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Composite Method Employing Pseudopotential at CCSD(T) Level

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1. Introduction

Thermochemical data are among the most fundamental and useful information of chemical species which can be used to predict chemical reactivity and relative stability. Thus, it is not surprising that an important goal of computational chemistry is to predict thermochemical parameters with reasonable accuracy (Morgon, 1995a). Reliability is a critical feature of any theoretical model, and for practical purposes the model should be efficient in order to be widely applicable in estimating the structure, energy and other properties of systems, as isolated ions, atoms, molecules(Ochterski et al., 1995), or gas phase reactions(Morgon, 2008a).

What is the importance of these studies?

For instance gas phase reactions between molecules and ions, and molecules and electrons are known to be important in many scientifically and technologically environments. On the cosmic scale, the chemistry that produces molecules in interstellar clouds is dominated by ion-molecule reactions. Shrinking down to our own planet, the upper atmosphere is a plasma, and contains electrons and various positive ions. Certain anthropogenic chemical compounds (including SF_6 and perfluorocarbons) can probably not be destroyed within the troposhere or stratosphere, but may be removed by reactions with ions or electrons in the ionosphere. Recent years have seen a massive growth in the industrial use of plasmas, particularly in the fabrication of microelectronic devices and components. The chemistry within the plasma, much of which involves ion-molecule and electron-molecule reactions, determines the species that etch the surface, and hence the outcome and rate of an etching process. Much of the chemistry that is often labelled as 'organic' or 'inorganic' involves ion-molecule reactions, usually carried out in the presence of a solvent. For instance, S_N2 reactions, such as OH^- + CH_3Cl, fall into this category. To gain a clearer picture of how these (gas phase) reactions occur, it is advantageous to study them removed from the (very great) perturbations due to the solvent.

So, the need for thorough studies of ion-molecule and electron-molecule reactions are thus well established, ranging from the astrophysical origins of molecules, through the survival of the earth's atmosphere, to modelling the plasmas that underpin many advanced processing technologies. There is intrinsic interest too in the studies, as they help to explore the nature and progress of binary encounters between molecules and ions, and molecules and electrons. At the most basic level answers are needed to the following questions - how fast does a reaction proceed? and what are the products of the reaction? What determines which

reactions occur? and what products are formed? Beyond these may come questions about the detailed dynamics of the reaction, such as how changing the energy of the reactants may influence the progress and outcome of the reaction.

Many powerful experimental techniques have been developed to give the basic data of reaction rate coefficients and products (usually just the identification of the ion product). These results are part of the raw data needed to understand and model the complex chemistry occurring in the diverse environments identified above. There is much information that is not directly available from the experimental data. This includes identification of the neutral products of a reaction, knowledge of the thermochemistry of the reaction, and characterization of the pathway that connects reactants to products. By invoking some general rules, the experimental observations can be used to provide partial answers. Thus the fast flow techniques that are used to provide much of the experimental data on ion-molecule reactions can only detect the occurrence of very rapid reactions (k >= 10^{-12} cm^3 s^{-1}), which places an upper bound on the exothermicity of the reaction of +20 kJ mol^{-1}. In cases where there are existing reliable enthalpies of formation of each of the species in a proposed pathway to an observed ion product, this rule can test whether the suggested neutral products may be correct. In other cases, where the enthalpy of formation of just one of the species involved in a reaction (usually the product ion) is unknown, the observation of a specific reaction pathway can be used to place a bound on the previously unkown enthalpy of formation. Finally for reactions which are known to be exothermic, if the experimenal rate coefficient is observed to be less than the capture theory rate coefficient, then it is usual to conclude that there must be some bottleneck or barrier to the reaction.

What can theoretical calculations add to the experimental data?

Three important and fundamental gas-phase thermochemical properties from a theoretical and experimental point of view are the standard heat of formation ($\Delta_f H^o_{gas}$), the electron (EA) and proton (PA) affinities. Thus, it is not surprising that an important goal of computational chemistry is to predict such thermochemical parameters with reasonable accuracy, which can be useful in the gas phase reaction studies. Proton transfer reactions are also of great importance in chemistry and in biomolecular processes of living organisms(Ervin, 2001). Absolute values of proton affinities are not always easy to obtain and are often derived from relative measurements with respect to reference molecules. Relative proton affinities are usually measured by means of high pressure mass spectrometry, with triple quadrupole and ion trap mass spectrometers (Mezzache et al., 2005) or using ion mobility spectrometry (Tabrizchi & Shooshtari, 2003). The importance and utility of the EA extend well beyond the regime of gas-phase ion chemistry. A survey of examples illustrates the diversity of areas in which electron affinities play a role: silicon, germanium clusters, interstellar chemistry, microelectronics, and so on.

The standard heat of formation, which measures the thermodynamic stability, is useful in the interpretation of the mechanisms of chemical reactions (Badenes et al., 2000).

On the other hand, theoretical calculations represent one attempt to study absolute values of electron or proton affinity and other thermochemical properties (Smith & Radom, 1991). However, accurate calculations of these properties require sophisticated and high level methods, and great amount of computational resources. This is particularly true for atoms of the 2nd, 3rd, ..., periods and for calculating properties like the proton and electron affinity

of anions. Gaussian-n theories (G1, G2, G3, and G4) (Curtiss et al., 1997; 1998; 2000; 2007) have given good results for properties like proton and electron affinities, enthalpies of formation, atomization energies, and ionization potentials. These theories are a composite technique in which a sequence of well-defined ab initio molecular orbital calculations is performed to arrive at a total energy of a given molecular species. There are other techniques that have been demonstrated to predict accurate thermochemical properties of chemical species, and are alternative to the Gaussian-n methods: the Correlation Consistent Composite Approach (ccCA)(DeYonker et al., 2006), the Multireference Correlation Consistent Composite Approach (MR-ccCA)(Oyedepo & Wilson, 2010), the Complete Basis Set Methods (CBS) and its versions: CBS-4M, CBS-Lq, CBS-Q, CBS-QB3, CBS-APNO(Montgomery Jr. et al., 2000; Nyden & Petersson, 1981; Ochterski et al., 1996; Peterson et al., 1991), and Weizmann Theories (W1 to W4)(Boese et al., 2004; Karton et al., 2006; Martin & De Oliveira, 1999; Parthiban & Martin, 2001).

Recently, we have implemented and tested a pseudopotential to be used with the G3 theory for molecules containing first-, second-, and non-transition third-row atoms (G3CEP) (Pereira et al., 2011). The final average total absolute deviation using this methodology and the all-electron G3 were 5.39 kJ mol^{-1} and 4.85 kJ mol^{-1}, respectively. Depending on the size of the molecules and the type of atoms considered, the CPU time was drastically decreased.

2. Computational methods

In this chapter we have developed a computational model similar to version of the G2(MP2, SVP) theory (Curtiss et al., 1996). Both theories are based on the additivity approximations to estimate the high level energy for the extended function basis set. While G2(MP2,SVP) is based on the additivity approximation to estimate the QCISD(T) energy for the extended 6-311+G (3df,2p) basis set: E[QCISD(T)/ 6-311+G(3df,2p)] E[QCISD(T)/6-31G(d)] + E[MP2/6-311+G(3df,2p)] - E[MP2/6-31G(d)]. Our methodology employs CCSD(T) energies in addition to the the valence basis sets adapted for pseudopotential (ECP) (Stevens et al., 1984) using the Generator Coordinate Method (GCM) procedure (Mohallem & Dreizler, 1986; Mohallem & Trsic, 1985).

The present methodology which relies on small basis sets (representation of the core electrons by ECP) and an easier and simpler way for correcting the valence region (mainly of anionic systems) appears as an interesting alternative for the calculation of thermochemical data such as electron and proton affinities or heat of formation for larger systems.

2.1 Development of basis sets

The GCM has been very useful in the study of basis sets(Morgon, 1995a;b; 2006; 2008b; 2011; Morgon et al., 1997). It considers the monoelectronic functions $\psi(1)$ as an integral transform,

$$\psi(1) = \int_0^\infty f(\alpha)\, \phi(\alpha, 1)\, d\alpha \tag{1}$$

where $f(\alpha)$ and $\phi(\alpha, 1)$ are the weight and generator functions respectively (gaussian functions are used in this work), and α is the generator. The existence of the weight functions (graphical display of the linear combination of basis functions) is an essential condition for the use of GCM. Analysis of the behavior of the weight functions by the GCM permits the

atomic basis set to be adapted in such a way as to yield a better description of the core electrons (represented by ECP) and the valence orbitals (corrected by addition of the extra diffuse functions), in the molecular environment. With the exception of some simple systems the analytical expression of the weight functions is unknown. Thus, an analytical solution of the integral transform (Eq. 1) is not viable in most cases, and suggests the need of numerical techniques to solve Eq. 1 (Custodio, Giordan, Morgon & Goddard, 1992; Custodio, Goddard, Giordan & Morgon, 1992). The solution can be carried out by an appropriate choice of discrete points on the generate coordinate, represented by:

$$\alpha_{i,(k)} = exp[\Omega_{o,(k)} + (i-1) \cdot \Delta\Omega_{(k)}], \quad i = 1, 2, 3, \ldots N_{(k)} \tag{2}$$

The discretization of the set is defined by the following parameters: an initial value (Ω_o), an increment ($\Delta\Omega$), and by the number of primitives used (N) for a given orbital k (s, p, d, $\ldots$). The search for the best representation is obtained using the total energy of the electronic ground state as the minimization criterion.

The SIMPLEX search method (Nelder & Mead, 1965) can be adapted to the any electronic structure program to provide the minimum energy of the ground state of the atom corresponding to the optimized discretization parameters.

The basic procedure consists of the following steps:

(a) search of the optimum discretized parameter set for the atoms using the GCM for variation on the generator coordinate space. The core electrons are represented by a pseudopotential. The discretization parameters (Ω_o and $\Delta\Omega$) are defined with conjunction with this ECP;

(b) the minimum energy criterion is observed and the characteristics of the atomic orbital weight functions are analyzed;

(c) extra functions (polarizaton or diffuse funcions - s, p, d and f) are obtained by observing the convergent behavior of the weight functions of the outer atomic orbitals (s and p). These extra functions are needed for the correct description of the electronic distribution in an anion (diffuse character of electronic cloud).

To the heavy atoms f type polarization functions are not available in these valence basis sets for this kind of ECP(Stevens et al., 1984). So, it was need to define the value of these f functions for Br and I atoms. The determination of the best value was carried out considering the smaller difference between the PAs (experimental and theoretical) values considering the Br^- and I^- anions. The f exponent values found are 0.7 and 0.3 for Br and I atoms, respectively.

In fact two sets of basis functions are used, a small basis and a larger basis, with extra diffuse and polarization functions, B0 and B1, respectively. Calculations with basis B1 are naturally much more expensive than those employing basis B0, so it is important to have computational schemes that perform the minimum number of calculations using basis B1.

For instance, the B0 basis set is defined as: (31) for H; (311/311) for C, O, F, S, and Cl; and (411/411) Br and I. For more refined energy calculations (B1 basis set are used), this set was augmented with additional diffuse and polarization functions (p for H and s, p, d, and f for heavy atoms) to yield a (311/11) set for H; (311/311/11/1) for C, O, F, S, and Cl; and (411/411/11/1) for Br and I atoms.

2.2 Molecular calculations

In many problems to be addressed by electronic structure methodology, high accuracy is of crucial importance. In order to obtain energies that may approach chemical accuracy ($\approx$10 kJ.mol^{-1}) calculations must take account of electron correlation. The 'ideal' methodology would have been a multi-reference configuration interaction all electron calculation with several large, flexible basis sets to enable extrapolation to the complete basis set limit. Depend on the size of the systems, performing accurate calculations (methodology and basis sets) represents a significant challenge.

Morgon *et al.* (Morgon, 1998; Morgon et al., 1997; Morgon & Riveros, 1998) have been developing techniques to tackle such problems. These are centered around the use of effective core potentials, in which the inner electrons are represented by an effective potential derived from calculations on atoms. The electronic wavefunction itself then only contains the outer electrons.

The procedure to the molecular calculations employing this methodology is:

(a) optimization of the molecular geometries and vibrational analysis are carried out at HF/B0 level. The harmonic frequencies confirm that the stationary points correspond to minima and are used to compute the zero-point energies;

(b) further optimization is carried out at MP2/B0 level;

(c) at the MP2 equilibrium geometry corrections to the total energies are performed at higher level of theory. First, this is carried out at CR-CCSD[T]/B0 level (Completely Renormalized Coupled-Cluster with Single and Double and Perturbative Triple excitation) (Kowalski & Piecuch, 2000) (or at CCSD(T)/B0 level for EA calculations), and later by addition of extra functions (s, p, d, and f) at MP2/B1 level.

Thus, these results coupled to additive approximations for the energy yield an effective calculation at a high level of theory,

$$\approx E[CR - CCSD[T]/(B1)] = E[CR - CCSD[T]/(B0)] +$$

$$+ E[MP2/(B1)] - E[MP2/(B0)] + ZPE[HF/(B0)] * scal \qquad (3)$$

where *scal* (0.89) is the scaling factor on the vibrational frequencies.

The CR-CCSD[T] (Completely Renormalized Coupled-Cluster with Single and Double and Perturbative Triple excitation) methodology refers to size-extensive left eigenstate completely renormalized (CR) coupled-cluster (CC) singles (S), doubles (D), and noniterative triples (T). This approach is abbreviated as CR-CCL and is appropriately described by Piecuch(Piecuch et al., 2002) and Ge(Ge et al., 2007).

An alternative model was developed for the study of heat of formation. This model employs valence basis sets aug-CCpVnZ (n = 2, 3, and 4) (Dunning, 1989). These basis sets were adapted to ECP using the GCM and are identified by ECP+ACCpVnZm (m = modified). The energies are obtained through the extrapolations to the complete basis set limit (CBS) using Peterson mixed exponential/Gaussian function extrapolation scheme (Feller & Peterson, 1999).

$$E(MP2) = E_{CBS} + B \, exp[-(x - 1)] + C \, exp[-(x - 1)^2] \qquad (4)$$

where x = 2, 3, and 4 come from ECP+ACCpV2Zm, ECP+ACCpV3Zm and ECP+ACCpV4Zm energies, respectively.

For this electronic property, molecular calculations consist of:

(a) optimization of the molecular geometries and vibrational analysis are carried out at HF/ECP+ACC2Zm level. The harmonic frequencies are employed to characterize the local minima and to compute the zero-point energies;

(b) further optimization is carried out at MP2/ECP+ACC2Zm level;

(c) at the MP2 equilibrium geometry corrections to the total energies are performed at higher level of theory. First, at CR-CCL/ECP+ACC2Zm level, and calculations by addition of extra functions ($s, p, d,$ and f) at MP2/ECP+ACC3Zm and MP2/ECP+ACC4Zm levels. The E[MP2/ECP+ACC5Zm] is estimated throught the Eq. 4.

(d) Finally, the results are coupled through additive approximations, and the energy corresponds to an effective calculation at a high level of theory,

$$\approx E[CR - CCL/ECP + ACC5Zm] = E[CR - CCL/ECP + ACC2Zm] + $$
$$+ E[MP2/ECP + ACC5Zm] - E[MP2/ECP + ACC2Zm] - \qquad (5)$$
$$+ ZPE[HF/ECP + ACC2Zm] * scal + E(HLC)$$

where *scal* is the scaling factor on ZPE.

The method also includes an empirical higher-level correction (HLC) term. This term is given by either Eq. 6 or Eq. 7 depending on whether the species is a molecule or an atom:

$$HLC_{molec.} = -C \cdot n_\beta - D \cdot (n_\alpha - n_\beta) \qquad (6)$$

$$HLC_{atom} = -A \cdot n_\beta - B \cdot (n_\alpha - n_\beta) \qquad (7)$$

In these equations, n_α and n_β are the numbers of α and β electrons, respectively. The parameters A (4.567mH), B (2.363mH), C (4.544mH), and D (2.337mH) were obtained by fitting to the experimental data of heats of formation.

It is important to note that since it only depends on the number of α and β valence electrons, the HLC cancels entirely from most reaction energies, except when the reactions involve a mixture of atoms and molecules (as in heats of formation and bond dissociation energies) and/or when spin is not conserved (Lin et al., 2009).

It should be also noted that the absolute values of the calculated energies have no real significance, as no common energy zero for different atoms has been used. This arises from how the effective core potentials are constructed. When differences are formed, the differences between the zeros cancel, to leave for instance the difference in energy between the products and reactants of a reaction.

Additionally, an alternative approach for molecular geometry optimization and harmonic frequencies calculation can be considered through the use of the DFT (B3LYP, M06, ...).

3. Results and discussion

3.1 Basis sets

The existence of the weight functions (graphic representations of the linear combination of the atomic orbitals) is the fundamental condition to use the GCM. The analysis of the behavior of the weight functions by the GCM allows the fitting of the atomic basis sets in order to get a

better description of the electrons in the molecular environment. The analysis of the weight functions of the outermost atomic orbitals suggested the need for improvements of the basis sets for the heavy atoms. Observing the plots of the weight functions of the outermost orbitals it is possible to establish the best fit of the basis sets. Using the atom of Cl as an example, the representation of the weight function of the atomic orbital 3s is shown in Fig. 1. The continuous line represents the plot of the weight function of the original primitive basis set for the all electron system. The dashed line represents the same weight function obtained using the pseudopotential. This figure shows that the 10 inner functions (large α) have a contribution close to zero towards the description of the weight function. The vertical solide line cutoff of the basis set indicates precisely where the pseudopotential starts to represent the core atomic region.
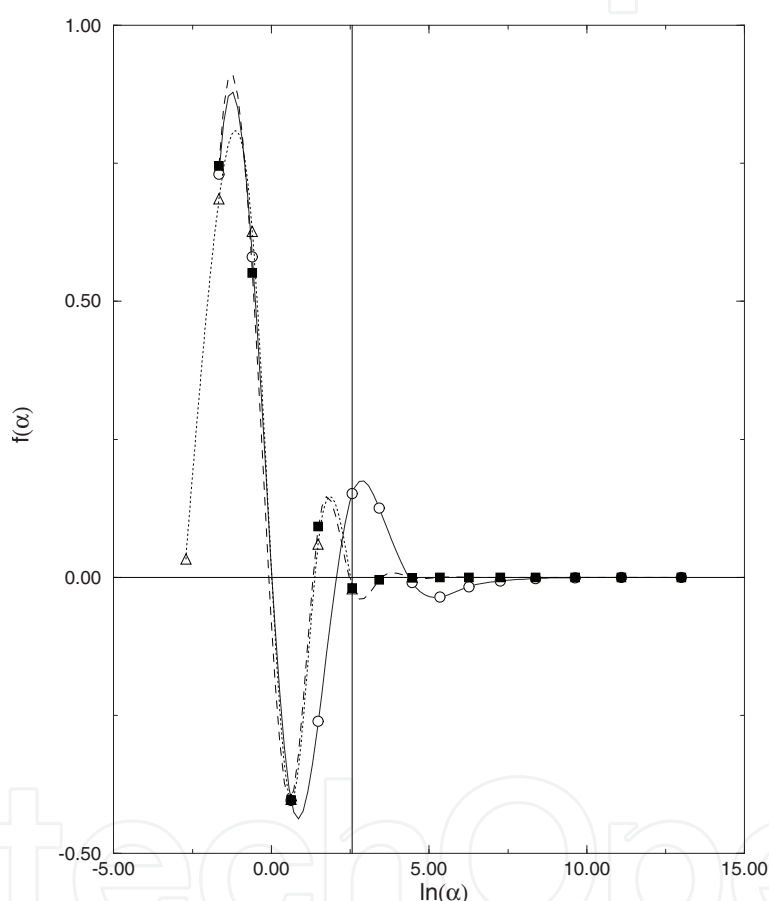

Fig. 1. Weight functions for the 3s atomic orbital of Cl in systems with all electrons (ae, continuous line), with the pseudopotential (pp, dashed line), with the addition of one diffuse function plus pseudopotential (dif+pp, dot-dashed line) and the cutoff point line represented by the vertical solid line.

3.2 Proton affinity

Proton affinity is a very sensitive property of the electronic structure and it is appropriate to test our methodology. Table 1 shows the results of the acidity (in kJ.mol^{-1}) for a set of anions systems. These results were obtained using the B0 and B1 basis sets and Eq. 3. A comparison is also presented with experimental results. One can observe that our theoretical results are

very close to the experimental errors (well within 5 kJ.mol^{-1}) with root mean square deviation of 4.14 kJ mol^{-1}.

System	PA$_{Calc.}$	PA$_{Exp.}^a$
F$^-$	1556.17 (-2.17)	1554.0
CH$_2$F$^-$	1710.21 (0.79)	1711 ± 17
Cl$^-$	1395.56 (-0.56)	1395.0
CH$_2$Cl$^-$	1658.18 (-1.18)	1657 ± 13
Br$^-$	1354.80 (-1.80)^b	1353.0 ± 8.80
CHClBr$^-$	1563.4 (0.82)	1560.0 ± 13.00
CH$_2$Br$^-$	1640.54 (2.46)	1643 ± 13
I$^-$	1315.10	1315.0
CH$_2$I$^-$	1617.47 (-1.47)	1616 ± 21
Acetamide,2,2,2-trichloride	1493,6	1436 ± 8.8
Formamide-N,N-dimethyl	1671.34 (-1.34)	1670.0 ± 17.00
Formamide	1510.13 (-5.13)	1505.0 ± 8.80
methyl cyclopentanol	(2.88)	1559.00 ± 8.40
2,methyl cyclopentanol	(2.99)	1558.00 ± 8.40
CH$_2$CHCHI$^-$	1555.24 (-4.24)	1551.0 ± 8.8
δ_{rmsd}	4.14	

^{a}Experimental values from NIST Webbase - http://webbook.nist.gov/chemistry/.
^{b}(PA$_{Exp.}$ - PA$_{Calc.}$).

Table 1. Proton Affinity (kJ.mol^{-1}) calculated with the method given by Eq. 3 and comparison with experimental values.

3.3 Electron affinity

In the Table 2 are the electron affinities calculated with the CCSD(T)/B1 energy from Eq. 3. It also shows a comparison between our results and the experimental values, where experimental data are available. The root mean square deviation (δ_{rmsd}) calculated is 0.15 eV.

The use of pseudopotential is competitive, mainly in systems containing S, Cl, and Br atoms. The computational time is almost constant for analogous systems with Cl and Br atoms, because in these cases we have an equal number of outer electrons. In calculations involving all electrons the computational performance is totally different and increases with the number of electrons. The CR-CCSD[T]/ECP computational demand is decreased by 10% when compared with all-electron calculations. For molecules containing Cl, Br or I atom the time is drastically decreased (Morgon, 2006).

3.4 Heat of formation

In the Table 3 are the heats of formation calculated with the CCR-CL/ ECP+ACC5Zm from Eq. 6. It also shows a comparison between our results and the experimental values, where experimental data are available. The average error using this methodology with respect to experimental results is closer to 10 kJ.mol^{-1}.

System	$EA^a_{Calc.}$	$EA^b_{Exp.}$
Br	3.36 $(-)^c$	-
Br_2	2.53 (-0.11)	2.42
CBr_3	2.49 (0.08)	2.57 ± 0.12
CCl_3	2.22 (-0.05)	2.17 ± 0.10
CF_3	1.74 (0.08)	1.82 ± 0.05
CF_3COO	4.56 (-0.10)	4.46 ± 0.18
$CH_2=CH$	0.71 (-0.04)	0.67 ± 0.02
$CH_2=CHCHBr$	0.96 (-)	-
$CH_2=CHCHF$	0.50 (-)	-
$CH_2=CCH_3$	0.69 (-0.13)	0.56 ± 0.19
$CH_2=NO_2$	2.40 (0.07)	2.48 ± 0.01
CH_2Br	0.91 (-0.12)	0.79 ± 0.14
CH_2BrCOO	3.99 (-0.01)	3.98 ± 0.16
CH_2Cl	0.70 (0.04)	0.74 ± 0.16
CH_2ClCOO	4.02 (-0.11)	3.91 ± 0.16
CH_2F	0.17 (0.08)	0.25 ± 0.18
CH_2FCOO	4.55 (-0.76)	3.79 ± 0.16
CH_3	0.08 (0.00)	0.08 ± 0.03
CH_3CH_2O	1.75 (-0.03)	1.71
CH_3CH_2S	2.02 (-0.07)	1.95
CH_3O	1.53 (0.05)	1.57
CH_3S	1.75 (0.12)	1.87
$CHBr_2$	1.74 (-0.03)	1.71 ± 0.08
$CHBr_2COO$	4.37 (-0.11)	4.26 ± 0.16
$CHClBr$	1.64 (-0.17)	1.47 ± 0.04
CHF_2COO	4.25 (-0.10)	4.15 ± 0.16
Cl	3.60 (0.01)	3.61
Cl_2	2.55 (-0.15)	2.40 ± 0.20
F	3.34 (0.06)	3.40
F_2	2.92 (0.08)	3.00 ± 0.07
Formamide-N,N-dimethyl	0.65 (-)	-
Formamide	3.34 (-)	-
HS	2.27 (0.05)	2.32
NH_2	0.70 (0.07)	0.77 ± 0.01
OH	1.77 (0.06)	1.83
iPrO	1.87 (0.01)	1.87
nPrO	1.74 (0.05)	1.79 ± 0.03
δ_{rmsd}	0.15	

[a]The higher level correction (HLC) from G3 theory was added to the final energy.
[b]Experimental values from NIST Webbase - http://webbook.nist.gov/chemistry/.
[c]($EA_{Exp.}$ - $EA_{Calc.}$).

Table 2. Electron Affinity (eV) calculated with the method given by Eq. 3, and comparison with experimental values.

Molecule	Point Group	Ground State	$\Delta_f H_{gas}^o$ calc	$\Delta_f H_{gas}^o$ exp[a]
OF	$C_{\infty v}$	$^2\Pi$	110.999 (2.21)[c]	108.78
OF$_2$	C_{2v}	$^1A_1$	28.582 (4.06)	24.52
OCl	$C_{\infty v}$	$^2\Pi$	103.482 (2.26)	101.22
OCl$_2$	C_{2v}	$^1A_1$	92.341 (4.48)	87.86
SF	$C_{\infty v}$	$^2\Pi$	8.661 (-4.31)	12.97
SF$_2$	C_{2v}	$^1A_1$	-289.573 (7.08)	-296.65
SF$_3$	C_s	$^2A'$	-512.605 (-9.57)	-503.03
SF$_4$	C_{2v}	$^1A_1$	-775.362 (-12.20)	-763.16
SF$_5$	C_{4v}	$^2A_1$	-887.770 (20.68)	-908.45
SF$_6$	O_h	$^1A_{1g}$	-1218.986 (1.48)	-1220.47
SCl	$C_{\infty v}$	$^2\Pi$	153.843 (-2.62)	156.47
SCl$_2$	C_{2v}	$^1A_1$	-19.262 (-1.69)	-17.57
SCl$_3$	C_s	$^2A'$	22.346 (-14.47)	36.82[b]
SCl$_4$	C_{2v}	$^1A_1$	-15.301 (-12.38)	-2.92[b]
SCl$_5$	C_{4v}	$^2A_1$	-38.76 (-2.78)	-35.98[b]
SCl$_6$	O_h	$^1A_{1g}$	-87.54 (-4.7)	-82.84[b]

[a] Experimental values from NIST Webbase - http://webbook.nist.gov/chemistry/.
[b] Ref. (Ditter & Niemann, 1982).
[c] ($\Delta_f H_{gas}$ Calc. - $\Delta_f H_{gas}$ Exp.).

Table 3. Heats of formation (in kJ mol^{-1}) with the method given by Eq. 6, and comparison with experimental values.

4. Conclusions

The proton and electron affinities and the heats of formation of some simple systems obtained by the procedure outlined in this paper are in very good agreement with experimental values. These results can be compared with those obtained by sophisticated and computationally more expensive calculations. ECP-based methods have been shown to be powerful, and of affordable computational cost for the systems addressed in this work. This is due to three features:

1) the number of steps employed during the calculations,
2) the smaller basis sets used in our methodology, and
3) the use of ECP.

The use of adapted basis functions for atoms by the Generator Coordinate Method along with the use of the pseudopotential allows a high quality calculation at a lower computational cost.

The present methodology - Eqs. 3 and 6, which relies on small basis sets (representation of the core electrons by ECP) and an easier and simpler way for correcting the valence region (mainly of anionic systems) appears as an interesting alternative for the calculation of thermochemical data such as electron and proton affinities and enthalpies of formation for larger systems.

The CCSD(T)/B1 method have been shown to be powerful, and of affordable computational cost for the systems containing atoms of the 2nd and 3rd periods.

5. Acknowledgments

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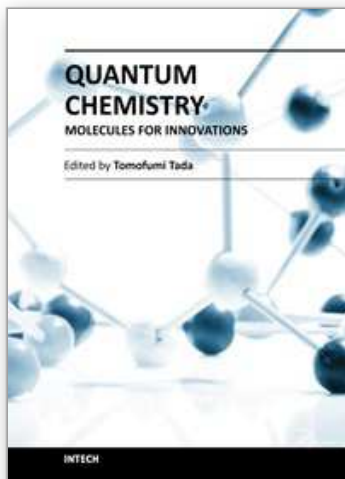
Quantum Chemistry - Molecules for Innovations

Edited by Dr. Tomofumi Tada

Molecules, small structures composed of atoms, are essential substances for lives. However, we didn't have the clear answer to the following questions until the 1920s: why molecules can exist in stable as rigid networks between atoms, and why molecules can change into different types of molecules. The most important event for solving the puzzles is the discovery of the quantum mechanics. Quantum mechanics is the theory for small particles such as electrons and nuclei, and was applied to hydrogen molecule by Heitler and London at 1927. The pioneering work led to the clear explanation of the chemical bonding between the hydrogen atoms. This is the beginning of the quantum chemistry. Since then, quantum chemistry has been an important theory for the understanding of molecular properties such as stability, reactivity, and applicability for devices. This book is devoted for the theoretical foundations and innovative applications in quantum chemistry.

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