A revisit of thermodynamic properties of ethanol
– a theoretical approach

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Abstract: In this study we investigate the effect of the ratio of the two conformers, gauche and anti, on the thermodynamic properties of ethanol using accurate *ab initio* calculations and modern statistical calculations. Specifically, accurate electronic structure calculations at the composite CBS-QB3 method were carried out to determine stable structures and their molecular properties (e.g., vibrational frequencies, rotational constants, etc.). Within the statistical mechanics framework, the calculated molecular properties were used to calculate thermodynamic properties with the inclusion of the rigorous hindered internal rotation (HIR) treatment for the rotation of the CH_3 group along the C-C bond. The thermodynamic properties of ethanol can be calculated by averaging those of the two conformers using K_{eq} and then compared with literature data. Alternatively, the data were also calculated using the most stable conformer, anti, with the implicit inclusion of the gauche conformer through the HIR treatment of the OH group along the C-O bond. The results from two approaches are in good agreement with the literature data for heat of formation ($\Delta_f H$), entropy (S) and heat capacity (C_p) for a wide temperature range. Since the later approach is less expensive, it is recommended to use for larger alcohol systems where it is very time-consuming to explore all possible conformers.

Keywords: Ethanol, Conformers, Thermodynamic Properties, Hindered Internal Rotation, CBS-QB3.

1. Introduction:

Over the past few decades, the development of computational science with the increasing in accuracy, reducing effort and friendly user interface has open a new door for chemistry research[1,2]. Ethanol is a typical molecule for chemistry ab initio study because of its simple structure and enormous applications, particularly in combustion as alternative fuel candidate.
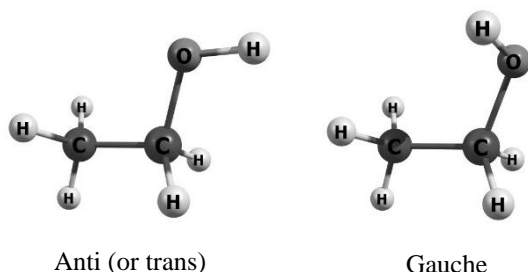

Figure 1. The gauche and anti conformers of ethanol

Ethanol has two stable forms with a small different in the electronic energy: the gauche form with the hydroxyl hydrogen point close to the ethyl group and anti form with the hydroxyl hydrogen point symmetrically away from the ethyl group[3] (cf. *Figure 1*). Many research papers confirmed the present and reported the ratio of the two conformers at low temperature. An early study of Barsnes and Hallam[4], by comparing the intensity of two OH peaks in IR spectra, estimated the ratio anti:gauche at 25 K is about 2:1. Two independent studies by Kaka, Quade[5] and Durig, Lasen[6] showed that the two conformers have energy different is about 42 cm^{-1}. Another study by Shaw and coworkers[7] using IR and VCD spectra determined the ratio anti:gauche as

42:58. Meanwhile, some calculation about the torsional barriers of the two conformers showed that gauche form is more stable[8][9][10].

Table 1: Difference in energy (gauche–anti) calculated for ethanol by different methods

Level	ΔE (kcal/mol)
HF 6-31G*	-0.108[a]
HF 6-311+G**	-0.282[a]
B3LYP/6-31G*	0.318[a]
B3LYP/6-311G**	0.251[a]
B3LYP/6-311++G**	-0.041[a]
B3LYP/cc-pVTZ	0.031[a]
MP2/6-31+G*	-0.172[a]
MP2/6-311++G**	0.014[a]
MP2/cc-pVTZ	-0.067[a]
MP2/6-311++G(3df,3pd)	0.232[a]
MP2/cc-pVQZ	0.246[a]
MP2/aug-cc-pVQZ	0.249[a]
MP4/6-31+G**	-0.124[b]
CCSD(T)/6-311++G**	0.117[c]

Reference: a: from the work of Scheiner et al [3]
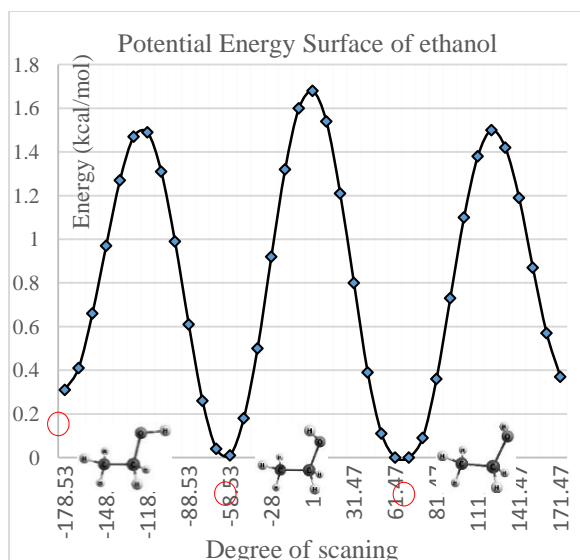b: from the work of Shaw et al[7]
c: from the work of Krueger [11]

Figure 2: The potential energy surface of ethanol gauche and anti conformers transformation

Recently, a study by Scheiner and Seybold[3] indicated that the energy of the two conformers is close and using different basic set show that the result may be reversed when energy is calculated by different methods (**Table 1**) and come up with the conclusion that the two conformers have nearly equal energies, and in vapor phase, the gauche form predominates because of its twofold degeneracy.

Acknowledge the orientation of recent ab initio research in the literature. In this study, we applied a similar but advance ab initio approach to determine the ratio of the two conformers gauche:anti in a range of temperatures. Then, we consider the ratio into ethanol thermodynamic properties calculation to see if this ratio has any impact to ethanol properties, where we expect to suggest a more authentic method for thermodynamic properties calculation.

2. Computational Details:
2.1 Ratio of the two conformer calculation:

Electronic structure optimization

All calculations were performed using Gaussian 09 package[12]. Electronic energies were calculated at high-level composite method CBS-QB3 developed by Peter and coworkers [13] with "chemical accuracy" to be normally defined as within ~ 1 kcal/mol of experimental data. In detail of calculation, optimized geometries and frequencies of the guest structure are obtained at the B3LYP/6-311G (2d, d, p) level of theory. The single-point energy corrections were performed at CCSD (T) / 6-31 + G (d') and MP4SDQ / CBSB4 levels and then extrapolated to the complete basis set limit. In this step, Gaussian 09 code only provided the local minimum of atomic orbital function, or the conformer has lowest energy close to the guest structure of a given species. Therefore, gauche and anti conformers are optimized respectively.

Thermodynamic properties calculations:

The molecular parameters of species obtained from electronic structure calculation will be used as inputs for a standard statistical mechanics treatment to compute thermodynamic properties of the species. If low-frequency modes corresponding to internal rotation represent, these modes must be treated as hindered rotors. For the two conformers, O-H bonding position corresponds to methyl group is fixed because each conformer will be calculated respectively, thus only methyl group is considered as hindered rotor. Hindrance potential energy correction is carried out using Gaussian 09 and then used as input for MSMC code. The hindrance potential is computed at either B3LYP/6-31G(d) or the MP2/6-31G(d) level of theory via relaxed potential energy scan in the steps of 10 degree of the dihedral angles corresponding to the rotation. The averaged reduced moments of inertia required for the hindered rotation treatment were calculated with the proposal by East and Radom[14], based on the original work of Kilpatrick and Pitzer [15]. The harmonic frequencies are scaled by a factor of 0.99 prior to calculate zero point energy (ZPE) and thermodynamic properties. The electronic energy of a species is converted into the corresponding heat of formation using the atomization method. The Schrödinger equation could be solved numerically by using the wave function of the free rotor as basic functions. The obtained energy levels are used to yield the partition function and contribution to the thermodynamic function ΔH_f, entropy S, and heat capacity C_p together with Gib free energy.

Ratio Gauche: anti

When Gib free energy is obtained for the two conformers, the ratio of the two conformers can be determined as K_{eq}, since the transformation between the gauche and anti conformers can be considered as an equilibrium at gas phase, and determined by the formula: $K_{eq} = e^{\frac{-\Delta G}{RT}}$. However, there is only one anti form but two gauche forms, which have the same characteristics and are mirror image of each other. Therefore, the ratio of gauche not only depend on the transformation between gauche and anti but also depend on the relative number of transformation types can occur. Anti form can transform into any of the two gauche form, while gauche form can either transform into another gauche form or to anti form. Therefore, the ratio of the gauche form should be doubled.

2.2 The revisit thermodynamic properties of ethanol

Previously, thermodynamic properties of gauche and anti conformers were calculated respectively. To examine the effect of the gauche:anti ratio into thermodynamic properties calculation, we suggest that the thermodynamic properties of ethanol should be the average thermodynamic properties of the two conformers. The results of this average calculation

would be compared with the results of the present approach, in which thermodynamic properties were calculated with the same method, but only the most stable conformer, anti, was used with the implicit inclusion of the gauche conformer through the hindered internal rotation (HIR) treatment of the OH group along the C-O bond . We also compare this result with some practical data and some data available in the some reliable database (e.g ATcT[i], NIST[ii]) at different temperature if available.

3. Results and Discussion:
3.1 The gauche: anti ratio:
Electronic structure calculation of the two conformers using Gaussian 09W was performed with the composite method CBS-QB3 gave the very close result of electronic energy and anti conformer is slightly negative (0.2 kcal/mol) to the gauche conformer. This result well agreed with the study by Scheiner and Seybold[3]. Using statistical mechanic calculation with the range of temperature between 298 and 1500 K, the acquired Gib free energies of the two conformers showed that the energy of anti form always slightly negative than the gauche form, with the differences no more than 0.015 kcal/mol. Anti form is confirmed to be the most stable conformer of ethanol. Thermodynamic calculation indicated the equilibrium has K_{eq} approximately 1 at room temperature. The transformation neither favor gauche nor anti conformer. The two conformers accounted for an equal amount. However, since the existent of 2 gauche forms as mentioned above, the ratio gauche:anti should be 2:1. When the temperature in increased to 1500K, the equilibrium constant is 1. The energy different between two conformers is not significant at high temperature. Consequently, the ratio gauche:anti is expected to be 2:1 but may not affect thermodynamic properties at this temperature.

Table 2. Ratio gauche:anti at different temperature

Tm	ΔG_{Gauche}	ΔG_{Anti}	$\Delta G(I)$	K_{eq}
298	-15.9796	-15.9837	0.0041	0.999998
300	-16.1093	-16.1134	0.0041	0.999998
500	-30.0952	-30.1062	0.0110	0.999997
1000	-72.7327	-72.7463	0.0136	0.999998
1500	-124.0967	-124.0978	0.0011	0.100000

Units: Temperature: Kelvin; ΔG: kcal/mol

(i) Active Thermochemical Tables (http://garfield.chem.elte.hu/Burcat/burcat.html; Accessed date: April, 29th 2016)
(ii) National Institute of Standards and Technology (http://webbook.nist.gov/chemistry/; Accessed date: April, 29th 2016)

3.2. Thermodynamic Properties:
Heat of formation at standard condition, entropy, and heat capacity at constant pressure results were carried out using MSMC code[1] with the method CBS-CB3 at the precision level of 256 bit.

Heat of formation:
Heat of formation of anti form is less than gauche form 0.4 kcal/mol (**Table 3**). Using the practical data as the reference points, the average result showed an improvement by 0.4 kcal/mol in accurate compared with the present method. The average result is also very close agree with the heat of formation data collected from ATcT and GA database, which is very reliable theoretical data for small molecules. Besides, the experimental data show a largest different in energy between the measurement is 0.2 kcal/mol, and the largest measurement error about 0.5 kcal/mol in the latest measurement. Therefore, ab inito methods can provide a confident reference.

Table 3: Heat of formation from this calculation and some experimental data

Method	ΔH_f	Error
Gauche	-56.0495	0.87
Anti	-56.4593	0.87
Anti+2Gauche	**-56.1861**	**0.87**
Anti with hinder	-56.6073	0.87
Practical data[16]	-56.095	0.0717
Practical data[16]	-56.238	0.1195
Practical data[16]	-56.238	0.47801

Units: ΔH_f: kcal/mol

Entropy and heat capacity:
Thank to the available practical data collected in a study by Green[16], theoretical calculations were carried out at the same condition of temperature. Both of the two approaches show a close relation. However, surprisingly, the present approach calculation results (A-H) are close to the practical result in these two thermodynamic properties than the average approach (A+G) (cf. **Figure 3** and **Figure 4**). Results by conventional method matched completely in the error ranges of the practical data for entropy and close to the practical data in heat capacity, while the results from the interested approach are more negative from 1 to 3 cal/mol for entropy, increasing by temperature and about 0.5 cal/mol for heat capacity. The elimination of hindrance potential energy of the OH rotated group in the calculation of the two conformers may lead to the incomplete description of ethanol behavior, cause the change in entropy and heat capacity. For these parameters, we suggest to include hindered internal rotation for all the rotated axis, which is a simple approach but perfection calculation.
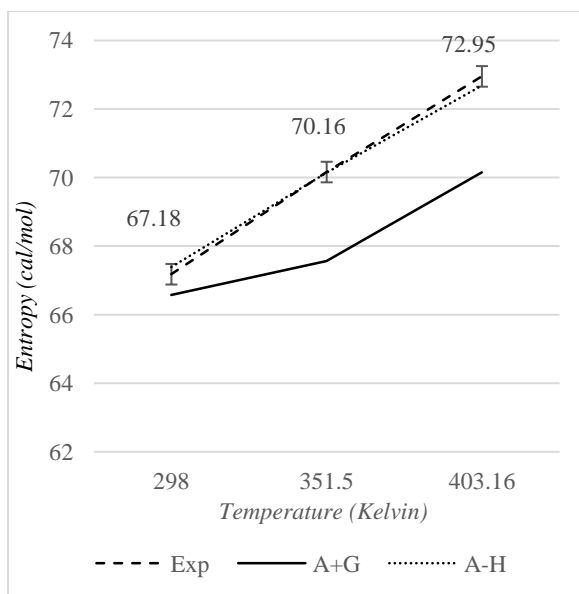
Figure 3: Entropy of this calculation (A+G), the present approach (A-H) and the practical data at temperature 298K to 403K.
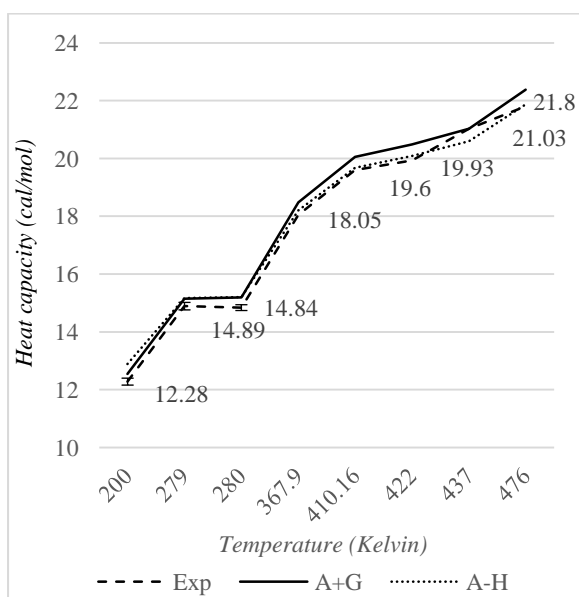

Figure 4: Heat capacity of this calculation (A+G), the present approach (A-H) and practical data at temperature 200K to 476K.

IV. Conclusion and Remarks:

The small gap in electronic energy between the two conformers have a sight effect to thermodynamic properties of ethanol. Ratio of gauche to anti conformer are determined to be approximately 2:1 at room temperature. At lower temperature, the inclusion of this ratio shows a significant improvement in heat of formation and acceptable results of entropy and heat capacity when compare with the present approach and some practical data. The energy gap decreased when temperature increase, which mean the ratio gauche to anti do not have significant effect to thermodynamic properties

of ethanol at high temperature (about 1500K). We suggest, from this research, the calculation with average conformers approach should be considered for a very accurate enthalpy while for a general thermodynamic calculation, the present approach shows considerable advantages.

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