

Thermochemical Data from *Ab Initio* Calculations. II. Total Correlation Energies, Schrödinger Energies, and Theoretical Heats of Formation*

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Bond correlation energies $\epsilon(\text{XY})$ have been derived by partitioning second-order Rayleigh–Schrödinger–Møller–Plesset (RSMP) correlation energies. Values of $\epsilon(\text{XY})$ depend on the type of bonding between atoms X and Y. They can be considered as comprising correlation energies of bond, lone, and inner-shell electron pairs of the group XY. Once a set of appropriate increments $\epsilon(\text{XY})$ has been obtained, it is possible to estimate unknown RSMP energies of larger molecules. This concept also can be used when estimating total correlation energies $E(\text{CORR})$. For this purpose $\epsilon(\text{XY})$ values have been derived from known $E(\text{CORR})$ energies of small molecules. It is shown that $|\epsilon(\text{XY})|$ increments increase linearly with the number n of electron pairs of the group XY. The function $\epsilon(n)$ becomes zero for $n = \frac{1}{2}$ (one uncorrelated electron) and passes through -0.042 for $n = 1$, which is approximately the correlation energy of the bonding electron pair of H_2 or a $1s$ inner-shell pair. With the aid of estimated $E(\text{CORR})$ and HF limit energies, Schrödinger energies and theoretical heats of formation of relatively large molecules are obtained.

I. INTRODUCTION

In the past few years, noteworthy progress in calculation of correlation energies of molecules has been made.¹ A relatively simple way of computing correlation-corrected molecular energies is provided by second-order RSMP perturbation theory.^{2,3} It has been shown that RSMP calculations can be carried out with large basis sets ($N \geq 80$) for medium-sized molecules (five heavy atoms).⁴ Nevertheless, the computational cost of RSMP calculations on medium-sized and large molecules are still rather high. Especially for investigations with augmented DZ basis sets, a semiempirical way of estimating RSMP correlation corrections is highly desirable.

As shown in Figure 2 of Part I,⁵ the prediction of energy lowerings caused by an improvement of both the basis set and the method implies *a priori* knowledge of correlation corrections, specifically their dependence on the basis set. For example, if second-order correlation energies $E^{(2)}(\text{B})$ or $E^{(2)}(\text{C})$ can be obtained empirically (step 2 in Fig. 2 of Part I), a direct estimation of RSMP molecular

energies for bases B and C becomes possible. Since on the other hand the effect of a basis set enlargement from B to C is also predictable (step 1 of Fig. 2, Part I), easily available $E(\text{SCF/B})$ energies will suffice to obtain an estimate of $E(\text{RSMP/C})$ values.

These estimates help to predict changes of relative molecular energies upon basis set and method improvement. Since the cost of an RSMP/C calculation can also be predicted,³ a cost-efficiency factor can be determined which indicates whether extension of calculations to the higher theoretical level is justified or not.

Estimates of $E^{(2)}(\text{X})$ energies for a large basis set X may also be used when trying to get an estimate of total correlation energies. The latter are needed to obtain Schrödinger energies and theoretical heats of formation. The estimation of these energies is the ultimate goal of this work. In order to get there we will proceed in the following way: First, a method of predicting second-order RSMP correlation energies is worked out (Secs. II–IV). Then, in Sec. V, total correlation energies $E(\text{CORR})$ are determined for a set of small molecules with the aid of experimental data and known $E(\text{HF})$ values.⁵ Energies $E(\text{CORR})$ will be used to analyze RSMP correlation corrections $E^{(2)}$ (Sec. VI) and to

* For Part I, see the preceding article in this issue. Abbreviations are used in the same manner as in Part I.

find a method of estimating total correlation energies of larger molecules (Sec. VII). In Sec. VIII, it will be examined as to whether a determination of theoretical heats of formation is feasible. Finally, the usefulness of this approach is demonstrated for an example.

II. ELECTRON PAIR CORRELATION ENERGIES

Different ways of semiempirically estimating correlation energies have been suggested by Hollister and Sinanoğlu.⁵ Their suggestions were based on earlier work of Sinanoğlu⁷ who demonstrated that for closed-shell molecules the major part of the total electron correlation energy $E(\text{CORR})$ results from electron pair contributions. Thus, to a first approximation the correlation energy may be obtained by

$$E(\text{CORR}) \approx \sum_{i \geq j}^M \epsilon_{ij} \quad (1)$$

where ϵ_{ij} stands for the pair contribution of two electrons in MOs i and j and the subscripts run over all M occupied orbitals.

If eq. (1) is used to estimate $E(\text{CORR})$, a total of $M(M+1)/2$ values ϵ_{ij} has to be known in advance. Molecular pair energies ϵ_{ij} can be related to typical atomic pair correlation energies as has been demonstrated by Hollister et al.⁶ Although this way of estimating ϵ_{ij} values is feasible, it requires special consideration of environmental effects on correlation, e.g., via a population analysis of SCF MOs.⁶ This makes the estimation of $E(\text{CORR})$ a rather troublesome method. In addition, it suffers from the ambiguities and drawbacks of a population analysis.⁸ Therefore, eq. (1) is used in the following in a simpler way.

According to classical models of chemical bond and electronic structure of closed-shell molecules, one can distinguish between electron bond pairs, nonbonding or lone pairs, and inner-shell pairs. MOs which have been subjected to a unitary transformation that maximizes intraorbital Coulomb interactions at the expense of interorbital interactions, namely so-called localized MOs,⁹ reflect this description to some extent. Thus the correlation energy can be thought of as being built-up by intraorbital pair energies of localized bond, lone-pair, and inner-shell MOs with the interorbital pair energies leading only to small contributions.

If one can identify for two bonded atoms X and Y characteristic pair energies, the correlation en-

ergy of the molecule XY is simply approximated by

$$E(\text{CORR}) \approx \sum_i \epsilon_i(\text{X}) + \sum_{i'} \epsilon_{i'}(\text{Y}) + \sum_l \epsilon_l(\text{X}) + \sum_{l'} \epsilon_{l'}(\text{Y}) + \sum_n \epsilon_n(\text{XY}) \quad (2)$$

where i, i', l, l', n run over all inner-shell, lone, and bond electron pairs. This approach, of course, is only useful if the pair energies are transferable from one molecule to another. Furthermore, it can only be applied if a description of the electronic structure of a molecule in terms of inner-shell, lone, and bond pairs is possible.¹⁰

Since environmental effects on inner-shell electrons are certainly small, their pair energies should be transferable. As for the bond pairs, there is indication from a partitioning of hydride correlation energies that typical increments can be assigned to bonds X—H (X = C, O, N, F).^{11,12} If this is also true for lone-pair electrons, an estimation of correlation energies for closed-shell molecules is straightforward, once appropriate pair correlation energies ϵ can be assigned to eq. (2).

III. PARTITIONING OF CORRELATION ENERGIES INTO GROUP CONTRIBUTIONS

At the level of second-order RSMP perturbation theory only pair excitations $ij \rightarrow ab$ from occupied MOs i and j to virtual orbitals a and b are considered.² This means that out of all possible many-electron correlations, only pair correlations contribute to $E^{(2)}$. Assuming that the MOs of a given molecule are completely localized, the correlation energy $E^{(2)}$ can be equated directly to the right-hand side of eq. (2). In order to examine this hypothesis, the following procedure has been carried out.

For a set of 21 small molecules correlation corrections $E^{(2)}(\text{X})$ are computed with X = B, C, and D (see Appendix of Part I). Since these calculations are based on delocalized MOs, they lead to $\epsilon_{ij}^{(2)}$ rather than $\epsilon_i^{(2)}$, $\epsilon_{l'}^{(2)}$, and $\epsilon_n^{(2)}$ values. Accordingly, eq. (2) has to be used in a different way. This can be done by collecting all terms in eq. (2) which contribute to a bonded group XY. They define a group correlation energy $\epsilon^{(2)}(\text{XY})$.¹³ Forming the sum of all group contributions $\epsilon^{(2)}(\text{XY})$, the energy $E^{(2)}$ can be approximated according to eq. (3):

$$E^{(2)} \approx \sum_{\text{all XY}} \epsilon^{(2)}(\text{XY}) \quad (3)$$

Equation (3), of course, implies that only appropriate fractions of inner-shell or lone-pair corre-

lation energies are included in $\epsilon^{(2)}(XY)$. Otherwise, certain $\epsilon_i^{(2)}$ and $\epsilon_j^{(2)}$ values are counted more than once in eq. (3).

Each group XY is not only characterized by the atoms X and Y but also by the type of bond connecting these atoms. One can expect different values $\epsilon^{(2)}(XY)$ when going from single to multiple bonding between X and Y. Since the number of bond pairs increases with the multiplicity of the bond, relationship (4)

$$|\epsilon^{(2)}(X-Y)| < |\epsilon^{(2)}(X=Y)| < |\epsilon^{(2)}(X\equiv Y)| \quad (4)$$

should hold.

The application of eq. (3) to computed correlation energies leads to a partitioning of $E^{(2)}$ values. First an X—H increment is determined by dividing the value $E^{(2)}$ of hydrides XH_p by the number p of X—H bonds. Then, $E^{(2)}$ of compounds H_pXYH_q is used to find $\epsilon^{(2)}(XY)$:

$$\epsilon^{(2)}(XY) = E^{(2)}(H_pXYH_q) - p\epsilon^{(2)}(X-H) - q\epsilon^{(2)}(Y-H) \quad (5)$$

In this way for the three basis sets B, C, and D 21 different group contributions $\epsilon^{(2)}(XY)$ have been determined. They are shown in Table I.

As expected the group correlation energies are in line with typical features of the classical description of the chemical bond. For example, absolute $\epsilon^{(2)}(XY)$ values of double bonds are about twice, those of triple bonds are about three times, as large as the corresponding values of the single bonds. From increments $\epsilon^{(2)}(XX)$ and $\epsilon^{(2)}(YY)$, the values $\epsilon^{(2)}(XY)$ can be estimated roughly.

IV. PREDICTION OF SECOND-ORDER RSMP CORRELATION ENERGIES $E^{(2)}$

Using the group contributions of Table I, correlation corrections $E^{(2)}(B)$ and $E^{(2)}(C)$ have been estimated for 26 three-heavy-atom molecules. In Tables II (basis B) and III (C) estimated values are compared with directly computed $E^{(2)}$ energies. It is interesting to note that an approximation of $E^{(2)}$ with group increments $\epsilon^{(2)}(XY)$ leads mostly to an underestimation of $|E^{(2)}|$. This may indicate the deficiency of the localization picture. The more delocalized the MOs used in the RSMP calculation are, the more negative the difference $E^{(2)}$ may become.

For both basis sets a standard deviation σ of ca. 3 kcal/mol is found. This is encouraging in view of a semiempirical realization of step 2 of Figure 2 in Part I. It is obvious that the RSMP/C energies of the three-heavy-atom molecules investigated in

Table I. Bond correlation energies $\epsilon^{(2)}(XY)$ in hartree for basis sets B, C, and D.^a

Bond	Basis B	Basis C	Basis D	Source
H-H	-0.01738	-0.01738	-0.02524	H ₂
C-H	-0.02522	-0.03549	-0.04204	CH ₄
C-C	-0.04095	-0.06242	-0.06337	C ₂ H ₆
C=C	-0.08380	-0.12127	-0.12097	C ₂ H ₄
C≡C	-0.13651	-0.18734	-0.18544	C ₂ H ₂
N-H	-0.03904	-0.05768	-0.06377	NH ₃
N-H	-0.06893	-0.10485	-0.10537	N ₂ H ₄
N=N	-0.14043	-0.21056	-0.21101	N ₂ H ₂
N≡N	-0.24158	-0.31704	-0.31704	N ₂
O-H	-0.06470	-0.09426	-0.09956	OH ₂
O-O	-0.12799	-0.18356	-0.18353	O ₂ H ₂
O=O	-0.24383	-0.33837	-0.33837	O ₂
F-H	-0.12958	-0.18115	-0.18549	HF
F-F	-0.26897	-0.36592	-0.36592	F ₂
C-H	-0.05407	-0.08277	-0.08362	CH ₃ ·NH ₂
C-H	-0.12114	-0.16933	-0.16966	CH ₂ ·NH ₂
C≡N	-0.19217	-0.25769	-0.25661	HCN
C-O	-0.07863	-0.11742	-0.11792	CH ₃ ·OH
C=O	-0.17174	-0.23906	-0.23883	CH ₂ ·O
C≡O	-0.21427	-0.29011	-0.29011	CO
C-F	-0.14055	-0.20108	-0.20116	CH ₃ ·F

^a Derived from the energies of Table VI of Part I.⁵

this work can be predicted from the corresponding single determinant basis B energies. The standard deviation of estimated RSMP/C values is 3.9 kcal/mol no matter in which sequence steps 1 (improvement of basis set) and 2 (improvement of method) are carried out.

It is concluded that an empirical approximation of $E^{(2)}$ energies with known group increments $\epsilon^{(2)}(XY)$ is possible. An estimation of large basis set RSMP calculations from simple SCF calculations becomes feasible as soon as appropriate basis set lowering and correlation contribution increments have been found from calculations on small molecules with suitable bond patterns.

V. CORRELATION ENERGIES FROM EXPERIMENTAL DATA

With the aid of estimated HF limit energies $E(\text{HF})$ (ref. 5), it is possible to derive molecular correlation energies from experimental data. In the case of a K-atomic nonlinear molecule of which heat of formation at T K, $\Delta H_f^\circ(T)$, and all 3K-6 vibrational frequencies ν_i are known, the molecular correlation energy $E(\text{CORR})$ can be found by equating experimental with theoretical energy differences.^{11,14-16} Equations (6)–(15) summarize

Table II. Comparison of computed RSMF correlation energies $E^{(2)}(B)$ with estimated values. (All energies E in hartree.)

Formula	Skeleton	Name, Conformation	$E(\text{RCMP}/B)$	$E^{(2)}(B)$		Diff ^a (kcal/mol)
				computed	estimated	
C_3H_8	C-C-C	Propane	-118.37751	-0.28540	-0.28369	1.1
C_3H_6	C-C=C	Propene	-117.17956	-0.27753	-0.27609	0.9
C_3H_4	C-C≡C	Propyne	-115.97637	-0.27575	-0.27835	-1.6
	C=C=C	Allene	-115.96623	-0.26870	-0.26798	0.4
C_2NH_7	C-C-N	Ethylamine, gauche	-134.34968	-0.30064	-0.29922	0.9
C_2NH_7	C-N-C	Dimethylamine	-134.33636	-0.30087	-0.29852	1.5
C_2NH_5	C=C-N	Vinylamine	-133.16234	-0.29219	-0.29162	0.4
	C-C=N	Acetaldimine, HCNH cis	-133.16791	-0.30313	-0.30203	0.7
	C=N-C	N-Methylformaldimine	-133.15146	-0.30740	-0.30133	3.8
C_2NH_3	C-C≡N	Acetonitrile	-132.03132	-0.30421	-0.30879	-2.9
	C≡C-N	Ethynylamine	-131.94942	-0.28842	-0.29388	-3.4
	C=C=N	Ketenimine	-131.95617	-0.30006	-0.29443	3.5
C_2OH_6	C-C-O	Ethanol, COOH trans	-154.16575	-0.31164	-0.31040	0.8
	C-O-C	Dimethyl ether	-154.14806	-0.31236	-0.30860	2.4
C_2OH_4	C-C=O	Acetaldehyde, HCCO cis	-152.99806	-0.31331	-0.31358	-0.2
	C=C-C	Vinyl alcohol, COOH cis	-152.97005	-0.30583	-0.30280	1.9
C_2OH_2	C=C=O	Ketene	-151.80346	-0.30896	-0.30599	1.9
	C≡C-O	Ethynol	-151.74939	-0.30803	-0.30503	1.9
CO_2H_4	O-C-O	Methane diol, HOCO gauche	-189.95661	-0.34061	-0.33710	2.2
	O-C-O	Methyl hydroperoxide, COOH trans	-189.87507	-0.34946	-0.34699	1.5
CO_2H_2	O-C=O	Formic acid, HOCO cis	-188.81730	-0.34670	-0.34029	4.0
CO_2	O=C=O	Carbon dioxide	-187.68511	-0.35715	-0.34348	8.6
C_2FH_5	C-C-F	Fluoroethane	-178.14994	-0.30840	-0.30762	0.5
C_2FH_3	C=C-F	Fluoroethylene	-176.95073	-0.30472	-0.30002	2.9
C_2FH	C≡C-F	Fluoroacetylene	-175.71955	-0.31007	-0.30228	4.9
CF_2H_2	F-C-F	Difluoromethane	-237.92905	-0.33726	-0.33154	3.6

^a Difference $\Delta E^{(2)} = E^{(2)}(\text{estimated}) - E^{(2)}(\text{computed})$. Average error $\bar{f} = 2.2$ kcal/mol; standard deviation $\sigma = 2.9$ kcal/mol.

the various steps of this procedure (compare also with Fig. 1 of Part I).

1. Correction of $\Delta H_f^\circ(T)$ to $\Delta H_f^\circ(0)$, i.e., the heat of formation at 0 K.

$$\Delta H_f^\circ(0) = \Delta H_f^\circ(T) - H^{\text{TRANS}}(T) - H^{\text{ROT}}(T) - \Delta H^{\text{VIB}}(T) - RT + \sum_{\text{ELEM}} \Delta \Delta H_f^\circ(\text{ELEMENT}) k(\text{ELEMENT}) \quad (6)$$

where

$$H^{\text{TRANS}}(T) = 3/2(RT) \quad (7)$$

$$H^{\text{ROT}}(T) = 3/2(RT) \quad (8)$$

and

$$\begin{aligned} \Delta H^{\text{VIB}}(T) &= H^{\text{VIB}}(T) - H^{\text{VIB}}(0) \\ &= N_A \sum_i^{3K-6} h\nu_i / [\exp(h\nu_i/kT) - 1] \quad (9) \end{aligned}$$

(N_A = Avogadro number). The external heat content is given by RT . The last term in eq. (6) comprises the ΔH_f° changes of the elements in their standard state. It becomes necessary because both at T and 0 K $\Delta H_f^\circ(\text{ELEMENT}) = 0$. Values $\Delta \Delta H_f^\circ$ are multiplied by appropriate weighting factors k which reflect the composition of the molecule in question.

Table III. Comparison of computed RSMP correlation energies $E^{(2)}(C)$ with estimated values. (All energies E in hartree.)

Formula	Skeleton	Name, Conformation	$E(\text{RSMP}/C)$	$E^{(2)}(C)$		Diff ^a (kcal/mol)
				computed	estimated	
C_3H_8	C-C-C	Propane	-118.67302	-0.41108	-0.40876	1.4
C_3H_6	C=C=C	Propene	-117.46786	-0.39910	-0.39666	1.5
C_3H_4	C-C≡C	Propyne	-116.25529	-0.39173	-0.39174	0.0
	C=C=C	Allene	-116.24806	-0.38779	-0.38214	3.5
C_2NH_7	C-C-N	Ethylamine, gauche	-134.68614	-0.44015	-0.43800	1.3
C_2NH_7	C-N-C	Dimethylamine	-134.67575	-0.43970	-0.43616	-2.2
C_2NH_5	C=C-N	Vinylamine	-133.48492	-0.43075	-0.42588	3.0
	C-C=N	Acetaldimine, HCNH cis	-133.49991	-0.43330	-0.43161	-1.1
	C=N-C	N-diethylformaldimine	-133.48617	-0.43672	-0.42976	4.4
C_2NH_3	C-C≡N	Acetonitrile	-132.35056	-0.42491	-0.42659	1.1
	C≡C-N	Ethynylamine	-132.26265	-0.42071	-0.42096	0.2
	C=C=N	Ketenimine	-132.28154	-0.42698	-0.41947	4.7
C_2OH_6	C-C-O	Ethanol, COOH trans	-154.52765	-0.45332	-0.45158	1.1
	C-O-C	Dimethyl ether	-154.51409	-0.45254	-0.44781	3.0
C_2OH_4	C-C=O	Acetaldehyde, HCCO cis	-153.35705	-0.44429	-0.44346	0.5
	C=C-O	Vinyl alcohol, COOH cis	-153.32731	-0.44407	-0.43944	2.9
C_2OH_2	C=C=O	Ketene	-152.15925	-0.43527	-0.43132	2.5
	C≡C-O	Ethynol	-152.09627	-0.43842	-0.43452	2.4
CO_2H_4	O-C-O	Methane diol, HOCO gauche	-190.39372	-0.49819	-0.49436	2.4
	C-O-O	Methyl hydroperoxide, COOH trans	-190.28942	-0.50551	-0.50171	2.4
CO_2H_2	O-C=O	Formic acid, HOCO cis	-189.24611	-0.49196	-0.48624	3.6
CO_2	O=C=O	Carbon dioxide	-188.11696	-0.48414	-0.47812	3.8
C_2FH_5	C-C-F	Fluoroethane	-178.51871	-0.44254	-0.44097	1.0
C_2FH_3	C=C-F	Fluoroethylene	-177.31240	-0.43433	-0.42883	3.5
C_2FH	C≡C-F	Fluoroacetylene	-176.07243	-0.43153	-0.42391	4.8
CF_2H_2	F-C-F	Difluoromethane	-238.37297	-0.47823	-0.47314	3.2

^a See footnote a of Table II; $\bar{f} = 2.4$ kcal/mol; $\sigma = 2.8$ kcal/mol.

2. Calculation of the "experimental" molecular energy $E(\text{EXP})$ from eq. (10):

$$E(\text{EXP})^{\text{MOLECULE}} = \sum_{\text{ATOM}}^K E(\text{EXP})^{\text{ATOM}}$$

$$= \Delta H_f^\circ(0)^{\text{MOLECULE}} - \sum_{\text{ATOM}}^K \Delta H_f^\circ(0)^{\text{ATOM}} \quad (10)$$

In order to solve eq. (10) estimates of $E(\text{EXP})^{\text{ATOM}}$ are taken from the work of Cade and Huo¹⁷ (see Table IV).

3. Consideration of the zero-point vibrational energy $E(\text{VIB})$ and the atomic corrections $E(\text{NM})$

leads to a theoretical energy $E(\text{THEO})$ of a motionless molecule.

$$E(\text{THEO})^{\text{MOLECULE}} = E(\text{EXP})^{\text{MOLECULE}} - E(\text{VIB}) - \sum_{\text{ATOM}}^K E(\text{NM}) \quad (11)$$

where

$$E(\text{VIB}) = \frac{1}{2} N_A h \sum_i^{3K-6} \nu_i \quad (12)$$

The atomic correction $E(\text{NM})$ results from the motion of the nucleus relative to the center of

Table IV. Atomic energies (hartree) and heats of formation (kcal/mol) from Pople and Binkley (ref. 11).

Atom	$E(\text{REL})^{\text{a}}$	$E(\text{THEO})^{\text{b}}$	$E(\text{EXP})^{\text{c}}$	$\Delta H_{\text{f}}^{\circ}(0)^{\text{d}}$	$\Delta H_{\text{f}}^{\circ}(298)^{\text{d}}$
H	~ 0	-0.500	-0.4995	51.631(1)	52.100(1)
C	-0.014	-37.8575	-37.8558	169.58(45)	170.89(45)
N	-0.028	-54.6143	-54.6122	112.5(1.0)	113.0(1.0)
O	-0.050	-75.1127	-75.1101	58.989(30)	59.559(30)
F	-0.084	-99.8088	-99.8059	18.36(40)	18.86(40)

^a References 19.^b Estimated from $E(\text{EXP})$ according to eq. (11).^c Reference 17.^d Reference 20. Numbers in parentheses are uncertainties.**Table V.** Theoretical and experimental energies of small molecules. (E values in hartree; $\Delta H_{\text{f}}^{\circ}$ values in kcal/mol).

Molecule	$E(\text{HF})^{\text{a}}$	$E(\text{CORR})^{\text{b}}$	$E(\text{REL})^{\text{c}}$	$E(\text{THEO})^{\text{d}}$	$E(\text{VIB})^{\text{e}}$	$E(\text{EXP})$	$\Delta H_{\text{f}}^{\circ}(0)$	$\Delta H_{\text{f}}^{\circ}(298)^{\text{f}}$
H ₂	-1.1336	-0.0409	~ 0	-1.1745	0.01004	-1.1635	0	0
CH ₄	-40.219	-0.293	-0.014	-40.526	0.04320	-40.4786	-15.97	-17.89
C ₂ H ₂	-76.860	-0.471	-0.028	-77.359	0.02578	-77.3291	54.32	54.19
C ₂ H ₄	-78.080	-0.503	-0.028	-78.611	0.04923	-78.5561	14.51	12.49
C ₂ H ₆	-79.270	-0.550	-0.028	-79.848	0.07214	-79.7691	-16.52	-20.24
NH ₃	-56.226	-0.334	-0.028	-56.588	0.03287	-56.5517	-9.34	-11.02
N ₂	-108.997	-0.540	-0.056	-109.593	0.00539	-109.5830	0	0
N ₂ H ₂ ^g	-110.053	-0.581	-0.056	-110.690				48.7
N ₂ H ₄	-111.243	-0.623	-0.056	-111.922	0.04747	-111.8683	26.18	22.80
OH ₂ ^h	-76.070	-0.363	-0.050	-76.483	0.02052	-76.4586	-57.10	-57.80
O ₂ ^h	-149.670	-0.647	-0.100	-150.417	0.00360	-150.4082	0	0
O ₂ H ₂	-150.860	-0.693	-0.100	-151.653	0.02516	-151.6213	-31.08	-32.58
FH	-100.071	-0.379	-0.084	-100.534	0.00943	-100.5207	-65.13	-65.14
F ₂	-198.785	-0.725	-0.168	-199.678	0.00202	-199.6703	0	0
CH ₃ NH ₂ ⁱ	-95.274	-0.582	-0.042	-95.898	0.06242	-95.8294	-1.91	-5.50
CH ₂ NH ₂ ⁱ	-94.086	-0.543	-0.042	-94.671				
HCN	-92.920	-0.506	-0.042	-93.468	0.01557	-93.4477	32.39	32.3
CH ₃ OH	-115.106	-0.615	-0.064	-115.785	0.04961	-115.7295	-45.36	-47.96
CH ₂ O	-113.932	-0.572	-0.064	-114.568	0.02567	-114.5369	-27.35	-27.95
CO	-112.791	-0.528	-0.064	-113.383	0.00478	-113.3736	-27.20	-26.42
CH ₃ F	-139.110	-0.629	-0.098	-139.837	0.03817	-139.7929	-54.08	-56.0

^a See Part I.⁵^b Calculated from eqs. (6)–(15). See also refs. 11 and 16.^c From atomic values.¹⁹^d From eq. (11).^e Vibrational frequencies from ref. 21.^f From ref. 20.^g $E(\text{CORR})$ estimated from values for N₂ and N₂H₄.^h Energy of the lowest triplet state.ⁱ $E(\text{CORR})$ estimated from values of HCN and CH₃NH₂.

mass. It is approximated according to Bethe and Salpeter¹⁸ by

$$E(\text{NM})^{\text{ATOM}} = E(\text{EXP})^{\text{ATOM}} [1 - (M_N + m_e)/M_N] \quad (13)$$

with M_N and m_e being nuclear and electron mass.

4. *Estimation of relativistic effects with the aid of atomic values $E(\text{REL})$ ¹⁹ in order to obtain molecular Schrödinger energies $E(S)$.*

$$E(S) = E(\text{THEO}) - \sum_{\text{ATOM}}^K E(\text{REL})^{\text{ATOM}} \quad (14)$$

(The designation "MOLECULE" is only used in those cases where confusion between molecular and atomic values is possible.)

5. *Determination of molecular correlation energies $E(\text{CORR})$ from $E(S)$ and HF limit energies*

$$E(\text{CORR}) = E(S) - E(\text{HF}) \quad (15)$$

In Table V correlation energies obtained in this way are depicted for 21 small molecules. Also shown are the corresponding molecular energies $E(\text{HF})$, $E(\text{REL})$, $E(\text{THEO})$, $E(\text{VIB})$, and $E(\text{EXP})$ as well, as the heats of formation at 0 and at T K. Heats of formation²⁰ and vibrational frequencies²¹ have been taken from the literature. Energies of hydrides XH_p originate from Pople et al.¹¹ Deviations of true correlation energies $E(\text{CORR})$ are expected to be lower than 0.005 hartree.

VI. THEORETICAL CORRELATION ENERGIES

The correlation energies of Table V can be used in order to analyze RSMP correlation corrections $E^{(2)}$. It is possible to determine which fraction of the total correlation energy $E(\text{CORR})$ is covered by $E^{(2)}$ values. These data, given in percent, are summarized in Table VI for basis sets A, B, C, and D. By inspection of Table VI several observations can be made.

- (1) $E^{(2)}$ energies of basis sets like A and B cover only 5–40% of $E(\text{CORR})$.
- (2) Augmentation of the basis by polarization functions leads to a significant improvement of $E^{(2)}$ values. The relative changes from B to C and C to D are larger than the corresponding changes of the orbital errors.⁵
- (3) Even with basis D only 50–60% of $E(\text{CORR})$ are obtained.
- (4) The variation of percentage figures of Table

Table VI. Correlation corrections $E^{(2)}$ of small molecules given in percent of the total correlation energy $E(\text{CORR})$.^a

Molecule	Basis A	Basis B	Basis C	Basis D
H ₂	31.2	42.4	42.4	64.4
CH ₄	19.6	34.5	48.5	57.4
C ₂ H ₂	33.0	40.6	55.3	57.2
C ₂ H ₄	25.0	36.9	52.4	57.5
C ₂ H ₆	20.0	35.1	50.1	57.4
NH ₃	16.0	35.0	52.0	57.4
N ₂	28.7	44.8	58.8	58.8
N ₂ H ₂	20.6	39.2	56.1	58.3
N ₂ H ₄	14.2	36.1	53.9	57.9
OH ₂	11.5	36.0	52.2	55.0
O ₂		37.7	52.3	52.3
O ₂ H ₂	11.2	37.1	53.7	55.1
FH	5.3	34.6	48.1	49.0
F ₂	7.3	37.1	50.5	50.5
CH ₃ NH ₂	17.6	35.9	52.4	58.0
CH ₂ NH	24.5	38.8	54.6	58.5
HCN	35.3	44.6	58.7	59.1
CH ₃ OH	15.3	36.1	51.9	55.9
CH ₂ O	22.1	39.9	54.4	56.5
CO	27.7	42.1	55.6	55.6
CH ₃ F	11.4	35.0	49.1	52.0

^a For absolute $E^{(2)}$ values see Part I, Table VI.⁵

VI is, even in the case of basis D, relatively large.

As for the magnitude of $E^{(2)}$ values, one has to bear in mind that even for an infinite basis set second-order correlation corrections will not converge to $E(\text{CORR})$ since they do not comprise many-electron correlations, especially the important pair-pair contributions.¹ It is obvious from observations (1)–(3) that only extended basis sets lead to reasonable values of $E^{(2)}$. Thus an extrapolation to a limiting value $E^{(2)}$ close to $E(\text{CORR})$ is impossible with the data of Table VI.

VII. GROUP ADDITIVITY PROPERTY OF MOLECULAR CORRELATION ENERGIES

In order to obtain reasonable estimates of $E(\text{CORR})$ for larger molecules, the group contribution method developed in Sec. III is also applied for total correlation energies. Such a method was first suggested by Moffat.¹⁵ By relating electronic energies to the thermodynamic function of the

Table VII. Bond correlation increments $\epsilon(XY)$.

Bond	n^a	$\epsilon(XY)$ (hartree)		Source
		Moffat ^b	this work	
H-H	1		-0.041	H ₂
C-H	1.25	-0.074	-0.073	CH ₄
C-C	1.5	-0.124	-0.112	C ₂ H ₆
C=C	3	-0.249	-0.211	C ₂ H ₄
C≡C	4.5	-0.317	-0.325	C ₂ H ₂
N-H	1.66	-0.120	-0.111	NH ₃
N-N	2.33	-0.221	-0.179	N ₂ H ₄
N=N	4.66		-0.359	N ₂ H ₂
N≡N	7		-0.540	N ₂
O-H	2.5	-0.179	-0.181	OH ₂
O-O	4	-0.380	-0.331	O ₂ H ₂
O=O	8		-0.647	O ₂
F-H	5		-0.378	FH
F-F	9		-0.725	F ₂
C-N	1.92	-0.233 ^c	-0.141	CH ₃ NH ₂
C=N	3.83	-0.405 ^d	-0.286	CH ₂ NH
C≡N	5.75	-0.431	-0.433	HCN
C-O	2.75	-0.350	-0.215	CH ₃ OH
C=O	5.5	-0.450	-0.426	CH ₂ O
C≡O	7		-0.528	CO
C-F	5.25	-0.435 ^e	-0.410	CH ₃ F

^a Number of electron pairs contributing to XY.

^b Reference 15.

^c Source HCONH₂.

^d Source C₂H₅N.

^e Source FCN.

internal energy, Moffat assumed that molecular correlation energies are group additive. Because of a lack of suitable $E(\text{HF})$ values, SCF energies obtained with different basis sets X had to be used to approximate the molecular correlation energy thus leading to values $E'(\text{CORR})$ considerably lower than $E(\text{CORR})$:

$$E'(\text{CORR}) = E(\text{CORR}) - \Delta E(\text{ORB}/X) \quad (16)$$

Nevertheless, the assumption of a group additivity property of the correlation energy proved to be valid to a first approximation.¹⁵

This observation is largely confirmed by the results of Sec. III. On the other hand, the reduction of $E(\text{CORR})$ to contributions of localized electron pairs shows that a group additivity method will become less successful for larger molecules. Since $\epsilon(XY)$ energies derived from a small molecule do not contain all many-electron correlations of a large molecule, the absolute value of $E(\text{CORR})$ will be underestimated. In addition, delocalization effects in large molecules cannot be covered by the

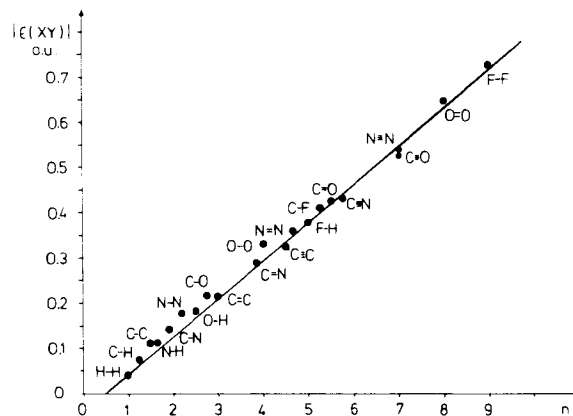


Figure 1. Dependence of the bond correlation energies $\epsilon(XY)$ on the number of electron pairs n of the group XY.

group contribution method. This, of course, can partially be compensated by taking $\epsilon(XY)$ values from larger molecules with electronic structures similar to those of the molecules which have to be investigated.

By partitioning of the molecular correlation energies listed in Table V, the bond increments $\epsilon(XY)$ shown in Table VII have been found. Because of eq. (16) they are less negative than the group contributions of Moffat,¹⁵ which are also depicted in Table VII.

As discussed in Sec. III, values $\epsilon(XY)$ possess features which are typical for the classical picture of the chemical bond. However, the group correlation energies are not parallel to any thermochemical bond property, e.g., to bond energies. In Figure 1, it is illustrated that the bond increments $|\epsilon(XY)|$ increase linearly with the number (n) of electron pairs. The function $\epsilon(n)$ becomes zero for $n = 0.5$, i.e., in the case of one electron which can move uncorrelated in molecular space. If another electron is added, a pair correlation energy of -0.042 hartree results. This value describes the amount of correlation of the H₂ bond pair or of a 1s inner-shell pair.²² The $|\epsilon(XY)|$ energies increase per electron pair by 0.084 hartree thus suggesting that a single electron contributes -0.042 hartree to the group correlation energy.²³ The scattering of ϵ values around the line²⁴

$$\epsilon(n) = -0.084n + 0.042 \quad (17)$$

indicates that environmental effects as well as the type of the contributing electron pair influence the magnitude of $\epsilon(XY)$. If bond-pair contributions dominate the magnitude of $|\epsilon(XY)|$, it comes out somewhat lower; if lone-pair contributions dominate, it comes out somewhat higher than calculated with eq. (17).

Table VIII. HF limit, correlation, and Schrödinger energies of three-heavy-atom molecules. (All energies in hartree.)

Formula	Skeleton	Name	E(HF)	E(CORR)	E(S)	E(THEO)
C ₃ H ₈	C-C-C	Propane (1)	-118.327	-0.807	-119.134	-119.176
C ₃ H ₆	C-C=C	Propene (2)	-117.135	-0.760	-117.895	-117.937
C ₃ H ₄	C-C≡C	Propyne (3)	-115.930	-0.729	-116.659	-116.701
	C=C=C	Allene (4)	-115.928	-0.713	-116.641	-116.683
C ₂ NH ₇	C-C-N	Ethylamine (5)	-134.323	-0.840	-135.163	-135.219
C ₂ NH ₇	C-N-C	Dimethylamine (6)	-134.313	-0.831	-135.144	-135.200
C ₂ NH ₅	C=C-N	Vinylamine (7)	-133.133	-0.793	-133.926	-133.982
	C-C=N	Acetaldimine (8)	-133.145	-0.801	-133.946	-134.002
	C=N-C	N-Methylformaldimine (9)	-133.136	-0.792	-133.928	-133.984
C ₂ NH ₃	C-C≡N	Acetonitrile (10)	-132.004	-0.764	-132.768	-132.824
	C≡C-N	Ethynylamine (11)	-131.921	-0.761	-132.682	-132.738
	C=C=N	Ketenimine (12)	-131.934	-0.754	-132.688	-132.744
C ₂ OH ₆	C-C-O	Ethanol (13)	-154.166	-0.873	-155.039	-155.117
	C-O-C	Dimethyl ether (14)	-154.153	-0.868	-155.021	-155.099
C ₂ OH ₄	C-C=O	Acetaldehyde (15)	-153.006	-0.830	-154.836	-153.914
	C=C-O	Vinyl alcohol (16)	-152.976	-0.826	-153.802	-153.880
C ₂ OH ₂	C=C=O	Ketene (17)	-151.818	-0.783	-152.601	-152.679
	C≡C-O	Ethynol (18)	-151.751	-0.794	-152.545	-152.623
CO ₂ H ₄	O-C-O	Methane diol (19)	-190.014	-0.938	-190.952	-191.066
	O-O-O	Methyl hydroperoxide (20)	-189.901	-0.946	-190.847	-190.961
CO ₂ H ₂	O-C=O	Formic acid (21)	-188.874	-0.895	-189.769	-189.883
CO ₂	O=C=O	Carbon dioxide (22)	-187.754	-0.852	-188.606	-188.720
C ₂ FH ₅	C-C-F	Fluoroethane (23)	-178.186	-0.887	-179.073	-179.185
C ₂ FH ₃	C=C-F	Fluoroethylene (24)	-176.989	-0.840	-177.829	-177.941
C ₂ FH	C≡C-F	Fluoroacetylene (25)	-175.751	-0.808	-176.559	-176.671
CF ₂ H ₂	F-C-F	Difluoromethane (26)	-238.049	-0.966	-239.015	-239.197

This is line with Snyder's suggestion that lone pairs lead to larger correlation contributions than localized bond pairs.²⁵ The $\epsilon(XY)$ increments derived from $E^{(2)}$ energies show a similar dependence on the number of electron pairs. But the scattering of values is somewhat stronger, which seems to depend on the basis [$r^2(B) = 0.9901$; $r^2(C) = 0.9910$; $r^2(D) = 0.9926$] as well as on the limitations of a second-order perturbation approach.

VIII. FROM SCF ENERGIES TO SCHRÖDINGER ENERGIES AND THEORETICAL HEATS OF FORMATION

As described in Part I (ref. 5), HF limit energies can be estimated from $E(A)$ and $E(C)$ values. Once

$E(\text{HF})$ has been obtained, the group contributions of Table VII are utilized to obtain an approximation of $E(\text{CORR})$ which then leads to an estimate of the Schrödinger energy. For illustration the $E(S)$ value of formic acid is estimated in this way:

$$\begin{aligned} E(\text{HF}) &\approx E(A) - [E(A) - E(C)]/0.955 \\ &\approx -186.21060 - (2.54355)/0.955 \\ &\approx -188.874 \text{ hartree} \end{aligned}$$

$$\begin{aligned} E(\text{CORR}) &\approx \epsilon(\text{C}=\text{O}) + \epsilon(\text{C}-\text{O}) \\ &\quad + \epsilon(\text{C}-\text{H}) + \epsilon(\text{O}-\text{H}) \\ &\approx -0.895 \text{ hartree} \end{aligned}$$

$$\begin{aligned} E(S) &\approx -188.874 - 0.895 \\ &\approx -189.769 \text{ hartree} \end{aligned}$$

This procedure has been applied to 26 three-

Table IX. Theoretical and experimental heats of formation $\Delta H_f^\circ(0)$. (Energies E in hartree, ΔH_f° values in kcal/mol.)

Molecule	$E(\text{THEO})$	$E(\text{VIB})^a$	$E(\text{EXP})$	$\Delta H_f^\circ(0)$		Diff ^c	$\Delta H_f^\circ(298)^b$
				theo	exp		
Propane	-119.176	0.10031	-119.067	-21.5	-19.4	-2.1	-24.8
Propene	-117.937	0.07695	-117.852	10.6	8.5	2.1	4.9
Propyne	-116.701	0.05389	-116.640	40.9	46.1	-5.2	44.4
Allene	-116.683	0.05312	-116.623	51.7	47.4	4.3	45.6
Dimethyl amine	-135.200	0.08941	-135.102	9.0	0.8	8.2	-4.4
Acetonitrile	-132.824	0.04393	-132.773	9.9	22.6	-12.6	20.9
Dimethyl ether	-155.099	0.07735	-155.013	-40.3	-39.7	-0.6	-44.0
Acetaldehyde	-153.914	0.05298	-153.853	-43.8	-37.1	-6.6	-39.7
Ketene	-152.679	0.03059	-152.641	-13.6	-13.5	-0.1	-14.2
Formic acid	-189.833	0.03258	-189.842	-90.8	-88.8	-2.0	-90.6
Carbon dioxide	-188.720	0.01155	-188.702	-105.0	-94.0	-11.0	-94.0
Difluoromethane	-239.197	0.03207	-239.156	-123.3	-105.0	-18.3	-108.1

^a Vibrational frequencies from ref. 21; exceptions are propene: B. Silvi, P. Labarbe, and J. P. Perchard, *Spectrochim. Acta, Part A*, **29**, 263 (1973); dimethylamine: G. Dellepiane and G. Zerbi, *J. Chem. Phys.*, **48**, 3573 (1968); acetaldehyde: J. C. Evans and H. J. Bernstein, *Can. J. Chem.*, **34**, 1083 (1956); difluoromethane: E. K. Plyler and W. S. Benedict, *J. Res. Nat. Bur. Stand.*, **47**, 202 (1951).

^b From ref. 20.

^c Difference $\Delta H_f^\circ(\text{theo}) - \Delta H_f^\circ(\text{exp})$. Average error $\bar{f} = 6.1$; standard deviation $\sigma = 8.1$ kcal/mol.

heavy-atom molecules for which $E(A)$ and $E(C)$ energies have been calculated or taken from the literature.²⁶ Results are listed in Table VIII which contains also theoretical energies $E(\text{THEO})$.

In order to make an assessment of the usefulness of estimated Schrödinger energies, they have been used to determine theoretical heats of formation $\Delta H_f^\circ(0)$ [see eqs. (10)–(14)] for those molecules of Table VIII for which all vibrational frequencies are available from experimental studies. These data are summarized in Table IX together with experimental ΔH_f° values and theoretical energies.

The differences between theory and experiment are as high as 18 kcal/mol. On the other hand, the computed standard deviation of 8 kcal/mol is relatively low. The errors originate from (1) deficiencies of the group contribution method used to determine $E(\text{CORR})$, (2) an erroneous extrapolation to $E(\text{HF})$ values, (3) inaccuracies of experimental values $\Delta H_f^\circ(T)$ and ν_i , or (4) any of the approximations made in eqs. (6)–(15).

Probably, the errors (3) and (4) are small in the cases considered. As for the relative contribution of (1) and (2) to absolute errors, it is impossible at the moment to make any assessment. Nevertheless, the data of Table IX provide some evidence that an estimation of heats of formation is possible. Theoretical ΔH_f° values will be useful in those cases where an accuracy of 5–10 kcal/mol is sufficient to solve a given problem.

Although ΔH_f° values have been obtained here with the aid of experimental frequencies, it is in principle possible to calculate all 3K-6 vibrational fundamentals. Then, theoretical heats of formation can be estimated directly from SCF energies.

Alternatively, zero-point vibrational energies $E(\text{VIB})$ and temperature corrections $\Delta H_f^\circ(0) - \Delta H_f^\circ(298)$ can be estimated by analyzing the corresponding values of small molecules (Table V) and deriving appropriate group contribution data as done in the case of the total correlation energies.²⁷ Utilizing these data and applying eqs.

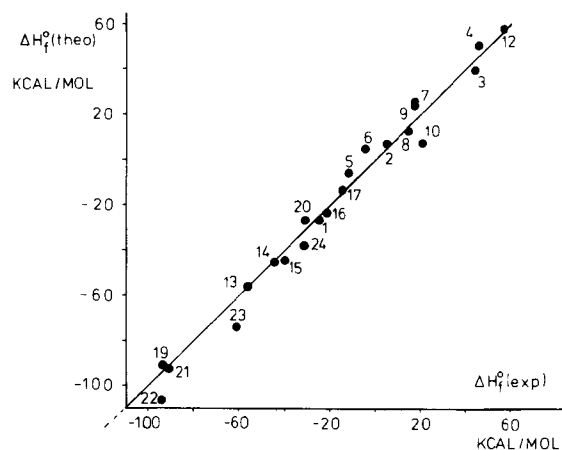


Figure 2. Comparison of theoretical and experimental heats of formation.

Table X. Theoretical and experimental heats of formation $\Delta H_f^\circ(298)$. (Energies E in hartree, ΔH_f° values in kcal/mol.)

Molecule	$E(\text{VIB})^a$	$E(\text{EXP})^b$	$\Delta H_f^\circ(0)$	$\Delta H_f^\circ(298)$		Diff ^e
				theo ^c	exp ^d	
<u>1</u>	0.101	-119.066	-21.1	-26.6	-24.8	-1.8
<u>2</u>	0.078	-117.851	11.2	7.4	4.9	2.5
<u>3</u>	0.055	-116.639	41.6	39.7	44.4	-4.7
<u>4</u>	0.055	-116.621	52.9	50.8	45.6	5.2
<u>5</u>	0.091	-135.119	-1.9	-5.6	-11.4	5.8
<u>6</u>	0.092	-135.099	10.7	5.2	-4.4	9.6
<u>7</u>	0.068	-133.906	29.1	25.8	(17.9)	(7.9)
<u>8</u>	0.068	-133.926	16.6	13.0	14.8	-1.8
<u>9</u>	0.068	-133.908	27.9	23.8	17.5	6.3
<u>10</u>	0.044	-132.773	10.0	7.3	20.9	-13.6
<u>11</u>	0.045	-132.686	64.6	62.7		
<u>12</u>	0.045	-132.692	60.8	58.5	(56.8)	(1.7)
<u>13</u>	0.079	-155.029	-51.6	-56.0	-56.2	0.2
<u>14</u>	0.079	-155.011	-40.3	-44.8	-44.0	-0.8
<u>15</u>	0.055	-153.850	-41.9	-44.3	-39.7	-4.6
<u>16</u>	0.056	-153.816	-20.5	-23.2	(-21.3)	(-1.9)
<u>17</u>	0.032	-152.640	-12.7	-13.4	-14.2	0.8
<u>18</u>	0.032	-152.584	22.4	21.6		
<u>19</u>	0.056	-191.001	-87.7	-91.0	(-93.5)	(2.5)
<u>20</u>	0.054	-190.898	-23.1	-26.5	(-30.9)	(4.4)
<u>21</u>	0.032	-189.843	-91.2	-92.5	-90.6	-1.9
<u>22</u>	0.008	-188.705	-107.2	-106.5	-94.0	-12.5
<u>23</u>	0.067	-179.109	-70.8	-74.6	-61.0	-13.6
<u>24</u>	0.044	-177.889	-35.5	-37.6	-31.6	-6.0
<u>25</u>	0.021	-176.643	16.2	16.1		
<u>26</u>	0.033	-239.155	-122.7	-124.7	-108.1	-16.6

^a Estimated from $E(\text{VIB})$ values of small molecules (see Table V).

^b Calculated from the $E(\text{THEO})$ energies of Table VIII according to eq. (11).

^c Theoretical $\Delta H_f^\circ(298)$ values derived from $\Delta H_f^\circ(0)$ enthalpies by using appropriate corrections for temperature effects.

^d Experimental $\Delta H_f^\circ(298)$ enthalpies from ref. 20. Values in parentheses have been obtained from group contribution tables published by S. W. Benson et al. (ref. 20d).



^e Difference $\Delta H_f^\circ(\text{theo}) - \Delta H_f^\circ(\text{exp})$. Average error $\bar{j} = 5.5$; standard deviation $\sigma = 7.5$ kcal/mol.

(6)–(10), theoretical estimates of $\Delta H_f^\circ(298)$ are obtained from energies $E(\text{THEO})$. Theoretical and experimental $\Delta H_f^\circ(298)$ values of compounds 1–26 are compared in Table X and Figure 2. Again, the computed standard deviation is ca. 8 kcal/mol, but decreases to 6.2 kcal/mol if compound 26, CH_2F_2 , is excluded. This is comparable to what has been found in previous calculations of heats of formation^{16,28–30} which were based on computed SCF or

SCF/CI reaction energies and experimental ΔH_f° values of small molecules^{16,28,30} or closed-shell ions²⁹ under the assumption $\Delta E(\text{CORR}) = 0$.

In Table X, eight molecules are listed for which experimental heats of formation are not known. For some of them, estimates of $\Delta H_f^\circ(298)$ have been obtained from thermochemical group contribution tables published by Benson et al.^{20d} These values agree well with theoretical estimates.

Table XI. Theoretically and empirically estimated heats of formation $\Delta H_f^\circ(298)$ of molecules involved in the ozonolysis reaction. (E in hartree, ΔH_f° in kcal/mol.)

Molecule	Substituents X; Y	$E(S)^a$	$E(\text{THEO})$	$E(\text{VIB})$	$E(\text{EXP})$	$\Delta H_f^\circ(0)$	this work	RE^b	$H_f^\circ(298)$	
									TC ^c	MINDO ^d
	H; H	-304.084	-304.262	0.074	-304.182	6	-1	0	-6	-28
	CH ₃ ; H	-343.396	-343.588	0.102	-343.477	3	-5	-7		
	CH ₃ ; CH ₃	-382.709	-382.915	0.131	-382.775	-3	-12	-14	-23	
XCHOO	H	-189.562	-189.676	0.030	-189.638	38	36	38	30	16
	CH ₃	-228.892	-229.020	0.059	-228.950	23	20	23	14	-4
	H; H	-304.163	-304.341	0.075	-304.260	-43	-49	-50	-50	-65
	CH ₃ ; H	-343.476	-343.668	0.104	-343.555	-46	-54	-58		
	CH ₃ ; CH ₃	-382.789	-382.995	0.133	-382.853	-52	-61	-68	-79	

^a From ref. 4.

^b Estimated from *ab initio* reaction energies⁴ and the $\Delta H_f^\circ(0)$ values of O₃ and C₂H₄.

^c Thermochemical estimates from refs. 32 and 33.

^d MINDO/3 results from refs. 34 and 35.

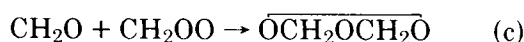
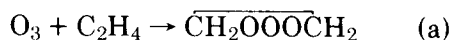
Therefore, the latter are especially helpful in those cases (11, 18, 25) where estimation from group contribution data is not possible.

IX. APPLICATION OF THEORETICAL HEATS OF FORMATION

In order to demonstrate the usefulness of theoretically estimated ΔH_f° values, molecular energies and heats of formation of some highly unstable peroxides are shown in Table XI. These molecules are of considerable interest since they play an important role in the ozonolysis reaction, i.e., the ozonation of olefins.³¹ Due to a severe lack of data on experimental heats of formation, various thermochemical estimates of ΔH_f° values utilizing group contributions tables^{32,33} or *ab initio* energy differences⁴ have been published. ΔH_f° values in question are based on the semiempirical MINDO/3 method.^{34,35}

The data of Table XI reveal that the theoretical estimates of ΔH_f° are more positive than the thermochemical ones, deviations ranging from 1–18 kcal/mol. MINDO/3 values, however, deviate by 10–28 kcal/mol.

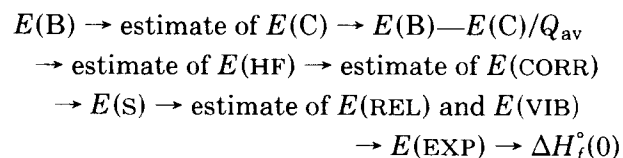
More important than the computed ΔH_f° values themselves are the reaction enthalpies derived therefrom. In the case of the ozonolysis [reactions (a), (b), (c)]:



reaction enthalpies of -43, 5, and -54 kcal/mol are obtained from the $\Delta H_f^\circ(0)$ data of Table XI and the known heats of formation of O₃, C₂H₄, and CH₂O. These results have to be compared with the best set of *ab initio* reaction energies (-49, 14, -63 kcal/mol) so far computed for reactions (a)–(c).⁴ Both sets of reaction data are in reasonable agreement. Theoretical estimates of ΔH_f° suffice to predict the strong exothermicity of reactions (a) and (c) as well as the weak endothermic character of (b). These predictions are of importance for the elucidation of the ozonolysis mechanism.

X. CONCLUSIONS

A relatively simple way of obtaining theoretical estimates of heats of formation has been described. As discussed in Parts I and II, it is possible in principle to derive theoretical ΔH_f° values from single-point RHF/B calculations:



In order to obtain more reliable ΔH_f° values it is necessary, however, to base estimates of $E(\text{HF})$ on at least two computed SCF energies, for example, $E(\text{A})$ and $E(\text{C})$ as described in Part I.

Estimated HF limit energies and correlation energies are helpful when analyzing the influence of basis set errors or correlation effects on computed energy differences. They can be used directly to derive theoretical reaction enthalpies in

those cases where no experimental data are available and an accuracy of ± 10 kcal/mol is considered to be sufficient. As an example of such a situation, the ozonolysis reaction discussed in Sec. IX may be considered.

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