

Introduction to Statistical Molecular Thermodynamics

Statistical thermodynamics vs classical thermodynamics

Classical thermodynamics encompasses a powerful set of laws but none of them offering any kind of molecular insight.

Statistical thermodynamics was developed to connect *microscopic* properties to the already well established *macroscopic* behavior of substances.

Statistical thermodynamics uses the **probability theory** to relate the **averages** of **molecular properties** to bulk **thermodynamic properties**, the properties like internal energy, entropy, enthalpy, etc.

Thermodynamic functions can be computed from the **partition functions** (Q) (the central one is internal energy) ,which plays the major role in statistical thermodynamics.

Partition function (Q) is to statistical mechanics what the **wave function** (Ψ) is to quantum mechanics which is a tool to express all of the properties that you might interested.

Thermochemistry output from Gaussian

How various thermochemical values are computed in *Gaussian*??

B3LYP/6-31G(d)

- Thermochemistry -

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

```
Zero-point correction=          0.045144 (Hartree/Particle)
Thermal correction to Energy=    0.048008
Thermal correction to Enthalpy=   0.048952
Thermal correction to Gibbs Free Energy= 0.027817
Sum of electronic and zero-point Energies= -40.471353
Sum of electronic and thermal Energies= -40.468489
Sum of electronic and thermal Enthalpies= -40.467545
Sum of electronic and thermal Free Energies= -40.488680
```

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	30.125	6.415	44.482
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	34.261
Rotational	0.889	2.981	10.146
Vibrational	28.348	0.453	0.075

How is energy stored in a molecule?

Connecting *macroscopic* thermodynamics to a molecular understanding requires that we know how energy is distributed on a *microscopic* scale.

Electronic energy. Changes in the **kinetic** and **potential** energy of one or more electrons associated with the *molecule*.

Kinetic Energy:

Translational energy. The entire *molecule* move (translate) in space.

Rotational energy. The entire *molecule* can rotate about its center of mass in space.

Vibrational energy. The nuclei can move *relative to one another* in space.

To specify completely the position in space of a molecule having n nuclei, we require $3n$ coordinates (3 Cartesian coordinates for each nucleus). We say that there are *$3n$ degrees of freedom*.

Degrees of freedom can be divided as translational (**3**), rotational (**linear molecule = 2; nonlinear molecule = 3**), or vibrational (**linear molecule = $3n-5$; nonlinear molecule = $3n-6$**)

Total Energy

The total energy of a molecule can be expressed as a sum over all the degrees of freedom.

For diatomic and polyatomic:

$$\mathcal{E} = \mathcal{E}_{\text{trans}} + \mathcal{E}_{\text{rot}} + \mathcal{E}_{\text{vib}} + \mathcal{E}_{\text{elec}}$$

D_e for diatomics.

$$\mathcal{E}_{n_x n_y n_z} = \frac{h^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$

$n_x = 1, 2, 3, \dots$
 $n_y = 1, 2, 3, \dots$
 $n_z = 1, 2, 3, \dots$

$$\mathcal{E}_J = \frac{\hbar^2}{2I} J(J+1)$$

$J = 0, 1, 2, \dots$
 For linear molecules

$$\mathcal{E}_v = h\nu \left(v + \frac{1}{2} \right)$$

$v = 0, 1, 2, \dots$
 For each vibrational degree of freedom

For monoatomic:

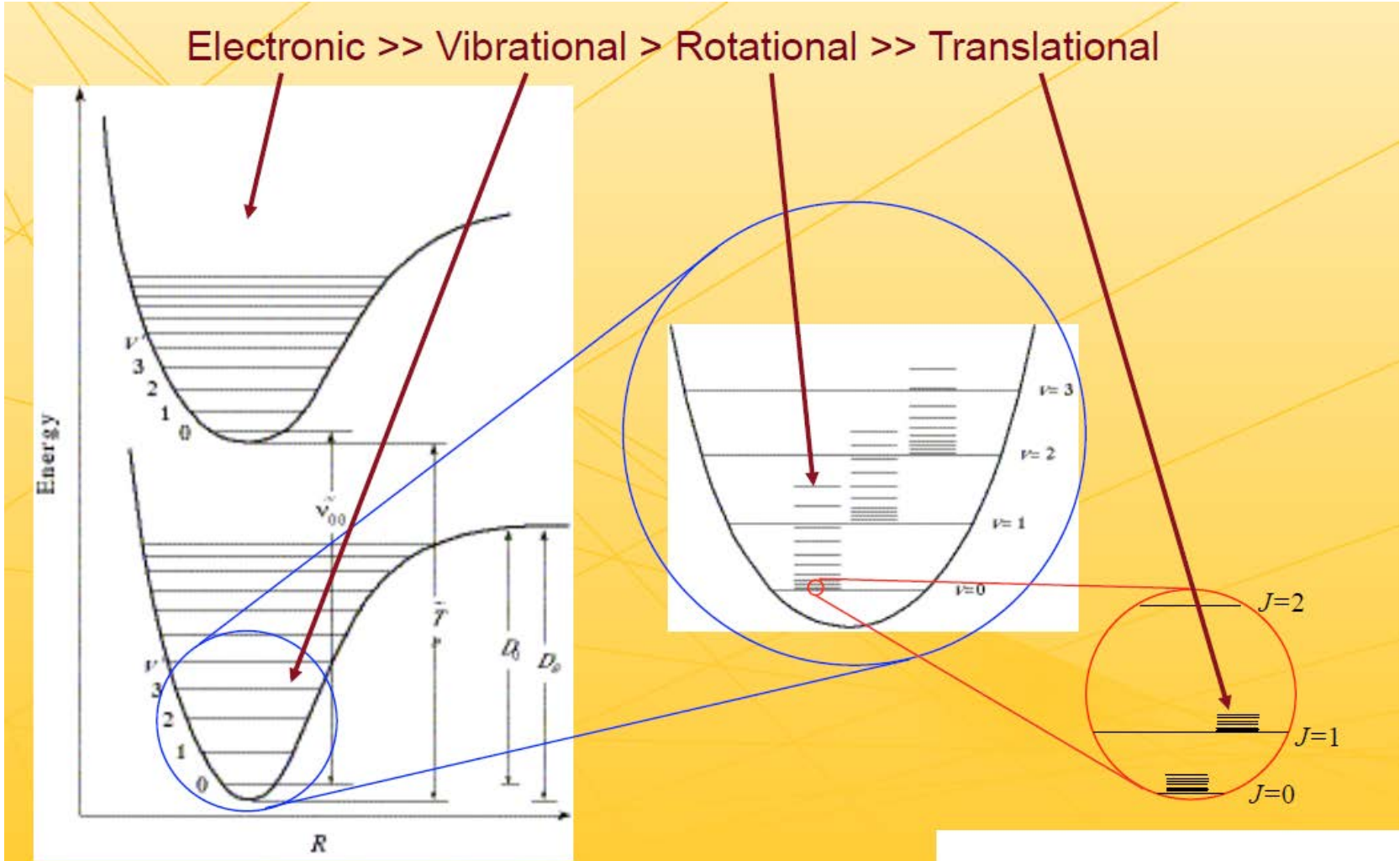
$$\mathcal{E}_{\text{atomic}} = \mathcal{E}_{\text{trans}} + \mathcal{E}_{\text{elec}} \quad (\text{sum})$$

total energy
translational energy
electronic energy

For an ideal *monatomic* gas the *only* degrees of freedom are translational and electronic.

Spacing of Energy Levels

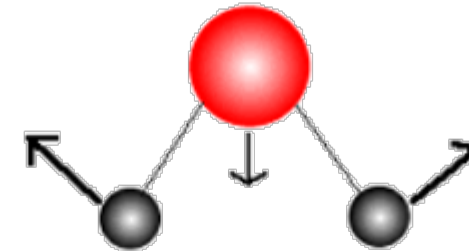
There is a general trend in energy spacing



Polyatomic vibrations: normal modes

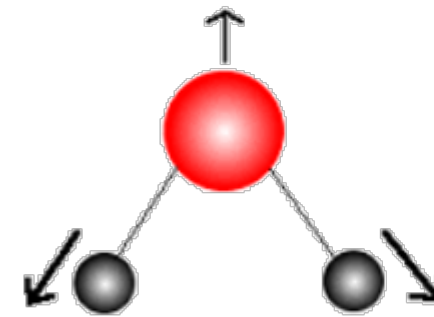
Polyatomic molecules have more than one vibration, and we can consider each of the vibrational degrees of freedom as independent harmonic oscillators. We refer to the characteristic **independent** vibrational motions as *normal modes*.

E.g., water has 3 normal modes:



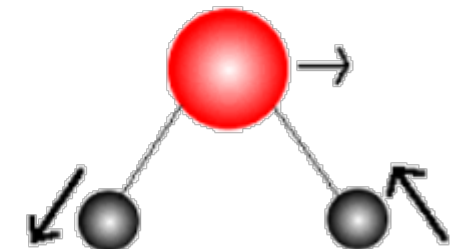
BEND

$$\tilde{\nu} = 1595 \text{ cm}^{-1}$$



SYMMETRIC STRETCH

$$\tilde{\nu} = 3686 \text{ cm}^{-1}$$



ANTI-SYMMETRIC STRETCH

$$\tilde{\nu} = 3725 \text{ cm}^{-1}$$

Since the normal modes are independent of one another, the total vibrational energy is simply the sum all of them:

$$\mathcal{E}_{\text{vib}} = \sum_{j=1}^{n_{\text{vib}}} h\nu_j \left(\nu_j + \frac{1}{2} \right)$$

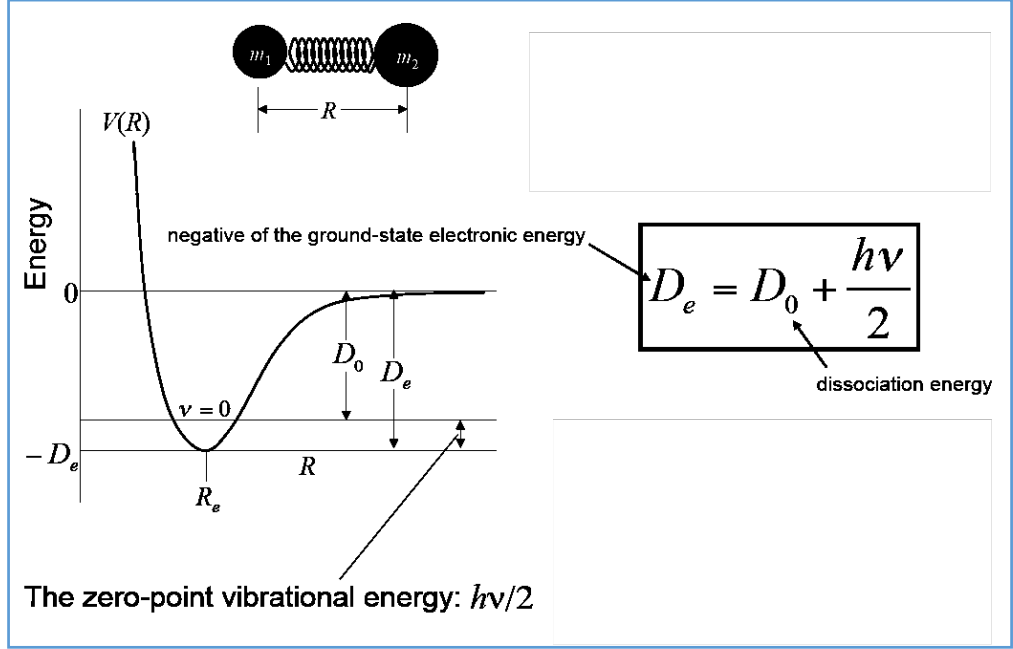
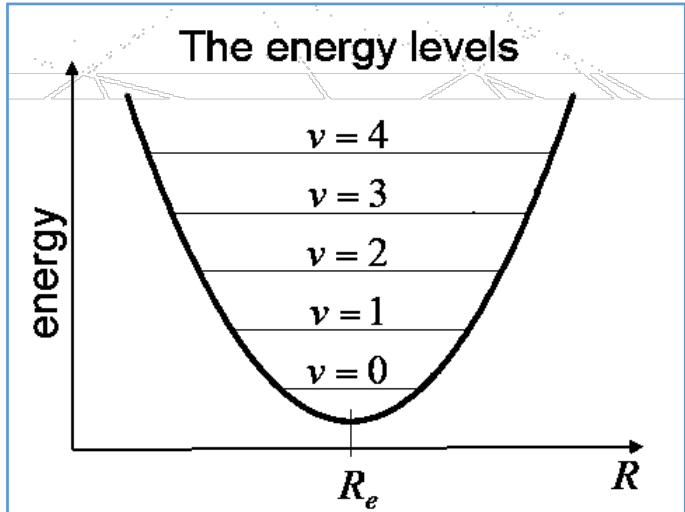
Vibrational Energy Levels & Bond Dissociation energy

$$\epsilon_{\text{vib}} = \sum_{j=1}^{n_{\text{vib}}} h\nu_j \left(\nu_j + \frac{1}{2} \right)$$

$\nu = 0, 1, 2, \dots$

$$\epsilon_0 = \frac{1}{2} h\nu$$

- For a diatomic the difference between the ground-state electronic energy and the negative of the bond dissociation energy is the **zero-point vibrational energy**.



The energy of the lowest state is NOT zero. The difference is called **zero-point energy**.

For example, for $\text{H}_2(\text{g})$:
 $D_e = 458 \text{ kJ} \cdot \text{mol}^{-1}$
 $D_0 = 432 \text{ kJ} \cdot \text{mol}^{-1}$
 $\tilde{\nu} = 4401 \text{ cm}^{-1} (= 52 \text{ kJ} \cdot \text{mol}^{-1})$

Behavior of partition Function

The partition function Q is a measure of the number of “accessible” states at a given temperature

$$S = k_B \ln W \qquad p_j(N, V, T) = \frac{e^{-E_j(N, V)/k_B T}}{Q(N, V, T)}$$

For simplicity, if *ground state* to be *non-degenerate* and define its energy as zero. Then all other state energies are positive and :

$$Q(N, V, T) = \sum_j^{\text{states}} e^{-E_j(N, V)/k_B T} \qquad \underline{\underline{Q(N, V, T) = 1 + \sum_j^{\text{excited states}} e^{-E_j(N, V)/k_B T}}}$$

As $T \rightarrow 0$, $Q \rightarrow 1$ and, as $T \rightarrow \infty$, $Q \rightarrow$ total number of states

As the “density of states” $\rightarrow 0$, $Q \rightarrow 1$ and, as it $\rightarrow \infty$, $Q \rightarrow$ total number of states

As a result, Q tells us how many energy states the system can access at the specified N , V and T .

Sources of components for thermodynamic quantities

The equations used to calculate the contributions to entropy, energy, and heat capacity resulting from : **translational, electronic, rotational vibrational motions** ($\epsilon = \epsilon_{\text{trans}} + \epsilon_{\text{rot}} + \epsilon_{\text{vib}} + \epsilon_{\text{elec}}$)

➤ The starting point in each case is the partition function $q(V, T)$

Entropy (S) :
$$S = Nk_B + Nk_B \ln \left(\frac{q(V, T)}{N} \right) + Nk_B T \left(\frac{\partial \ln q}{\partial T} \right)_V$$

Internal thermal energy (E) :
$$E = Nk_B T^2 \left(\frac{\partial \ln q}{\partial T} \right)_V$$

Heat capacity C_V :
$$C_V = \left(\frac{\partial E}{\partial T} \right)_{N, V}$$

$$\begin{aligned} q(V, T) &= \sum_j e^{-\beta(\epsilon_{\text{trans}} + \epsilon_{\text{rot}} + \epsilon_{\text{vib}} + \epsilon_{\text{elec}})_j} \\ &= \sum_i e^{-\beta \epsilon_{\text{trans}, i}} \sum_j e^{-\beta \epsilon_{\text{rot}, j}} \sum_k e^{-\beta \epsilon_{\text{vib}, k}} \sum_l e^{-\beta \epsilon_{\text{elec}, l}} \\ &= q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}} \end{aligned}$$

These three equations will be used to derive the final expressions used to calculate the different components of the thermodynamic quantities printed out by Gaussian.

Contributions from translation & rotational motions

Translational motion:

$$q_t = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V.$$

$$\left(\frac{\partial \ln q_t}{\partial T} \right)_V = \frac{3}{2T}$$

$$\begin{aligned} E_t &= N_A k_B T^2 \left(\frac{\partial \ln q}{\partial T} \right)_V \\ &= RT^2 \left(\frac{3}{2T} \right) \\ &= \frac{3}{2} RT \end{aligned}$$

Rotational motion:

diatomic and linear polyatomic molecules:

$$\begin{aligned} q_r &= \frac{1}{\sigma_r} \left(\frac{T}{\Theta_r} \right) \\ E_r &= RT^2 \left(\frac{\partial \ln q_r}{\partial T} \right)_V \\ &= RT^2 \left(\frac{1}{T} \right) \\ &= RT \end{aligned}$$

non-linear polyatomic molecules:

$$\begin{aligned} q_r &= \frac{\pi^{1/2}}{\sigma_r} \left(\frac{T^{3/2}}{(\Theta_{r,x} \Theta_{r,y} \Theta_{r,z})^{1/2}} \right) \\ E_r &= RT^2 \left(\frac{\partial \ln q_r}{\partial T} \right)_V \\ &= RT^2 \left(\frac{3}{2T} \right) \\ &= \frac{3}{2} RT \end{aligned}$$

Contributions from electronic motion

$$q_e = \omega_0 e^{-\epsilon_0/k_B T} + \omega_1 e^{-\epsilon_1/k_B T} + \omega_2 e^{-\epsilon_2/k_B T} + \dots$$

Where ω is the degeneracy of the each energy level.

Gaussian assumes that the first electronic excitation energy is much greater than $k_B T$.

Therefore, the **first** and **higher excited states** are assumed to be **inaccessible** at room temperature.

Further, the energy of the ground state is set to **zero**: $q_e = \omega_0$,

$$E = N k_B T^2 \left(\frac{\partial \ln q}{\partial T} \right)_V$$

The electronic internal thermal energy is zero.

Contributions from vibrational motion

- The contributions to the partition function composed of a **sum** of the contributions from **each vibrational mode**, K .
- Only the **real modes** are considered; modes with imaginary frequencies (i.e. those flagged with a minus sign in the output) are ignored.
- Gaussian uses the **bottom of the well** (BOT) as the **zero of energy** to determine the other thermodynamic quantities, but also prints out the $V=0$ (ground state of vibrational energy levels) partition function.
- The only difference between the two references is the additional factor of $\frac{1}{2} h\nu$, (which is the **zero point vibrational energy**) in the equation for the internal energy E_{vib} .

$$E_{\text{v}} = R \sum_K \Theta_{\text{v},K} \left(\frac{1}{2} + \frac{1}{e^{\Theta_{\text{v},K}/T} - 1} \right)$$

Gaussian Output : Thermochemistry

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Zero-point correction=                0.045144 (Hartree)
Thermal correction to Energy=          0.048008  $E_{tot} = E_t + E_r + E_v + E_e$ 
Thermal correction to Enthalpy=        0.048952  $H_{corr} = E_{tot} + k_B T$ 
Thermal correction to Gibbs Free Energy= 0.027817  $G_{corr} = H_{corr} - TS_{tot}$   $S_{tot} = S_t + S_r + S_v + S_e$ 
Sum of electronic and zero-point Energies= -40.471353  $\epsilon_0 + \epsilon_{ZPE}$ 
Sum of electronic and thermal Energies= -40.468489  $\epsilon_0 + \epsilon_{tot}$ 
Sum of electronic and thermal Enthalpies= -40.467545  $\epsilon_0 + H_{corr}$ 
Sum of electronic and thermal Free Energies= -40.488680  $\epsilon_0 + G_{corr}$ 

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References

1. Ochterski, Joseph W. "Thermochemistry in gaussian." *Gaussian Inc* (**2000**): 1-19.
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Thank you!