Homolytic dissociation energies from GVB-LSDC calculations

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GVB-LSDC provides a reasonable account of correlation effects needed for the calculation of bond dissociation energies. 27 homolytic dissociation reactions have been calculated with GVB-LSDC/6-31G(d). GVB-LSDC bond dissociation energies are better than both HF, HF-LSDC, and GVB results. The average error is 4 kcal/mol.

1. Introduction

The calculation of reaction energies for homolytic bond dissociation is one of the major goals in quantum chemistry. Knowledge of bond dissociation energies D_e (or D_0) are necessary to predict the outcome of radical reactions and to analyze the mechanism of chemical reactions in general. In addition, the D_e (D_0) values of a molecule provide an insight into its stability and bonding features. Therefore, much effort has been put into an accurate calculation of D_e values. As is well known, highly accurate D_e values can be obtained by MRD-CI and other methods that provide a balanced description of static and dynamic correlation effects needed for a proper description of the potential hypersurface along the dissociation coordinate [#1]. However, these methods are rather expensive and, therefore, they cannot be applied for large molecules in a routine way.

We present here an economic way of routinely calculating bond dissociation energies. Our approach is based on a simplified determination of correlation effects employing a generalized valence bond (GVB) [3] reference wave function in connection with a local spin density correlation functional (LSDC) originally suggested by Stoll and co-workers [4] [#2]. GVB can be considered as a simple MCSCF approach that is known to describe homolytic dissociation qualitatively correct. The LSDC method, on the other hand, has been designed to cover the dynamic part of the correlation energy by efficiently describing the Coulomb hole in molecules [4]. It has been applied to calculate various molecular properties [4]. An attempt to obtain reasonable dissociation energies with an HF based LSDC approach (HF-LSDC) has been less successful [6]. However, this failure actually underlines the necessity of using LSDC in connection with a wave function that leads to a qualitatively correct description of homolytic dissociation [7].

In the following we will present GVB-LSDC dissociation energies for 27 dissociation reactions of AH, AA, and AB bonds where A and B are both heavy atom elements. Our sample set comprises dissociation of diatomic as well as polyatomic molecules. In particular, dissociation of bonds typical of organic compounds are investigated. The purpose of this work is not to calculate highly accurate D_e values. Instead, we present here an economic way of calculating D_e values with a reasonable accuracy using moderate basis sets of the VDZ + P type.

2. Computational methods

The GVB method has been used in the perfect pairing approximation (GVB-PP) [3]. The initial guess for the GVB-PP calculation has been constructed from localized MOs calculated at the HF level. All electron pairs involved in bonding have been described as correlated pairs, i.e. for ethane, ethene,

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[#1] For reviews see ref. [1]; for some selected examples see ref. [2].

[#2] For related work see, e.g., ref. [5].

and acetylene one, two, and three electron pairs, respectively, have been correlated. Test calculations that included electron pairs of neighbouring bonds did not lead to any improvement. However, in the case of heteroatoms with electron lone pairs it turned out to be crucial also to describe these lone pairs as correlated pairs in the GVB calculation. Electron lone pairs can increase bonding, for example, by anomeric delocalization into adjacent bonds [8]. Examples of bond strengthening by anomeric interactions are the OO bond in H_2O_2 and the NN bond in N_2H_4 in their equilibrium conformation [8,9]. Also, the in-plane lone pair at N in trans-diazene, N_2H_2, or acetaldimin, CH_2NH, can interact with the vicinal CH or NH bond to some extent. On the other hand, lone pairs that do not delocalize in the bond being broken, do not lead to any improvement for calculated D_e values. We have tested for all molecules considered a possible inclusion of electron lone pairs in the GVB calculation and, thereby, have obtained a set of lone pair participation numbers q that lead to the best set of calculated bond dissociation energies.

The LSDC approach has been used with the density functional of Vosko, Wilke, and Nusair (VWN) [10] along the lines described by Nordholm and Kemister [6]. For this purpose, a LSDC program has been rewritten for routine use at both the restricted and the unrestricted HF level within the ab initio package COLOGNE [11]. Two ways of using LSDC at the HF level of theory have been tested. First, the LSDC correlation energy has been calculated using the converged HF wave function. Secondly, the LSDC functional has been directly included into the SCF iterations. Both ways lead to correlations energies that differ not more than 3 mhartree for the molecules considered. This suggests that the LSDC functional depends only slightly on changes in the HF density and that it is sufficient to calculate the LSDC energy from the converged HF density. Because of this, the same approach has been taken at the GVB level. GVB-LSDC energies have been determined by feeding into the VWN functional calculated GVB densities.

All calculations have been carried out at experimental geometries (see compilation in ref. [12]) using the 6-31G(d) basis set [13]. This is a modest split valence basis set with polarization functions (VDZ+P) for heavy atoms and, therefore, it can be employed for rather large molecules. LSDC correlation energies change only slightly with the basis set [6] and, therefore, a VDZ+P is already sufficient to get reasonable correlation energies. This is important since the aim of this work is to present a method for calculating dissociation energies in both an effective and economic way.

Dissociation energies D_0 have been calculated from experimental heats of formation $\Delta H_f^0(0)$ taken from standard compilations [14]. Experimental vibrational frequencies [15] have been used to obtain from D_0 bond dissociation energies D_e. Only the latter can be directly compared with calculated values.

3. Results and discussion

In table 1, calculated HF, HF-LSDC, GVB, and GVB-LSDC dissociation energies D_e are compared with experimental values for 27 different dissociation reactions. In fig. 1, GVB-LSDC values are plotted against experimental D_e values. A more detailed analysis of calculated D_e energies is provided by fig. 2 where the errors of the theoretical D_e values are shown for each molecule.

HF dissociation energies are all too small. They underestimate dissociation energies on the average by 55 kcal/mol. Particularly large are the errors for C_2 (135) and N_2 (121 kcal/mol). The D_e values for F_2 (-35) and H_2O_2 (-1.5 kcal/mol) are negative. In view of the well-known failure of HF theory to describe homolytic dissociation correctly, these results are not astonishing [16].

More astonishing is the fact that HF-LSDC does not lead to a substantial improvement of D_e energies. Although D_e becomes larger by up to 60 kcal/mol, calculated values are still too small by 29 kcal/mol on the average. The dissociation energy of F_2 is still negative (-23.6 kcal/mol). Errors in HF-LSDC energies are as large as 100 kcal/mol (see, e.g. C_2 in table 1). We conclude that HF-LSDC is not able to lead to reasonable dissociation energies. This is at contrast with a more positive evaluation of HF-LSDC given by Kemister and Nordholm [6], but these authors only considered a limited set of diatomic molecules that did not allow any conclusion with regard to the usefulness of LSDC in the case of polyatomic molecules.

On the other hand, the failure of HF-LSDC has to

Table 1
Theoretical and experimental bond dissociation energies [a]

Molecule	Bond	q [b]	D_e(HF)	D_e(HF-LSDC)	D_e(GVB)	D_e(GVB-LSDC)	D_e(exp.)
1 LiH	Li H		31.1	49.5	41.3	59.8	57.6
2 BeH$_2$	Be H		74.5	100.1	82.1	107.7	100.2
3 BH$_3$	BH		88.7	112.7	96.9	120.9	112.8
4 CH$_4$	CH		85.8	109.8	95.5	119.4	112.1
5 NH$_3$	NH	0	79.9	103.8	91.2	115.1	116.3
6 H$_2$O	OH	1	81.0	105.6	100.8	125.4	125.7
7 F H	FH	2	87.0	111.2	115.4	139.6	140.9
8 HCl	ClH	2	70.7	93.0	82.2	104.4	106.4
9 Li$_2$	Li Li		1.7	14.0	8.9	21.2	24.4
10 C$_2$H$_6$	CC		69.3	86.8	78.8	96.3	96.5
11 C$_2$H$_4$	CC		118.5	156.9	145.1	183.5	179.8
12 C$_2$H$_2$	CC		180.3	199.3	215.0	234.0	234.4
13 C$_2$	CC		9.3	43.3	99.8	133.8	144.4
14 N$_2$H$_4$	NN	2	30.2	44.3	56.4	70.3	75.1
15 N$_2$H$_2$	NN	2	46.2	80.0	92.6	126.4	118.0
16 N$_2$	NN	2	107.4	167.1	163.3	223.0	228.4
17 H$_2$O$_2$	OO	2	−1.5	12.0	37.3	50.9	55.1
18 F$_2$	FF	4	−35.2	−23.6	35.6	47.1	38.2
19 Cl$_2$	Cl Cl	4	10.6	22.6	39.7	51.5	58.0
20 CH$_3$NH$_2$	CN	0	58.2	74.7	75.8	92.3	93.2
21 CH$_2$NH	CN	1	92.2	128.1	126.9	162.8	153.3
22 H C N	CN	1	154.1	193.4	186.9	226.2	227.3
23 CH$_3$OH	CO	1	58.7	75.2	78.5	95.0	98.0
24 CH$_2$O	CO	2	99.7	135.9	144.8	180.8	183.7
25 C O	CO	3	169.8	205.4	226.4	261.9	259.2
26 CH$_3$F	CF	3	68.7	84.6	98.0	113.8	113.9
27 ClF	Cl F	4	4.0	17.9	47.3	61.1	60.2

[a] All values in kcal/mol. [b] Lone pair participation number (see text).
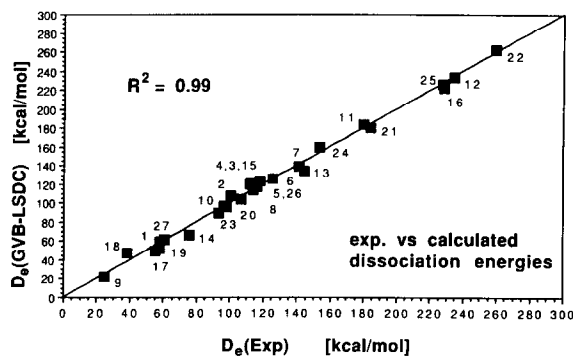

Fig. 1. Correlation of GVB-LSDC bond dissociation energies D_e (GVB-LSDC) with experimental dissociation energies D_e(exp.). R^2 is the correlation coefficient.

Fig. 2. Deviation of HF, HF-LSDC, GVB, and GVB-LSDC bond dissociation energies D_e from experimental dissociation energies D_e(exp).

be seen on the basis that the local spin density correlation functional yields only an estimate of dynamic correlation energy, but does not cover nondynamic
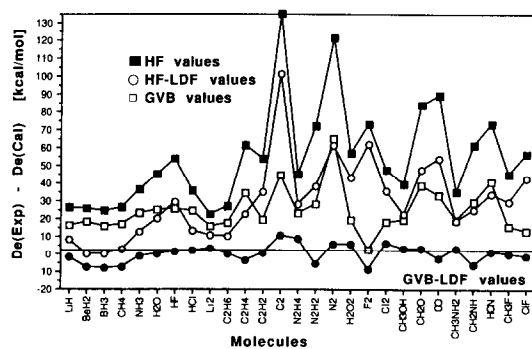
(static) correlation effects. Thus HF-LSDC cannot be better than any other single-determinant based ab initio approach in the case of homolytic dissociation

reactions. Errors as large as 50 kcal/mol are also obtained at the MP or CI level. Only when these calculations are calibrated by experimental data, significantly better results with an accuracy of ± 1 kcal/mol are obtained [17].

Contrary to single determinant methods, GVB describes homolytic dissociation correctly. This is reflected by the GVB D_e energies shown in table 1. Absolute GVB dissociation energies are still too small and the average error is with 24 kcal/mol still rather large, but relative trends in experimental dissociation energies are nicely reflected at the GVB level.

An almost dramatic improvement of calculated D_e energies is obtained at the GVB-LSDC level (see table 1 and figs. 1 and 2). The average error decreases to 4 kcal/mol which is exactly the error in experimental heats of formation of many of the dissociation products considered [14]. The largest error is calculated for C_2 (10.5 kcal/mol). Noteworthy is that for several dissociation reactions the D_e value is overestimated by GVB-LSDC. For example, LiH, BeH_2, BH_3, CH_4 and some double bonded compounds belong to this set. This has to do with the fact that 6-31G(d) does not provide a balanced description for these molecules and, hence, a relatively high basis set superposition error (BSSE) may result. The BSSE artificially increases theoretical D_e values.

Another source of error may be the heats of formation used to calculate "experimental" D_e energies. For BeH_2 and BH_3 no accurate experimental data are available and, therefore, theoretical ΔH_f^0 values [17] had to be taken to get D_e(exp.). For N_2H_2 and CH_2NH experimental ΔH_f^0 data are questionable or have been estimated [14]. Hence, errors obtained at the GVB-LSDC level may also reflect to some extent errors in experimental data used for comparison.

In conclusion it has to be stated that GVB-LSDC dissociation energies calculated in this work compare well with experimental values differing on the average by just 4 kcal/mol. This is far better than results that have previously been obtained by either HF, GVB, or LSDC methods. Future work has to show whether the same accuracy can be obtained for homolytic dissociation of bonds involving second row atoms. Some examples of these bonds have already been included in the present test set of molecules and the corresponding results are encouraging. Also, future research has to yield more information on possible basis set errors such as the BSSE, on the role of the density functional used, and on the fact that GVB results are not size consistent.

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