Fock limit. The estimate based on more accurate calculations lends support to this. All of the one-step hydrogenation energies for the C_2 hydrocarbons are also too negative, $6\text{-}31G^{**}$ values for $\Delta E_{\text{th}} - \Delta E_{\text{exp}}$ being -5.1, -3.8 and -3.6 kcal/mole for acetylene, ethylene and ethane respectively.

Table 5. Energy lowering per hydrogen atom (kcal/mole) due to addition of *p*-functions

Bond	Molecule	Energy lowering
H—H	H_2	1.4
C—H	CH_4	1.0
	C_2H_6	1.0
	C_2H_4	1.1
	C_2H_2	1.3
N—H	NH_3	2.4
	N_2H_4	2.2
	N_2H_2	2.0
O—H	H_2O	4.0
	H_2O_2	3.9
F—H	FH	5.3

The behavior of the three N_2 compounds is quite different. With the *sp* bases (4-31*G* and 6-31*G*), the theoretical hydrogenation energy of N_2 is too negative. Snyder and Basch [2] also found this. However, addition of polarization functions changes this sharply and the final (6-31*G***) result gives $\Delta E_{\text{th}} - \Delta E_{\text{exp}} = +4$ kcal/mole. The estimated Hartree-Fock limit, noted by Rauk, Allen and Clementi [14] is close to this. Inspection of Table 4 shows that the large change in ΔE_{th} due to inclusion of polarization functions is primarily due to the large extra *d*-lowering for the N_2 molecule, partly offset by extra hydrogen *p*-lowering for hydrogens in NH bonds. The other N_2 compounds diimide and hydrazine show similar changes of rather smaller magnitude.

We have already noted that the theoretical hydrogenation energy of the oxygen molecule is too positive, which is consistent with a smaller correlation correction for a triplet-state. For the remaining symmetrical single bonds in hydrogen peroxide and the fluorine molecule, the theoretical hydrogenation energies are too negative. In the case of F_2, an even more negative value of -149 kcal/mole is obtained if the estimated Hartree-Fock energies are used. This gives $\Delta E_{\text{th}} - \Delta E_{\text{exp}} = -15$ kcal/mole, a discrepancy already noted by Snyder and Basch [2]. It is evident that for this molecule, a significant change in ΔE_{th} occurs as the best of our basis sets is extended to the Hartree-Fock limit. This may well be due to the limitation of using only four primitive *p*-gaussians in the valence shell of fluorine since Snyder and Basch (using a basis with five primitive *p*-gaussians but without polarization functions) obtain a better result than 6-31*G*. It should also be noted that the fluorine molecule is somewhat exceptional in that no binding relative to separate fluorine atoms is obtained at the Hartree-Fock limit [15].

For the unsymmetrical molecules with two heavy atoms, the results of Table 3 are generally intermediate between those of the corresponding symmetrical systems. Thus, we have already noted that C_2 molecules give $\Delta E_{\text{th}} - \Delta E_{\text{exp}}$ too negative and N_2 molecules slightly too positive. For CN compounds, the corresponding values are slightly too negative. In the case of hydrogen cyanide, the value of $\Delta E_{\text{th}} - \Delta E_{\text{exp}}$ is about -4 kcal/mole with 6-31*G*** and with the estimated Hartree-Fock values. Among the other molecules, we may note that the value of ΔE_{th} for carbon monoxide changes sharply on addition of polarization functions. This is similar to the result for the isoelectronic molecule N_2.

Another related class of formal reactions that may be investigated in a similar way is the separation of multiple bonds into single bonds. For example, the reaction

$$H_2C=CH_2 + 2CH_4 \rightarrow 2H_3C-CH_3$$

is one in which the two "parts" of the CC double bond of ethylene are separated into CC single bonds in separate ethane molecules, the number of CH bonds remaining constant. It is the bond separation reaction [3] for ethylene, treated as a member of the cycloalkane series $(CH_2)_n$. The energy of the reaction is also the amount by which the double bond is stronger than two single bonds. The theoretical values for the energies of these reactions using the 6-31*G*, 6-31*G** and 6-31*G*** bases are compared with experimental data in Table 6. It is evident that addition of polarization functions improves the results leading to

Table 6. Energies of multiple bond separation reactions (kcal/mole)

Reaction	Calculated			Experimental
	6-31*G*	6-31*G**	6-31*G***	
$HC{\equiv}CH + 4CH_4 \rightarrow 3H_3C{-}CH_3$	− 47.3	− 53.8	− 52.7	− 51.1
$H_2C{=}CH_2 + 2CH_4 \rightarrow 2H_3C{-}CH_3$	− 18.3	− 22.0	− 21.2	− 21.0
$HC{\equiv}N + 2CH_4 + 2NH_3 \rightarrow 3H_3C{-}NH_2$	+ 8.3	+ 3.9	+ 1.4	+ 0.3
$H_2C{=}O + CH_4 + OH_2 \rightarrow 2H_3C{-}OH$	− 0.2	+ 0.6	+ 0.8	+ 3.3
$N{\equiv}N + 4NH_3 \rightarrow 3H_2N{-}NH_2$	+103.4	+110.0	+111.6	+112.3
$HN{=}NH + 2NH_3 \rightarrow 2H_2N{-}NH_2$	+ 10.8	+ 15.1	+ 15.5	+ 16.5

Table 7. Hydrogenation energy errors $\Delta E_{th} - \Delta E_{exp}$ with the 6-31G^{**} basis (kcal/mole)

	Single bonds				Double bonds			Triple bonds	
	C	N	O	F	C	N	O	C	N
C	−3.6	−1.5	+0.3	+3.2	−7.5		− 2.0	−12.5	−3.2
N		+1.5				+2.1	+ 4.1		+4.0
O			−6.3				+19.6[a]		
F				−3.2					

[a] Triplet state

Table 8. Estimated hydrogenation energy errors $\Delta E_{th} - \Delta E_{exp}$ at the Hartree-Fock limit (kcal/mole)

	Single bonds				Double bonds			Triple bonds	
	C	N	O	F	C	N	O	C	N
C	−4	−1	−2	− 3	−8	−2	−4	−12	−3
N		+1	−2	− 5		+2	−4		+3
O			−6	−10					
F				−15					

excellent agreement with experiment for both 6-31*G** and 6-31*G***. (Close correspondence between 6-31*G** and 6-31*G*** results is expected since all hydrogens remain bonded to the same type of other atom in these reactions).

The success of the comparison with experiment displayed in Table 6 suggests that the energies of these reactions would continue to be given well at the Hartree-Fock limit. If this is so, it would follow that the correlation contribution to the energy of a double (or triple) bond would be close to two (or three) times the correlation contribution to the corresponding single bond.

Next, it is useful to summarize the differences between theoretical and experimental hydrogenation energies in chart form so that trends are apparent. Table 7 does this for the 6-31*G*** basis. It may be noted that the values for double and triple bonds are roughly two and three times those for single bonds. This reflects the successful comparison in Table 6. Finally, we may make an attempt to estimate the residual error in all the theoretical hydrogenation energies at the Hartree-Fock limit. Table 8 displays such an estimate based on the discussion in this paper. The numbers are arrived at in the following steps.

(1) Values for double and triple bonds are taken to be respectively twice and thrice those for single bonds in accordance with the hypothesis put forward above.

(2) Available evidence suggests that the 6-31G^{**} values for CC, CN and NN bonds are close to the Hartree-Fock limit.

(3) For the FF bond in the fluorine molecule, the Hartree-Fock value of about -15 kcal/mole is 12 kcal/mole more negative than the 6-31G^{**} result. It is therefore suggested that the value for the C–F bond in methyl fluoride should be reduced by 6 kcal/mole, giving -3 kcal/mole as the estimated limiting error.

(4) Values for the remaining bonds are interpolated roughly to give the complete table.

It should be emphasized that the numbers given in Table 8 are only tentative and may have to be modified in the light of future studies with larger basis sets. However, they do sum up our present assessment of the performance of Hartree-Fock theory in predicting hydrogenation energies.

Acknowledgement. We are grateful to Dr. R. Ditchfield of Bell Telephone Laboratories for test output from POLYATOM and for some discussions. The invaluable expertise of Mr. David Rodgers, Chief Engineer, Computation Center, Carnegie-Mellon University, at both the hardware and software aspects of the UNIVAC 1108 considerably lightened the task of programming.

This research was supported in part by the National Science Foundation under Grant GP 25617.

References

1. Snyder, L. C.: J. chem. Physics **46**, 3602 (1967); – Thermochemistry and the electronic structure of molecules. Houston, Texas: The Robert A. Welch Foundation Research Bulletin No. 29 August 1971.
2. Snyder, L. C., Basch, H.: J. Amer. chem. Soc. **91**, 2189 (1969).
3. Hehre, W. J., Ditchfield, R., Radom, L., Pople, J. A.: J. Amer. chem. Soc. **92**, 4796 (1970).
4. Radom, L., Hehre, W. J., Pople, J. A.: J. Amer. chem. Soc. **93**, 289 (1971).
5. Pople, J. A., Gordon, M. S.: J. Amer. chem. Soc. **89**, 4253 (1967).
6. Roothaan, C. C. J.: Rev. mod. Physics **23**, 69 (1951).
7. Pople, J. A., Nesbet, R. K.: J. chem. Physics **22**, 571 (1954).
8. Ditchfield, R., Hehre, W. J., Pople, J. A.: J. chem. Physics **54**, 724 (1971).
9. Hehre, W. J., Ditchfield, R., Pople, J. A.: J. chem. Physics **56**, 2257 (1972).
10. Rothenberg, S., Schaefer III, H. F.: J. chem. Physics **54**, 2764 (1971).
11. Kari, R. E., Csizmadia, I. G.: J. chem. Physics **56**, 4337 (1972).
12. Dunning, Jr., T. H.: J. chem. Physics **55**, 3958 (1971).
13. Diercksen, G. H. F.: Theoret. chim. Acta (Berl.) **21**, 335 (1971).
14. Rauk, A., Allen, L. C., Clementi, E.: J. chem. Physics **52**, 4133 (1970).
15. Wahl, A. C.: J. chem. Physics **41**, 2600 (1964).
16. Hankins, E. D., Moscowitz, J. W., Stillinger, F. H.: J. chem. Physics **53**, 4544 (1970).

Professor J. A. Pople
Department of Chemistry
Carnegie – Mellon University
Pittsburgh, Pennsylvania 15213
USA