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## Notas de Física

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*A Semi-Empirical Alternative  
Approach to Explain  
Molecular Conformations*

by

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**ABSTRACT**

The semi-empirical energy partitioning has been reexamined, and developed further in order to introduce an alternative approach to study molecular conformations. This method is based in the definition of bond energy between atomic groups which is introduced in this paper from semi-empirical calculations. Different molecular systems (series  $H_2X_2$ ,  $X_2H_4$ ,  $CH_3-R$ ,  $NH_3$ ,  $C_2H_4$ ,  $CH_2NH$ ) are calculated to explain molecular conformations, barriers to rotation about double bond and inversion barriers. The obtained results, without geometry optimization, are in good agreement with experimental data and *ab-initio* method.

**Key words:** Conformational analysis - Inversion and Rotational barrier - Group Pair Bond Energy method - Atomic group energy - Semi-empirical energy partitioning

## INTRODUCTION

Due to the increased successful use of the conformational analysis many methods have been proposed recently. In general, the theoretical methods, in quantum chemistry, used in this subject can be divided into two groups; the *ab-initio* and semi-empirical procedures.

As is known all theoretical methods present a particular problem in the complete determination of the molecular conformations. For example; in the *Ab-initio* calculations the most important variables are the choice of geometry and selection of a basis set. These parameters are usually taken from the experimental geometry corresponding to the conformation of lowest energy. An actually complete *ab-initio* calculation would require that all geometrical parameters to be optimized for each conformation. In practice, this is almost intractable except for very simple molecules. Another known problem arises in the calculation of the great number of molecular integrals of one- and two-center, which is proportional to the fourth power of the number of functions that form the basis set in SCF calculations. In the *Semi-empirical* approach some of the examples that we will study later, we will stress the parameterization employed shows clearly that while some parameters allow correct predictions to be made over some molecular properties, nevertheless, they can lead to incorrect ones of other properties [1]. There are as well two essential limitations in the use of the semi-empirical approximation. The

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first one is associated with the choice of the appropriate parameters for the second-row atoms [2]. The other one is that this approach is, in some case, poorly suited to the calculations of rotational barriers around heteroatom-heteroatom bond [3].

We propose in this paper an alternative way to interpret the conformational analysis which has as well advantages and difficulties.

In the next section we discuss about this method. In the third section we present some results comparing them with the experimental and *ab-initio* calculations.

#### ENERGY PARTITION : ATOMIC GROUP ENERGY

Decomposition of the SCF energy (semi-empirical or *ab-initio*) into one- or more center terms has received considerable attention [4]. In particular within this framework the results obtained by CNDO method for molecular geometries, total energy and barriers to internal rotation and inversion are, in general, acceptable, making this method nowadays a very valuable tool in the hands of the quantum chemists for studying theoretically the conformational problems. In the Complete Neglect Differential Overlap - CNDO approximation only one and two center terms are considered in the calculation of the total energy  $E$ . This enable us to write  $E$  as,

$$E = \sum_A E_A + \sum_{A < B} E_{AB} \quad (1)$$

where

$$E_A = \sum_{\mu} P_{\mu\mu} U_{\mu\mu} + \frac{1}{2} \sum_{\mu, \nu} (P_{\mu\mu} P_{\nu\nu} - \frac{1}{2} P_{\mu\nu}^2) \gamma_{AA} \quad (2)$$

and

$$E_{AB} = \sum_{\mu, \nu} (2P_{\mu\nu} \beta_{\mu\nu} - \frac{1}{2} P_{\mu\nu}^2 \gamma_{AB}) + Z_A Z_B R_{AB}^{-1} - (P_{AA} Z_B + P_{BB} Z_A - P_{AA} P_{BB}) \gamma_{AB} \quad (3)$$

$P_{\mu\mu}$  is the total electron density on orbital  $\chi_{\mu}$ ,  $P_{\mu\nu}$  is an element of the bond order-electron density matrix,  $\gamma_{AB}$  is two-electron integral between an electron on atom A and one on B.  $Z_A$  is the core charge on atom A,  $R_{AB}$  is the internuclear distance and  $P_{AA} = \sum P_{\mu\mu}$ .  $U_{\mu\mu}$  is the mono-electronic contribution to the energy.

In order to study molecular conformations many authors have used different criterion of partitioning the semi-empirical energy. For instance, we remember briefly some important cases: Fischer and Kollmar [5] carried out a study over calculations into one- and two-center terms and into physical components. The two-center terms are a measure of the strength of the chemical bond; Allen [6] has partitioned the total energy in two terms, one repulsive and other attractive contributions to study the rotational barrier in hydrogen peroxide; Leibovicci and co-workers [7-12] have used the CNDO and INDO energy partition to the analysis the molecular conformation of many important molecular systems. In these papers the authors have also compared  $\sum E_{AB}$  (bonded) +  $\sum E_A$  and  $\sum E_{AB}$  (nonbonded) with the potential energy curve for internal rotation; Koehler, using different semi-empirical methods to partition the

total energy as a sum of the exchange, resonant and coulombic contribution has computed the rotational barriers in hydrazine [13] and formic acid [14]; Gordon [15] made a careful study of barriers to internal rotation of a series of molecules, indicating, in addition, the type of interactions to which the barrier owes its origin. He has partitioned the energy  $E_{AB}$  in three terms, as follows : the main contribution of the bonding (or antibonding) made by  $\chi_{\mu}$  on atom A and  $\chi_{\nu}$  on atom B, a term representing the stabilization due to exchange interaction and finally the contribution of the electrostatic interaction between atoms A and B.

In the case of the *ab-initio* approach interesting contributions have been done by Clementi and co-workers [16,17] and later by Musso and Magnasco [18] computing an *ab-initio* many-center expansions using an extended Gaussian basis.

Within this framework, some of these semi-empirical calculations using energy partition, to explain molecular conformations, have been in good agreement with experimental and *ab-initio* calculations, but in other cases, they have been less successful.

In order to make an attempt in this direction ( using semi-empirical methods ) we present here an alternative way of partitioning the total energy. A convenient feature of this analysis is the possibility of grouping the atoms of a molecule into atomic groups. Within the same idea as we have defined the Atomic Group Valence [19]  $V_G$  and Multicenter Bond Index [20]  $I_{ABC}$ , we assume that the molecule considered is formed by two group of atoms  $G_1$  and  $G_2$ . The groups  $G_1$  and  $G_2$  contain all atoms that builds the molecule. In analogy to the  $V_G$  definition we introduce the Group Pair Bond Energy as the sum of the atomic pair bond energy  $E_{AB}$

between all atoms A inside  $G_1$  and all atoms B inside  $G_2$ . For this we rewrite the right-hand side of equation (1) in a matricial form and we take the diagonal element  $E_{AA} = E_A$  ;

$$\begin{aligned}
 E &= \sum_{A, B} \frac{1}{2} (1 + \delta_{AB}) E_{AB} \\
 &= \sum_{i=1}^2 \sum_{A, B \in G_i} \frac{1}{2} (1 + \delta_{AB}) E_{AB} + E_G
 \end{aligned} \tag{4}$$

where

$$E_G = \sum_{\substack{A \in G_1 \\ B \in G_2}} E_{AB} \tag{5}$$

$E_G$  shows the peculiarity of each group within the molecule and it represents, in analogy with  $E_{AB}$ , a contribution in the necessary energy to bind the groups  $G_1$  and  $G_2$ . The Atomic Group Energy curve is obtained taking the group  $G_1$  fixed and we rotate, as rigid rotor,  $G_2$  around of the z-axis binding  $G_1 - G_2$ . Here all bond lengths and angles are held fixed during rotation; they assigned standard or experimental values.

## RESULTS and DISCUSSION

The procedure to be followed will be to explain the conformations of some important molecular system using the atomic group energy. We also treat the barriers to rotation about double bond. A part of this section is used to explain the inversion barriers using this alternative method. Our results will be compared with experimental data and with those ones of *ab-initio*

and semi-empirical methods. We show that our results to find the more stable conformation for all molecular systems here studied, using the alternative method, have been in good agreement with the experimental data. We would like to emphasize that our calculations have been done using the CNDO/2 method *without geometry optimization*.

**Series  $H_2X_2$**

- $H_2O_2$  ( Hydrogen peroxide )
- $H_2S_2$  ( Hydrogen persulphide )

The alternative methods here developed predict that the *gauche* conformation is the more stable for the  $H_2O_2$  molecule (see geometry in reference 21 p. 106). In this case the *trans*-conformer is more stable as *cis*-conformer which is in relative agreement with experimental results (Fig.1a). It is necessary to point out that the best results in the literature for  $H_2O_2$  from semi-empirical calculations are obtained using geometry optimization [15] and only these are in relative agreement with experimental data. The prediction of the *trans* barrier in the hydrogen peroxide molecule has been a challenge for the theoreticians, even at the level of *ab-initio* calculations. Both semi-empirical [15,16], without geometry optimization, and earlier *ab-initio* calculations predicted the molecule to be planar in the *trans* configuration [22,23]. More refined *ab-initio* calculations (with polarization functions included in the basis set together with geometry optimization) have reproduced both the dihedral angle and the *trans* barrier of hydrogen peroxide [24-26]. A similar analysis of spectral data for



$H_2S_2$  [27] reveals that the internal rotation splitting in the ground state is very much smaller than in  $H_2O_2$ . The results obtained using our approach (Fig.1b) with two cis and trans barriers, are in complete agreement with the most *ab-initio* calculation and the experimental evidence for a skew conformation for hydrogen persulphide (see geometry in reference 21 p. 152).

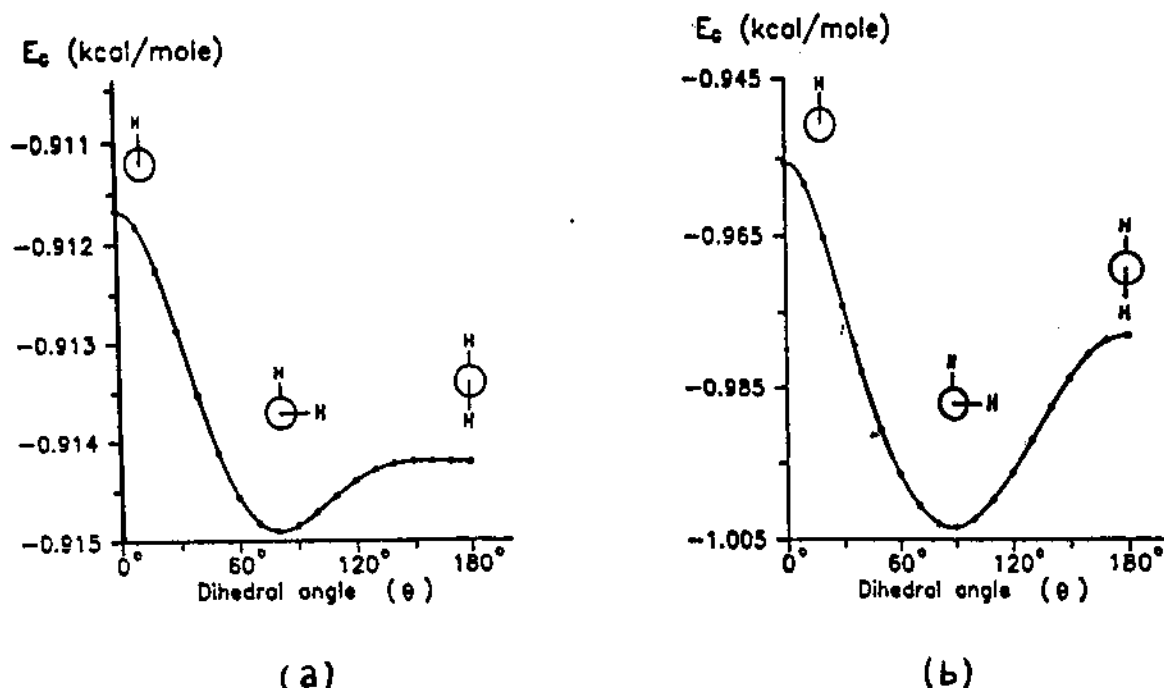


Fig.1  $E_c$  energy profile describing the rotation around the bond axis between the groups  $G_1$  and  $G_2$  in the (a) hydrogen peroxide molecule ( $H_2O_2$ ) and (b) hydrogen persulphide molecule ( $H_2S_2$ ). In both case the groups  $G_1 \subset \{HX\}$  and  $G_2 \subset \{XH\}$ , where  $X = O$  or  $S$ .

Hydrogen Peroxide is predict to have a twisted structure at STO-3G, which is consistent with a study by Stevens [28] using an STO basis directly. Using the 4-31G basis, a full optimization of the geometry leads to a trans structure and it is not until  $d$  functions are added on oxygen that a twisted structure is clearly

indicated. This was first demonstrate by Veillard [24], who found a dihedral angle  $123^\circ$  as compared with an experimental value  $111^\circ$ .

Hunt et al using the far infrared spectrum [29] yields a *cis* > *trans* barrier. All calculations overestimate the *cis* barrier and underestimate the *trans* barrier. The best results have been obtained by Dunning et al. [30] with a polarized basis and geometry optimization, which are required to obtain a *trans* barrier of more than a few tenths kcal/mole. But for *cis* barrier is only necessary the geometry optimization, since the barrier is not strongly influenced by polarization functions. Using an FSGO basis Cheney and Christoffersen [31] are fortuitous in view of the much poorer results obtained with comparable basis sets.

Series  $X_2H_4$

- $N_2H_4$  ( Hydrazine )
- $P_2H_4$  ( Diphosphine )

Our methods predict that the most stable conformation for the hydrazine molecule is the *gauche* one (Fig.2a). See the used geometry in the reference 32. The relative order of stability is *gauche* > *trans* > *cis* which is consistent with the *ab-initio* calculations [33,34]. The semi-empirical calculations fails badly in predicting the order of stability (*gauche* > *cis* > *trans*) [35]. The best semi-empirical results has been obtained by Gordon [15] using the CNDO with geometry optimization and Jesaitis [36] with INDO calculations.

Another important molecule belonging the series  $X_2H_4$  is the  $P_2H_4$  system. Many *ab-initio* and semi-empirical calculations have

been performed on the diphosphine molecule in recent years, see for example the table 1.12 in the reference [25]. The most *ab-initio* calculations predict the relative order of stability *trans* > *gauche* > *cis* in contradiction to the results obtained from the microwave data [37]. In this case our results has been in good agreement with the microwave results, which have predicted the dihedral angle  $\theta \approx 74^\circ$  (Fig.2b) to the more stable conformation (see geometry in the reference 21 p.152). We have obtained the following sequence of relative order of stability *gauche* > *trans* > *cis*. The Fig.2c is an ilustrative way to represent the conformational minima for the  $P_2H_4$  molecule as in the Fig.2b.

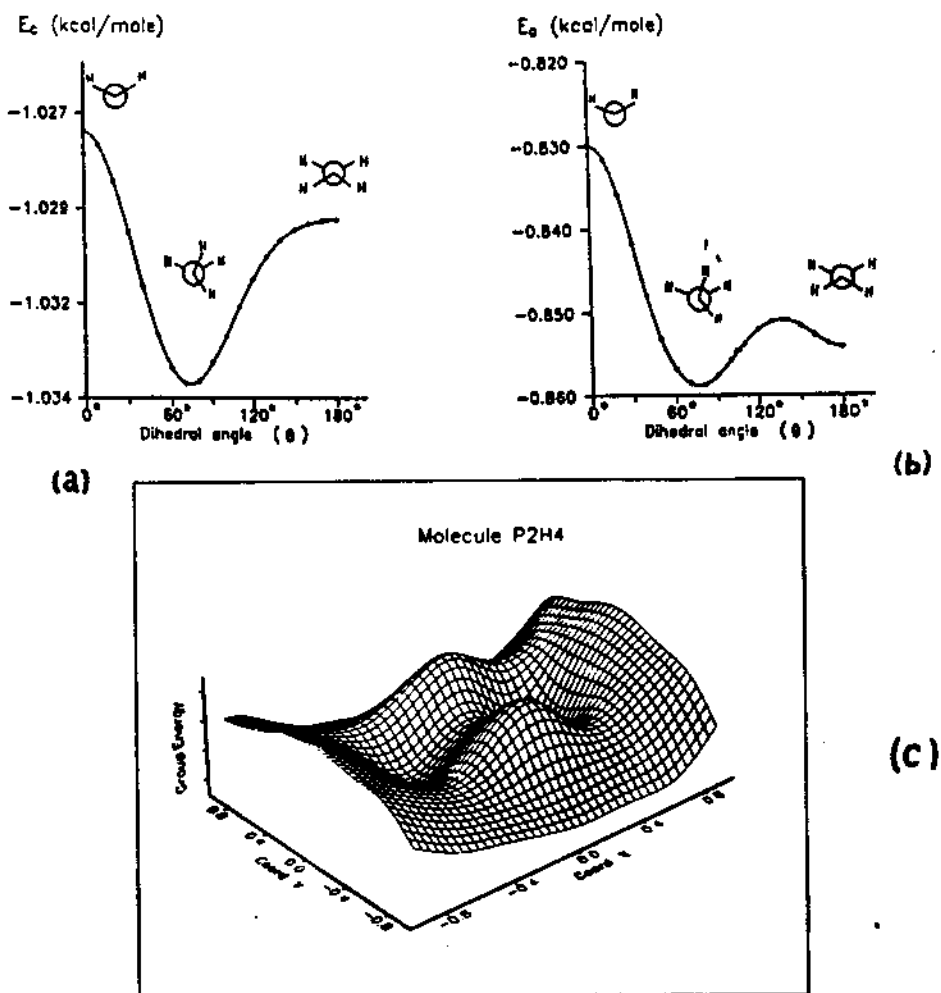


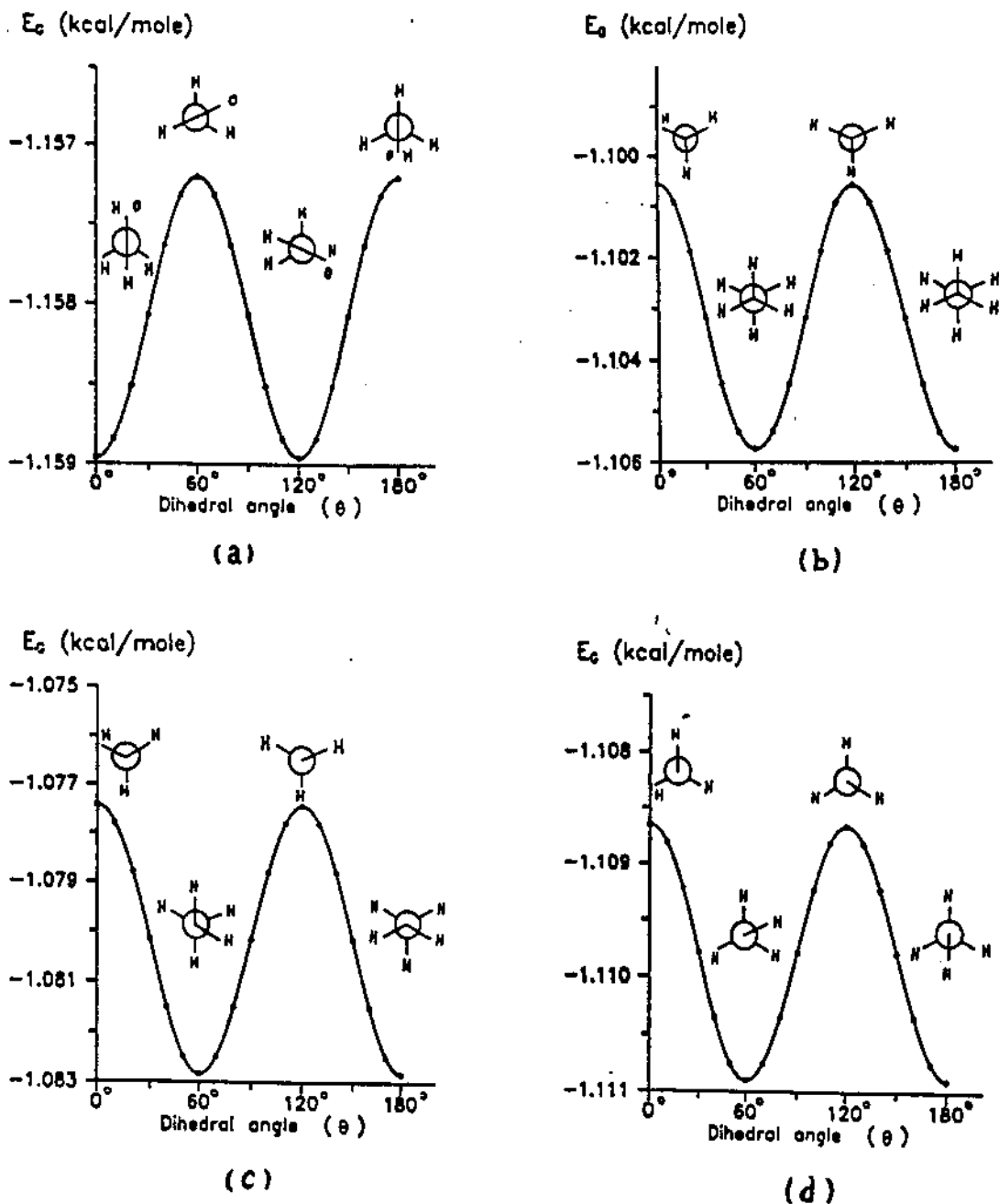
Fig.2  $E_G$  energy function describing the rotation around the bond axis between the groups  $G_1$  and  $G_2$  in the (a) hydrazine molecule ( $N_2H_4$ ) and (b) diphosphine molecule ( $P_2H_4$ ). In both cases the groups  $G_1 \subset \{HX\}$  and  $G_2 \subset \{XH_2\}$ , where  $X = N$  or  $P$ . (c) A 3D-surface for the  $E_G$  in terms of a hydrogen  $(x,y)$  coordinates in case of  $P_2H_4$ .

- Series  $\text{CH}_3 - \text{R}$
- $\text{CH}_3\text{COH}$  ( acetaldehyde )
  - $\text{CH}_3\text{CH}_3$  ( ethane )
  - $\text{CH}_3\text{NH}_2$  ( methylamine )
  - $\text{CH}_3\text{OH}$  ( methyl alcohol )

Within the series  $\text{CH}_3-$  (Radical) Jorgensen and Allen [32] have studied (in qualitative way) the  $\text{CH}_3-(\text{COH})$  compound using charge density analysis. They found that the conformation with a methyl hydrogen eclipsing the C-O double bond is most stable than the configuration with methyl hydrogen. In good agreement with the charge density approach and the experimental data the alternative method predict (Fig.3a) the same relative order of stability for the acetaldehyde molecule (see used geometry in the reference 38).

Based on CNDO calculations Gordon [15] has studied the possible conformations to the ethane, methylamine and methyl alcohol compounds. In this paper the staggered configuration is most stable for all three molecules. As is showed in the Figures 3a-d the conformational analysis using our methods predict the staggered conformation in the unperturbed ground states. The experimental and *ab-initio* results found for conformations in the series ethane [25,39], methylamine [40-43] (see geometries in the reference 38) and methyl alcohol [40-42,44] (see geometry in the reference 21 p.148) are well reproduced by both and normal CNDO calculations.

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**Fig.3** The  $E_G$  energy function describing internal rotation around the bond axis between the groups  $G_1$  and  $G_2$  in the (a) acetaldehyde where  $G_2 \subset \{ COH \}$ , (b) ethane where  $G_2 \subset \{ CH_3 \}$  (c) methylamine where  $G_2 \subset \{ NH_2 \}$  and (d) methyl alcohol where  $G_2 \subset \{ OH \}$ . In all compounds the group  $G_1$  contain the  $CH_3$  radical.

## INVERSION BARRIERS

Barriers of inversion have been the object of many theoretical methods; *ab-initio* and semi-empirical calculations, in recent years, see for example a good discussion about this subject in the references 21 and 25. The ammonia is probably the most important molecule in chemistry used in attempt to explain the barrier of inversion of molecular system because  $\text{NH}_3$  is an of most simple stable system which shows such a type of barriers. If the  $\text{NH}_3$  is pyramidal, it may exist in two conformations which are related by the transposition of the Nitrogen atom from one side of the  $\text{H}_3$  group to other. Then the atomic group energy curve as a function of the height of the pyramid is a symmetrical double minimum curve as is showed in Fig. 4. The used geometry is  $r(\text{NH}) = 1.424 \text{ \AA}$  and  $\langle(\text{HNH}) = 101.1^\circ$ .

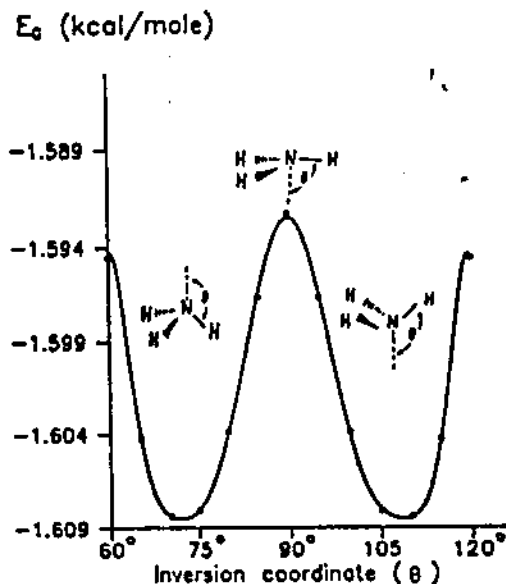


Fig.4  $E_G$  energy function describing pyramidal inversion in ammonia ( $\text{NH}_3$ ).

These results show that the alternative methods is a good device in order to explain inversion barriers and it is worth to emphasize that these results are comparable with those ones of *ab-initio* and semi-empirical calculations.

## DOUBLE BOND

Another interest in this direction is the study of the barriers to rotation about a double bond using the methods hier discussed. The compounds examined are  $C_2H_4$  and  $CH_2NH$  (see geometries in the reference 21 p.156).

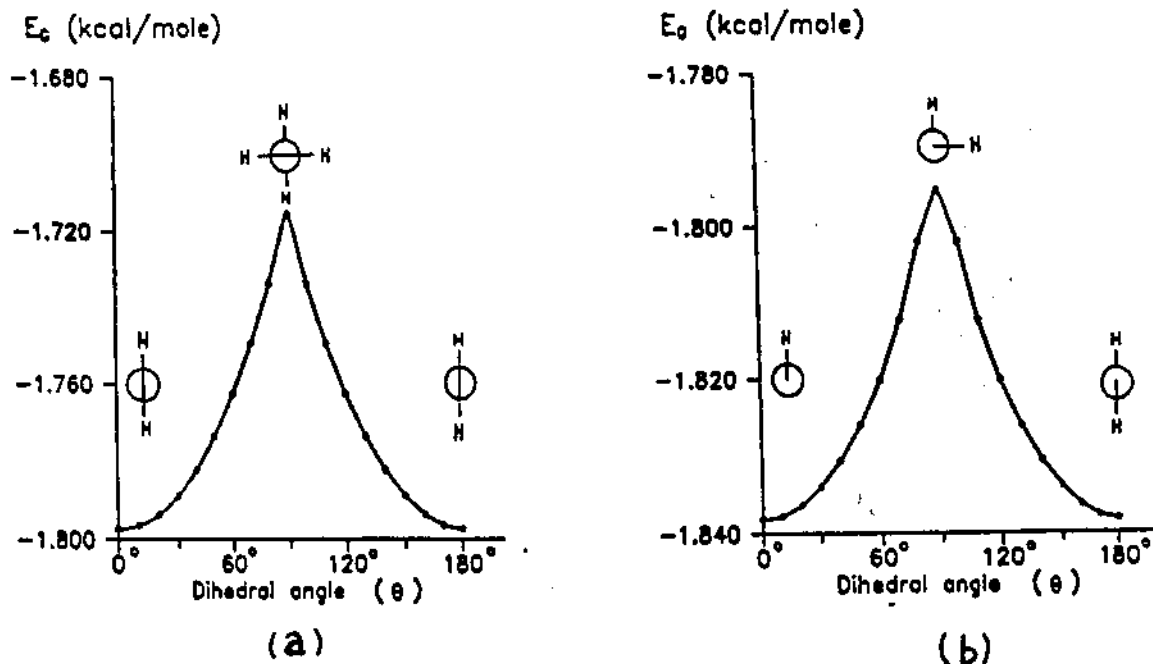


Fig.5 The  $E_G$  energy function describing internal rotation about double bond in the (a) ethylene ( $C_2H_4$ ) where  $G_2 \subset \{CH_2\}$ , and (b) methyleneimine ( $CH_2NH$ ) where  $G \subset \{NH\}$ . In both compounds the group  $G_2$  contain the  $CH_2$  radical.

In this case our methods predict the cis and trans conformation for both compounds as the most stable conformations (Fig.5a,b). These predictions are confirmed using *ab-initio* [45] and experimental [46] calculations.

We conclude from these preliminary studies that the atomic group energy partitioning method can be a qualitative indicator of conformational preference, but there is still not quantitative relationship between barrier heights and the atomic group energy. In particular, there is no evidence for our knowledge that we can get the magnitudes of barriers from our approach but we expect to be successful in this direction as we will show in elsewhere.

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