

Hands-on Calculation of Thermal Correction to Gibbs Free Energy

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Objective

This manual presents a step-by-step calculation of the **thermal correction to Gibbs free energy** using molecular vibrational frequencies, following the statistical mechanics formalism as implemented in the Gaussian16 software package. There has been some confusion among beginners regarding whether the famous Gaussian16 implicitly incorporates the zero-point energy (ZPE) contribution into the reported thermal correction to Gibbs free energy. In my code, I have explicitly extracted the vibrational frequencies and other thermochemical parameters from the Gaussian output and recalculated the thermal correction to Gibbs free energy using the same statistical mechanical framework as employed by Gaussian. Our results confirm that Gaussian16 **does implicitly include the ZPE contribution** in its thermal correction to Gibbs free energy. Therefore, when computing the final Gibbs free energy by adding the thermal correction to the electronic energy, there is **no need to add ZPE separately**; otherwise, the Gibbs free energy will be overestimated by exactly the amount of the zero-point contribution.

Constants :

- Planck constant: $h = 6.62607015 \times 10^{-34} \text{ J} \cdot \text{s}$
- Boltzmann constant: $k_B = 1.380649 \times 10^{-23} \text{ J/K}$
- Speed of light: $c = 2.99792458 \times 10^{10} \text{ cm/s}$
- Gas constant: $R = 8.314462618 \text{ J/mol} \cdot \text{K}$
- Avogadro's number: $N_A = 6.02214076 \times 10^{23} \text{ mol}^{-1}$
- Temperature: $T = 298.15 \text{ K}$
- Pressure: $P = 101325 \text{ Pa}$
- Atomic mass unit: $1 \text{ amu} = 1.66053906660 \times 10^{-27} \text{ kg}$

1 Translational Contribution

The translational partition function q_{trans} for a molecule is given by the equation:

$$q_{\text{trans}} = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \times \frac{k_B T}{P}$$

Where m is the mass of the molecule, which will be taken from the Gaussian output file in amu and then converted into kg using the conversion factor provided in the Constants box. T is the temperature of interest in K, P is the pressure of interest in Pascal, and h is Planck's constant. All quantities are in SI units.

The internal energy U_{trans} and entropy S_{trans} for translational motion are given by:

$$U_{\text{trans}} = \frac{3}{2} RT$$

$$S_{\text{trans}} = R \left(1 + \frac{3}{2} + \ln q_{\text{trans}} \right)$$

2 Rotational Contribution

The rotational partition function q_{rot} is computed using the rotational moments of inertia which can be collected from Gaussian output file in atomic units (amu Bohr^2) and converting

them to SI units ($\text{kg}\cdot\text{m}^2$)/[1 bohr = $5.29177210903e-11$ m]:

$$q_{\text{rot}} = \sqrt{\pi} \left(\frac{8\pi^2 k_B T}{h^2} \right)^{3/2} \times \frac{\sqrt{I_{\text{prod}}}}{\sigma}$$

where I_{prod} is the product of the moments of inertia for the three axes of rotation, and σ is the symmetry number of the molecule.

The internal energy U_{rot} and entropy S_{rot} for rotational motion are given by:

$$U_{\text{rot}} = \frac{3}{2}RT$$

$$S_{\text{rot}} = R \left(\frac{3}{2} + \ln q_{\text{rot}} \right)$$

3 Vibrational Contribution

For vibrational modes, the vibrational partition function q_{vib} is calculated for each frequency ν in cm^{-1} (vibrational frequencies in wavenumbers) which can be easily grepped from Gaussian output file. The vibrational energy U_i and entropy S_i for each mode are given by:

$$\theta_i = \frac{hc\nu_i}{k_B}$$

$$x_i = \frac{\theta_i}{T}$$

$$U_i = R \left(\frac{\theta_i}{e^{x_i} - 1} + \frac{1}{2}\theta_i \right)$$

$$S_i = R \left(\frac{x_i}{e^{x_i} - 1} - \ln(1 - e^{-x_i}) \right)$$

The total vibrational internal energy U_{vib} and entropy S_{vib} are the sum over all vibrational modes:

$$U_{\text{vib}} = \sum_i U_i$$

$$S_{\text{vib}} = \sum_i S_i$$

4 Electronic Contribution

The electronic partition function q_{elec} is simplified, assuming the molecule has 2 electronic states (degeneracy $g_{\text{elec}} = 2$):

$$S_{\text{elec}} = R \ln g_{\text{elec}}$$

The electronic contribution is negligible for closed shell molecules.

5 Total Contributions

The total internal energy U_{total} , entropy S_{total} , enthalpy H_{total} , and Gibbs free energy G_{total} are calculated as:

$$U_{\text{total}} = U_{\text{trans}} + U_{\text{rot}} + U_{\text{vib}} + U_{\text{elec}}$$

$$S_{\text{total}} = S_{\text{trans}} + S_{\text{rot}} + S_{\text{vib}} + S_{\text{elec}}$$

$$H_{\text{total}} = U_{\text{total}} + RT$$

$$G_{\text{total}} = H_{\text{total}} - TS_{\text{total}}$$

Finally, the thermal correction to the Gibbs free energy is converted into Hartree units [$1 \text{ Hartree} = 2625.5 \text{ kJ/mol}$]:

$$G_{\text{Hartree}} = \frac{G_{\text{total}}}{1000 \times 2625.5}$$

6 Example Code

I have attached a simple Python code for a reactant-complex molecule, that calculates the thermal correction to the Gibbs free energy using vibrational frequencies, and the results from this code is matching well with the Gaussian16 output.