Improved atom equivalents method for converting density functional theory energies calculated on molecular mechanics structures to heats of formation

Pablo Duchowicz and Eduardo A. Castro*

CEQUINOR, Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C.C. 962, La Plata 1900, Argentina
E-mail: castro@dalton.quimica.unlp.edu.ar

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Abstract

We present an improved atom equivalents method for converting Density Functional Theory energies calculated on molecular mechanics structures to enthalpies of formation. The introduction of bond parameters to an original sent of atom parameters yields a sensible improvement of the enthalpy predictions. The comparison with other similar approaches shows that our present method is a rather better calculation scheme. Some further possible improvements are pointed out.

Keywords: Density functional theory energy, enthalpy of formation, atom equivalents method

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Introduction

The requirements of the ever increasing development of pure and applied chemistry demands a reliable and as large as possible databank on Thermodynamic and Kinetic values, such as bond dissociation enthalpies, standard molar enthalpies of formation, energies of activation, etc. Such data are of paramount importance to the understanding of chemical problems and fruitful applications, such as energetics of the chemical bonds, structural properties and reactivity, chemical industry, biochemistry, environmental chemistry and many other equally important[1].

Notwithstanding, there is a huge difference between the size of the experimental thermochemical databanks and the number of known molecules, and this gap increases steadily since it is not possible to measure the thermochemical properties for all the existing compounds and for the new one synthesized day after day. For the time being, the situation is such that thermochemical data on some classes of compounds, such as hydrocarbons and other aliphatic compounds, are well known and of quite reliable quality, but on other cases, like aromatic and heterocycle compounds, those data are scarce or even totally lacking. Hence, it is necessary to have credible and accurate enough methods for estimating the enthalpies of formation of different sort of compounds.

At present, there are several well-established theoretical schemes for the estimation of these properties, although each of them is suitable for a reduced set of molecules or/and they are questionable in some sense, so that it remains rather difficult to apply them routinely to arbitrary organic compounds.

In a recent contribution aiming to overcome the previously mentioned drawbacks, Rousseau and Mathieu have presented new atom equivalents to convert Density Functional Theory (DFT) energies calculated on molecular mechanics structures to formation enthalpies ($\Delta H^o{}_f$)[2]. The central purpose of the authors was to look for practical and widely applicable methods and more efficient procedures, and their results compare well with other similar schemes based on previous atom equivalents techniques. This study could demonstrate that cost-effective approaches to molecular formation enthalpies may be developed just combining DFT with an appropriate molecular mechanics force field.

The purpose of the present work is to take a step further on the method introducing bond parameters in order to take into account explicitly the neighborhood effects. This sort of correction has shown to be a suitable way to improve similar atom equivalents methods to compute $\Delta H^o{}_f$.[3-6]

Method

The well known idea of transferability has played a significant role in the whole area of physical chemistry. The very concepts of molecular size, molecular shape, and molecular structure are firmly settled in the modern chemistry around 200 years ago.[7]

The classical theory of the chemical compound structures conceived the molecule as a set of single interacting effective atoms. This well-known concept also implies the transferability and additivity of the molecular features connected with identical atoms and bonds. The principle of transferability has often been called for to analyse a wide variety of physical chemistry properties.[8-14] Whenever a chemical bond is regarded to be independent of its location in some molecular structure, or the additivity of several parameters like bond moments, covalent radii or bond energies, is accepted, the validity of the principle of transferability is being assumed and made evident. Consequently, theoretical physical chemists are in search of suitable parameters that might consistently carry the essential and meaningful chemical information assignable from one molecule to another, without major changes.[15]

In this regard, quite different sets of atom and group equivalents have been developed which allow a direct calculation of heats of formation from semiempirical and ab initio total electronic energies.[16-19] All these procedures are based upon the very concept of transferability and they give a reasonable agreement with the available experimental data.

Recently, Rousseau and Mathieu[2] have introduced new atom equivalents to convert BP/DN**//MMFF energies into ΔH^o_f and the results compare rather well with the results of previous similar schemes. The basic starting equation is where

$$\Delta H^o_f = E + ZPE + TR + ROT + VIB + kT + \sum_k H_k{}^\circ + \sum_k X'_k \qquad (1)$$

H^o_k is the formation enthalpy of the k gaseous atoms
X'_k is the atom equivalent
E is the total molecular electronic energy at the equilibrium geometry
ZPE is the zero-point energy
TR is the translational thermal energy
ROT is the rotational thermal energy
VIB is the vibrational thermal energy
kT converts energy into enthalpy

X'_k is obtained from a least-squares fit of suitable experimental data. Eq. (1) can be simplified at a rather large extent since the explicit inclusion of TR, ROT and kT contributions, using calculated data, does not improve significantly the results. Besides, the atomic formation enthalpies H^o_k are included within new empirical paramters Y_k together with ZPE and VIB, so that it is a usual practice in this sort of approximation to apply the following approximation.[23,30-34]

$$\Delta H^o_f = E + \sum_k Y_k \qquad (2)$$

The distinctive feature of this procedure proposed by Rousseau and Mathieu stems from the fact that it relies on DFT energies E calculated on molecular mechanics structures. Although numerical estimations based on Eq. (2) gives sensible ΔH_{of} values, the authors pointed out some possible future developments of atomic equivalents approaches. One of these consists on using different atomic equivalents according to the chemical environment of the atoms. However, this procedure should increase at a somewhat large extent the number of atomic parameters in order to take into account the great diversity of such environments. Consequently, a nearly equivalent method to consider the existing atoms in a network of specific chemical bonds is to extend Eq. (2) as follows where the index k-l runs over all chemical bonds an W is a constant.

$$\Delta H^o_f = E + \sum_k Y_k + \sum_k X_{k-l} + W \qquad (3)$$

On the basis of previous results for Y_k, we have determined X_{k-l} contributions as correction terms. That is to say, resorting to the Rousseau and Mathieu´s parameters, we have computed the new X_{k-l} bond parameters fitting them against experimental ΔH^o_f values through Eq. (3), employing previous Y_k´s.

In order to judge consistently the relative merits of the proposed methodology, we have resort to the same molecular sets as that used previously by Rousseau and Mathieu, and then we compare our results with their values as well as with those reported by Habibollahzdeh et al */35/* and Rice et al[36]. These specific choices are due these two works are based on atomic equivalents determined from DFT to estimate ΔH^o_f**.**

Results and Discussion

The training set used to derive the bond parameters together with ΔH^o_f calculated by Rousseau and Mathieu[2] and our present approach are given in Table 1, while in Table 2 we display atomic and bond parameters. Evidently, the training panel comprises a quite representative set of molecules including hydrocarbons, alcohols, ketones, aldehydes, ethers, carboxylic acids, nitriles, and halogenated hydrocarbons.

The analysis of results shown in Table 1 allows one to verify the improvements of predictions of heats of formation when introducing bond parameters. In particular, rms and maximum absolute deviation are lower for the present approach.

In Table 3 we present our estimations of ΔH^o_f for the prediction molecular panel together with other theoretical results for comparative purposes. Maximum deviations and rms errors are also included to facilitate the corresponding comparisons among the different models.

The analysis of results shows that bond parameters are indeed “correction terms” regarding atomic parameters (see relative magnitudes of these quantities in Table 2). Since dimethylfuroxan presents an oxygen atom linked to one aza nitrogen atom through a dative bond, it cannot be handled with the MMFF force field, hence the lack of calculated value of this molecule. Once again, the insertion of corrective bond terms in Eq. (2) to give Eq. (3) yields ameliorate results, since there is an improvement of rms and maximum absolute deviations. The comparison of the results arising from the different methods enables one to verify that the introduction of bond parameters into the approximation of atom equivalents for converting DFT energies calculated on molecular mechanics structures to formation enthalpies yields a rather satisfactory theoretical scheme. Since experimental uncertainties in the determination of enthalpies of formation are around 10 kJ/mol, the average deviations are rather sensible. It is also interesting to compare our present approach with Habibollahzadeh et al´s method, since this last one has been particularly designed to compute thermochemical data. Results of Table 3 show that maximum absolute deviations are similar, while our approach gives a lower root mean square deviation.

Table 1. Training set used to derive the bond parameters listed in Table 2

Molecule	$\Delta H°_f$ (BP/DN**)$^{2\,a}$	$\Delta H°_f$(this work)	$\Delta_1{}^{2\,b}$	Δ_2 (this work)^b
2,2,3,3-Tetrafluoro-1-propanol	-1061.3	-1064.6	7.3	4.0
Hexafluorobenzene	-956.0	-956.7	-2.5	-3.2
Tetrafluoromethane	-933.2	-939.1	18.6	12.69
Pentafluorobenzene	-806.0	-807.5	-4.0	-5.5
Chlorotrifluoromethane	-707.9	-711.3	7.9	4.5
Trifluoromethane	-697.1	-699.1	4.0	2.0
1,2,4,5-Tetrafluorobenzene	-646.8	-648.6	-11.0	-12.8
3-Methylbutanoic acid	-510.0	-509.4	1.0	1.6

Table 1. Continued

Trifluoroacetonitrile	-497.9	-499.1	7.2	6.0
Butanoic acid	-475.9	-473.8	-10.9	-8.8
Chlorodifluoromethane	-482.0	-482.1	-4.0	-4.1
2,3-Butanediol	-482.3	-480.8	22.4	23.9
Difluoromethane	-450.7	-448.3	-3.2	-0.8
1,2,4-Benzenetriol	-444.0	-444.1	-8.4	-8.5
Propyl formate	-462.7	-459.8	33.1	36.0
Methyl acetate	-410.0	-404.5	-15.1	-9.6
1,4-Dioxane	-315.3	-314.9	-18.1	-17.7
Hexanol	-315.9	-313.5	-10.2	-7.8
Cyclohexanol	-286.2	-292.7	-8.1	-14.6
2-Propanol	-272.6	-271.6	-3.4	-2.4
Acetamide	-238.3	-232.6	-15.8	-10.1
Urea	-235.5	-229.7	-13.6	-7.8
Ethanol	-243.8	-238.8	3.1	8.1
Cyclopentanol	-242.5	-247.0	2.0	-2.5
Fluoromethane	-234.3	-229.0	-1.7	3.6
Acetone	-217.1	-210.1	-6.1	0.9
N,N-Dimethylformamide	-192.4	-184.3	-22.3	-14.2
Formamide	-186.0	-173.3	-23.2	-10.5
Propanal	-185.6	-176.9	-10.0	-1.3
2,2,3-Trimethylbutane	-204.5	-2004.6	16.0	15.9
2,2-Dimethylbutane	-185.6	-185.0	9.9	10.5
Ethanal	-166.2	-156.7	-5.6	3.9
2-Methyl-2-nitropropane	-177.1	-179.3	5.4	3.2
2,3-Dimethylbutane	-177.8	-176.8	6.2	7.2

Table 1. Continued

Neopentane	-167.9	-166.7	0.6	1.8
Nitrobutane	-143.9	-144.3	-15.9	-16.3
2-Methylbutane	-153.7	-151.7	-3.7	-1.7
1-Fluoro-4-methylbenzene	-147.5	-148.8	0.7	-0.6
Isobutane	-134.2	-131.5	-4.2	-1.5
Ethoxyethene	-140.8	-137.7	3.0	6.1
n-Butane	-127.1	-124.0	-7.2	-4.1
Cyclohexane	-123.4	-130.0	-7.7	-14.2
Cyclooctane	-124.4	-130.3	2.6	-3.3
Cycloheptane	-118.1	-124.0	-2.3	-8.2
Chloroethane	-124.5	-122.7	4.3	6.1
Nitroethane	-102.3	-101.1	-14.4	-13.2
Propane	-104.7	-100.7	-9.3	-5.3
Formaldehyde	-115.9	-104.0	8.1	20.0
Chloroform	-103.2	-102.2	-1.3	-0.3
Butylamine	-91.9	-86.6	-5.3	0.0
Ethane	-83.7	-78.9	-7.3	-2.5
Methyl chloride	-83.7	-80.0	-3.9	-0.2
Hydrogen chloride	-92.3	-97.3	6.9	1.9
Cyclopentane	-76.4	-80.7	-5.6	-9.9
Phenol	-96.4	-105.0	14.6	6.0
Methane	-74.5	-69.5	-0.9	4.1
2-Methyl-1,2-propanediamine	-90.3	-84.7	18.1	23.7
Dinitromethane	-58.9	-58.2	12.4	13.1
Methylamine	-22.5	-14.4	-2.2	5.9
Dimethylamine	-19.5	-11.2	-5.0	3.3

Table 1. Continued

Tetrachloroethylene	-12.4	-15.2	1.4	-1.4
1,2,3-Trimethylbenzene	-9.5	-11.6	2.3	0.2
p-Xylene	18.0	17.1	-0.9	-1.8
2-Methyl-propanenitrile	23.4	24.4	-5.0	-4.0
Butanenitrile	33.6	35.1	-15.0	-13.5
1,2-Dimethylbenzene	19.1	18.3	0.1	-0.7
Cyclobutane	28.4	29.5	-8.3	-7.2
1,3-Dimethylbenzene	17.3	16.4	3.6	2.7
Acetaldimine	24.0	-0.6	9.2	-15.4
Propanenitrile	51.7	53.9	-9.7	-7.5
Methylbenzene	50.4	50.9	-2.0	-1.5
Chlorobenzene	51.8	51.3	-1.2	-1.7
Ethanenitrile	74.0	77.0	-12.0	-9.0
Ethylenediamine	84.1	90.2	-10.8	-4.7
Cyclopropylamine	77.0	80.7	-1.3	2.4
Benzene	82.9	84.9	-3.0	-1.0
N-Methylmethanimine	44.0	20.2	39.2	15.4
4-Methylpyridine	103.8	115.8	-12.0	0.0
1H-Imidazole	139.3	156.8	-25.7	-8.2
Hydrogen cyanide	135.1	141.1	-4.2	1.8
1H-Pyrazole	179.4	209.7	-30.3	0.0
Butyne	165.2	164.8	-0.1	-0.5
Dimethyl.diazene	148.6	122.5	26.1	0.0
Propyne	184.9	185.3	0.1	0.5
4-Pyridinecarbonitrile	283.5	295.0	-19.5	-8.0
Acridine	273.9	277.3	12.8	16.2

Table 1. Continued

Bicyclo[1.1.0]butane 1carbonitrile	304.5	300.1	38.6	34.2
Rms	-	-	12.6	10.1
Maximum absolute deviation	-	-	39.2	36.0

[a] unit kJ/mol.

[b] error with respect to the experimental data.[37]

Table 2. Atom and bond equivalents taken from Ref. 2 and derived in this work, respectively (kJ/mol)

Atom and bond types	Coordination	Y_k	X_{k-l}
H	1	1557.6	-
C	4	100,114.9	-
C	3	100,119.5	-
C	2	100,114.4	-
N	3	143,859.4	-
N (nitro)	3	143,908.2	-
N	2	143,856.5	-
N	1	143,846.6	-
O	2	197,426.1	-
O	1	197,427.9	-
F	1	262,042.9	-
Cl	1	1,208,399.3	-
C-C	-	-	-1.2215
C-H	-	-	0.6528
C-F	-	-	2.8234
C-O	-	-	0.4742
O-H	-	-	2.3221
$C-C_{arom}$	-	-	-0.6818
C-Cl	-	-	0.4643
C=O	-	-	3.4990
C≡N	-	-	-0.5397
N-H	-	-	0.8837

Table 2. Continued

C-N	-	-	-1.0563
N-O	-	-	0.5485
N=O	-	-	0.5485
C=C	-	-	-1.9198
C-N_{arom}	-	-	0.6690
N-N_{arom}	-	-	2.5135
C≡C	-	-	-3.2865
C=N	-	-	-8.0259
N=N	-	-	-9.5493

Constant term in Eq. (3) (W) equal to –0.4453.

Table 3. Enthalpies of formation (kJ/mol) for several compounds

Molecule	Exp. [38]	PIMM [2]	P1[2]	P2[2]	HGCMP[35]	This work
Chlorodifluoromethane	-482.0	-438.6	-472.6	-485.9	-461.7	-486.2
Methyl acetate	-411.5	-412.9	-423.3	-426.9	-405.6	-422.4
Ethylene glycol	-387.1	-411.1	-374.0	-386.1	-357.9	-380.0
Formic acid	-378.6	-371.8	-385.7	-392.7	-352.8	-387.1
1,4-Dioxane	-315.5	-307.2	-296.5	-300.8	-332.8	-299.6
1-Fluoropropane	-285.6	-285.1	-293.1	-296.2	-272.8	-293.6
Diethyl ether	-251.8	-253.0	-268.7	-267.2	-265.1	-262.7
Urea	-245.6	-211.4	-234.9	-241.6	-211.3	-236.2
Water	-241.6	-234.3	-227.9	-233.8	-197.8	-229.1
Acetamide	-238.1	-214.0	-248.3	-251.3	-224.5	-246.3

Table 3. Continued

Ethanol	-235.0	-242.1	-233.3	-240.7	-219.6	-235.6
Acetone	-217.1	-209.7	-224.1	-223.2	-196.3	-216.5
Methanol	-201.3	-219.6	-197.9	-204.5	-183.6	-197.7
Dimethylether	-183.9	-208.0	-189.9	-195.3	-184.7	-187.5
Neopentane	-168.0	-175.0	-169.0	-167.3	-154.5	-166.0
n-Butane	-125.5	-127.9	-132.6	-134.3	-127.3	-131.6
Methyl nitrate	-122.1	-189.9	-154.0	-158.2	-163.9	-151.7
Chloroethane	-112.0	-100.8	-108.1	-120.3	-117.9	-118.3
Formaldehyde	-108.5	-120.8	-108.8	-107.8	-79.8	-95.5
Propane	-104.6	-106.2	-113.4	-114.0	-105.8	-110.5
Nitroethane	-102.2	-121.8	-115.5	-116.7	-84.1	-116.3
Ethane	-83.6	-85.6	-91.4	-90.9	-84.7	-86.5
Nitromethane	-74.4	-97.2	-87.3	-86.9	-46.8	-85.2
Methane	-74.4	-65.3	-78.8	-75.4	-70.6	-70.5
Methyl nitrite	-66.5	-81.6	-30.0	-32.2	-81.0	-21.1
Ammonia	-46.0	-9.4	-41.8	-42.7	-22.9	-32.1
Benzaldehyde	-36.7	-45.1	-40.7	-45.3	-40.6	-40.9
Furan	-34.9	-61.7	-26.0	-42.5	-54.2	-44.3
Methylamine	-23.0	-23.5	-22.9	-24.7	-14.3	-16.8
Isobutene	-16.9	-2.7	-14.8	-15.9	-11.0	-15.0
Oxazole	-15.5	-40.6	-11.7	-29.7	-16.7	-22.3
Dimethylnitramine	-4.6	30.1	-26.7	-26.3	-11.2	-17.5
Propene	20.0	28.1	22.2	20.5	26.6	23.0
Vinyl chloride	37.2	20.8	36.4	22.3	14.3	23.8
Nitroethylene	37.6	2.0	45.0	41.0	59.4	41.7
4,5-dihydro-3-nitroisoxazole	39.0	-34.8	28.0	53.1	50.0	25.7
Chlorobenzene	51.8	52.4	64.1	50.4	39.3	49.8
Triamino-trinitrobenzene	51.8	-34.8	101.7	102.0	75.0	98.1
Ethylene	52.3	59.5	59.1	57.7	65.3	61.9
Cyclopropane	53.1	50.3	29.0	42.5	50.9	44.0
1,3-Dinitrobenzene	53.9	24.9	67.2	65.6	71.4	61.5
1,4-Dinitropiperazine	58.1	155.0	29.3	35.9	50.6	39.1

Table 3. Continued

4-Nitroaniline	58.9	34.6	87.3	83.6	54.0	83.3
1,3,5-Trinitrobenzene	62.3	46.5	81.1	80.0	76.2	74.1
Acetonitrile	64.4	87.9	81.6	62.0	64.2	83.0
Nitrobenzene	67.3	37.1	66.1	63.5	68.1	61.8
Isoxazole	78.6	104.4	69.9	55.4	64.7	61.9
Benzene	82.3	82.5	83.6	79.9	79.2	81.7
Aniline	86.9	90.2	85.5	80.7	77.9	83.0
Methylhydrazine	94.5	91.7	85.5	85.3	87.6	103.0
Dimethylfuroxan	102.2	123.9	-	-	68.6	-
Dimethylfurazan	107.2	160.4	80.8	76.0	82.6	87.2
Pyrrole	108.2	74.4	104.2	100.3	101.4	115.6
1,3-Butadiene	109.9	110.4	122.2	116.4	118.9	116.2
Pyridine	140.3	153.9	131.5	128.1	131.2	141.1
Indole	156.3	169.5	158.2	154.7	139.1	164.2
Propyne	184.7	185.1	184.3	185.0	178.2	185.4
Allene	190.3	-	177.7	183.0	188.4	186.1
RDX	191.4	240.7	178.7	185.1	167.6	197.1
Pyrimidine	195.7	203.5	174.1	171.1	196.9	195.1
Pyrazine	195.9	212.1	188.3	186.1	212.1	210.9
Acetylene	228.0	227.1	140.0	240.1	234.5	243.2
Pyridazine	278.1	284.3	258.7	258.4	282.2	278.7
Tetrazole	334.2	359.7	290.6	292.5	332.1	318.8
rms absolute deviation	-	28.7	15.7	15.5	17.1	13.6
Maximum absolute deviation	-	96.9	59.6	64.8	43.8	46.3

Conclusions

Following a similar basic perspective as that stated in Rousseau and Mathieu´s paper[2], we do not intend here to achieve for an extreme chemical accuracy but to look for a more efficient and simple way to estimate a fundamental thermodynamical quantity. This work aims to introduce an improvement into a recent method based on atom equivalents for converting DFT energies calculated on molecular mechanics structures to heats of formation. The improvement consists in inserting bond parameters in order to take into account the chemical environment of each atom within the molecule. This change does not introduce any further extra effort in the computational procedure so that the simplicity of the original approach[2] is kept. This sort of amelioration is not new and some previous applications have shown the convenience of inserting it within the context of similar calculation schemes[3-6]. The basic idea behind the methodology is consistent with the variety of atom types involved in force field definitions and present results seem to suggest a suitable way to define the optimal combination of force field, electronic structure model, and the set of atomic equivalents and bond parameters.

Regarding some possible future improvements of the method described here, perhaps it should be advisable to define atom and bond parameters for rather more specific sets of molecules. In fact, although it seems the procedure leads to a "parameters nightmare", it should be more sensible since it is nearly impossible to attain a satisfactory enough agreement between experimental and theoretical data when the fitting set is composed of quite different molecules. It must be taken into account that this sort of methodology is a semiempirical one, where results arising from first principle methods and empirical molecular mechanics procedures are used together with arbitrary fitting equations and experimental data.

At present, research along this line is under development in our laboratory and results will be presented elsewhere in the forthcoming future.

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