getThermo

User's Guide

Grupo de Espectroscopia Teórica e Modelagem Molecular – GET

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1 Introduction

The **getThermo** package was created to make possible obtain thermodynamic properties of chemical systems selecting normal modes to represent vibrational movement. This manual selection should be necessary in cases which the quantum mechanics package is unable to correctly discriminate vibrational modes. In this cases, for example in calculation of supermolecules frequencies, some rotational modes could be assigned as vibrational modes, resulting in incorrect values of thermodynamic properties.

This first version of **getThermo** is applicable to frequencies calculations in GAMESS package (*General Atomic and Molecular Electronic Structure System*)[1] and Gaussian09[2].

Procedure to obtain partition functions follows the same treatment as in GAMESS package. Briefly, the following equations are derived from statistical mechanics.[3]

Vibrational partition function, q_{vib}, is obtained by description of movement as an harmonic oscillator approximation. It depends of frequencies from Hessian calculation, ν_i, and temperature, T. (equation 1)

$$q_{vib} = \prod_i \left(\frac{1}{1 - e^{-\frac{hc}{k_B T}\nu_i}} \right) \tag{1}$$

Translational partition function, q_{trans}, is obtained through ideal gas Law approach. It is calculated based in total mass weight, M, and pressure, P. (equation 2)

$$q_{trans} = \frac{1}{P} \left(k_B T\right)^{5/2} \left(\frac{2\pi}{h^2} \frac{M}{N_A} \right)^{3/2} \tag{2}$$

Rotational partition function, q_{rot}, is obtained by description of movement as an rigid rotor approximation. It is calculated based in inertia moment in the three Cartesian coordinates, I_r, and temperature, T. (equation 3)

$$q_{rot} = \sqrt{\pi} \left(\frac{T^{3/2}}{\sqrt{\Theta_x}\sqrt{\Theta_y}\sqrt{\Theta_z}} \right) \tag{3}$$

Where Θ_r is given by the expression shown in equation 4.

$$\Theta_r = \frac{h^2}{8\pi^2 k_B} \frac{1}{I_r} \tag{4}$$

These partition functions are applied to obtain corrected total Gibbs Free Energy to the chemical system of interest.

2 Installation Instructions

The **getThermo** package contains a very simple shell-script called *install*. Running this script, the compilation of **getThermo** is executed and the binary *getThermo.x* placed at *build* folder.

If you want to compile **getThermo** manually, is recommended *gfortran* as FORTRAN compiler. The command is exemplified in following textbox.

```
gfortran -ffree-line-length-none getThermo.f90 -o getThermo.x
```

3 Software Structure

The **getThermo** package contais two programs: the *getThermo* shell-script and the *getThermo.x* binary.

The shell-script, wrote in BASH (*Bourne-Again SHell*), takes the user's input file, checking its suitability and generating the complete input read by *getThermo.x*. This complete input file is a temporary file created to each selected work, named *{Work}.getThermo.inp*. It's also execute the calculations indicated in input file and generate their output files.

The *getThermo.x* binary perform the thermodynamic properties calculations and it's executed within the *getThermo* shell-script. The code was wrote in FORTRAN 90/95 (*Mathematical FORmula TRANslation System*).

To run **getThermo** you should use only the *getThermo* shell-script, giving your input filename in a command like in the shown below. To avoid errors, this script **must** be executed in the folder which contain the input files.

```
$getThermoDirectory/getThermo {Input Filename}
```

After the calculation are created two kinds of output files. The *{Work}.getThermo.out* file contains the results for a single selected work. The *{Input Filename}.getThermo.tsv* (*Tab-Separated Values format*) contains all the results, organized in a table to simplify the post-treatment.

4 Input Description

The input file have an important and very simple rule to avoid syntax errors: **Only one command is permitted per line.** In multiple instance case, the **getThermo** shell-script takes only the last occurrence.

It's also possible to make comments in the input file. Any information after the keywords are ignored by **getThermo** shell script since you do not use keywords in this texts. In the same way, lines that do not contain any keyword are also ignored and can be used as a comment.

Each keyword has the syntax shown in the following box. The keyword and its value are separated by a equal character, '='.

```
KEYWORD={Keyword value}
```

For cases in which keywords contains array elements, these are separated by commas. In the following box, there's an example with three array elements.

```
KEYWORD={Keyword value #1},{Keyword value #2},{Keyword value #3}
```

4.1 Required Keywords

- **Output**: GAMESS or Gaussian09 output filename or folder which contains. The output file must to be from Hessian calculation type (keyword *RUNTYP=HESSIAN* in GAMESS input file or keyword *Freq* in Gaussian09 input file).
- **NVibMode**: Number of vibrational modes selected to thermodynamic properties calculations.

4.2 Optional Keywords

- **IMode**: An array containing the sequence of normal modes.

  The **getThermo** FORTRAN program excludes the firsts modes, the deselected by **NVibMode** keyword and the rotational and translational modes. In some cases, you should try to use this keyword to select correctly the interesting modes. Max dimension is equal **NVibMode** value given.

- **Temperature**: An array containing temperatures to be used in thermodynamic properties calculations.

  Default: 298.15 K

5 About Authors

getThermo is developed by Grupo de Espectroscopia Teórica e Modelagem Molecular (GET) from Instituto de Química of Universidade Federal do Rio de Janeiro (IQ/UFRJ), coordinated by Professor Alexandre Braga da Rocha.

Distribution of **getThermo** is given on our GitHub repository, under MIT License

The FORTRAN code and shell-scripts are developed by M.Sc. Carlos Eduardo de Moura and M.Sc. Ricardo Oliveira. Contact us for any question about **getThermo**.

References

[1] Michael W. Schmidt, Kim K. Baldridge, Jerry A. Boatz, Steven T. Elbert, Mark S. Gordon, Jan H. Jensen, Shiro Koseki, Nikita Matsunaga, Kiet A. Nguyen, Shujun Su, Theresa L. Windus, Michel Dupuis, and John A. Montgomery. General atomic and molecular electronic structure system. *Journal of Computational Chemistry*, 14(11):1347–1363, 1993.

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[3] D.A. McQuarrie. *Statistical thermodynamics*. University Science Books, 1973.