Quantum Chemistry

Lecture 25

Thermodynamic quantities calculated from quantum theory

NC State University

Introduction

The relationship between the solutions to the Schrödinger equation and the thermodynamic standard state must be understood first in order to relate calculated energies to experiment. The Hartree-Fock and DFT methods are usually applied to individual molecules, which implies that the molecules are in the gas phase. Yet, the temperature is not defined by the quantum mechanical solutions are the molecules are calculated in their center-of-mass coordinate system. Thus, the temperature can be assumed to be absolute zero. Although this is a completely contradictory set of conditions (i.e. a molecule in the gas phase at T = 0 K!), this is what we find by a simple analysis of the meaning of the Schrödinger equation.

Comparison with experiment

To a first approximation we should compare the calculated results to gas phase thermodynamic quantities, but this would also require appropriate corrections for zero point energy and for the kinetic energy or internal energy of the molecule.

First, we briefly review the key statistical mechanical equations that permit one to calculate enthalpy, entropy and also free energy. Second, we will examine the partition functions, which can be approximated in the classical (high temperature) limit for rotations and translations. On the other hand, we will consider only the zero point vibrational energy, which is a low temperature approximation. This is a reasonable approximation.

Molecular partition function

A vibrational frequency calculation must be carried out in order to calculate contribution of each of these normal modes to the partition function. The vibrational contribution to the entropy is significant.

The molecular partition function is the product of each of the three kinematic partition functions and the electronic partition function.

$$q = q_{trans} q_{rot} q_{vib} q_{elec}$$

For indistinguishable particles, the system partition function is

$$Q = \frac{q^N}{N!}$$

Calculation of the internal energy

For convenience the quantity β is defined as

$$\beta = \frac{1}{k_B T}$$

Using the statistical mechanical definition of the internal energy

$$U = -\left(\frac{\partial \ln Q}{\partial \beta}\right)$$

This form is very useful since we can ignore any contributions to Q that do not contain temperature.

Calculation of the free energy

The entropy is given by

$$S = \frac{U - U_0}{T} + k_B \ln Q$$

Finally, the Helmholtz free energy is given by

$$A = -k_B T \ln Q$$

Finally the pressure can be calculated from the partition function.

$$P = -\left(\frac{\partial \ln Q}{\partial V}\right)_T$$

Using the pressure one can calculate the both the enthalpy and Gibbs free energy.

Translational partition function

The partition function for translation is given by

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

The translation partition function can be calculated based on the molecular mass. Since all calculations described in this course have been carried out in a center-of-mass coordinate system (i.e. the center of mass is the origin), the translations have been projected out.

The translational energy of the molecules is the kinetic energy, which is $3/2 k_B T$ on a molecular basis, according to the kinetic theory of gases. On a molar basis we use $3/2 RT$, which provides a correction to the calculated energy. The remaining kinematic variables are rotation and vibration, which require consideration of the partition function since there can be temperature dependent population of the energy levels.

Rotational partition function

The partition function for rotation can be treated classically since the energy level spacing is much less than thermal energy,

$$\frac{\hbar^2}{2I_A} 2J \ll kT$$

where I_A is one of the moments of inertia.

In the general case there are three moments of inertia, I_A, I_B and I_C, which can be obtained following the geometry optimization. While there are some special cases such as spherical tops, the general case involves calculating the rotational partition function for each of three axes. The complete partition function is (degeneracy $g_j = 2J + 1$)

$$q_{rot} = \frac{1}{\sigma} \left(\sum_{J=0}^{\infty} g_J \exp\left\{ -\frac{\hbar^2 J(J+1)}{2I_A k_B T} \right\} \right)^{1/2} \left(\sum_{K=0}^{\infty} g_K \exp\left\{ -\frac{\hbar^2 K(K+1)}{2I_B k_B T} \right\} \right)^{\frac{1}{2}} \left(\sum_{L=0}^{\infty} g_L \exp\left\{ -\frac{\hbar^2 L(L+1)}{2I_C k_B T} \right\} \right)^{1/2}$$

Rotational partition function

In the high temperature limit (which is typically below room temperature), the partition function can approximated by:

$$q_{rot} = \frac{1}{\sigma}\left(\frac{2I_A k_B T}{\hbar^2}\right)^{1/2}\left(\frac{2I_B k_B T}{\hbar^2}\right)^{1/2}\left(\frac{2I_C k_B T}{\hbar^2}\right)^{1/2}$$

This is a general form for a molecule with three axes of rotation (a non-linear polyatomic). For a linear molecule (including diatomic molecules) there are only two terms. When we calculate the internal energy of rotation we will use the logarithm (see the internal energy expression). Thus, the energy of rotation is simply RT for a diatomic and 3/2 RT for a polyatomic.

For rotations in the classical limit we can insert the partition function into the expression for the rotational energy

$$U_{rot} = -N \left(\frac{\partial \ln q_{rot}}{\partial \beta} \right)$$

which is obtained using the substitution of the system partition function into the internal energy. For each rotational degree of freedom we find that

$$U_{rot} = \frac{N}{2} \left(\frac{\partial \ln \beta}{\partial \beta} \right) + \text{other terms}$$

This leads to

$$U_{rot} = \frac{N}{2} k_B T = \frac{1}{2} RT$$

for each rotational degree of freedom.

Vibrational partition function

The vibrational partition function is identical to the partition function of evenly spaced radiation levels. Since there 3N - 6 normal modes of vibration the partition function is the product of the single mode partition function. We use the index n to represent each normal mode of vibration. The result is:

$$q_{vib} = \prod_{n=1}^{3N-6} \frac{e^{-\frac{\hbar\omega_n}{2k_B T}}}{\left(e^{-\frac{\hbar\omega_n}{k_B T}} - 1\right)}$$

where we have included the contribution due to the zero point energy

$$\exp\left\{-\frac{\hbar\omega_n}{2k_B T}\right\}$$

in this calculation.

Calculation of the electronic partition function

For vibrations, the most important contribution is the zero point vibrational energy (ZPVE). If we consider only that contribution we have

$$U_{ZPVE} = -\sum_n \left(\frac{\partial \ln \left(\exp \left\{ -\frac{\hbar \omega_n \beta}{2} \right\} \right)}{\partial \beta} \right) = \sum_n \frac{\hbar \omega_n}{2}$$

The electronic partition function is calculated from the well depth D_o.

$$q_{elec} = e^{D_o/RT}$$

where D_o is conveniently given in units of kJ/mol. We see that the contribution to the energy is simply the well depth D_o.

Definition of enthalpy

In practice we use the total energy of each molecule obtained from the ab initio or DFT calculation. When the difference in binding energy for reactants and products is combined with the kinematic energy calculated from the partition function, it possible to obtain an accurate estimate for the enthalpy of reaction. Thus, we use the prescription:

$$\Delta_{rxn}H^o = \sum_{i,prod} \nu_i \left(D_{o,i} + \sum_{ni} \frac{\hbar\omega_{ni}}{2} \right) - \sum_{j,react} \nu_j \left(D_{o,j} + \sum_{nj} \frac{\hbar\omega_{nj}}{2} \right)$$

Example of H_2O

To obtain the enthalpy of reaction at T = 0 K. At a finite temperature we would need to correct each term by the translational and rotational partition function. In order to obtain the enthalpy we would also need to include the work term. Since H = U + PV and PV is the work term we can also use the ideal gas law (PV = RT) to write H = U +RT. Thus, the correction to the quantum mechanical energy is 4RT for a polyatomic and 7/2RT for a diatomic molecule.

We will use H_2O are our example calculation. Keeping in Mind that the reaction for formation of water from H_2 and O_2 Is also the same as the enthalpy of formation of water, we Will report the out from DFT calculations for the three molecules, H_2, O_2 and H_2O.

```
           Total Energy        Binding E
      -76.381619Ha      -0.3813040Ha

Standard thermodynamic quantities at  298.15 K  and   1.00 atm


 Zero point vibrational energy:      13.127 kcal/mol


 H,Trans:            0.889 kcal/mol
 H,Rot  :            0.889 kcal/mol
 H,pV   :            0.592 kcal/mol
 H,Vib - ZPVE:         0.002 kcal/mol
 S,Trans:           34.609  cal/mol.K
 S,Rot  :           11.919  cal/mol.K
 S,Vib  :            0.007  cal/mol.K
 C,Trans:            4.968  cal/mol.K
 C,Rot  :            2.981  cal/mol.K
 C,Vib  :            0.047  cal/mol.K
 =========================================
 H,Total - ZPVE:      2.372 kcal/mol
 S,Total:           46.535  cal/mol.K
 C,Total (p):         7.996  cal/mol.K
 G,Total:          -11.503 kcal/mol
```

```
      Total Energy          Binding E
    -1.166147Ha        -0.1666453Ha

Standard thermodynamic quantities at   298.15 K  and    1.00 atm

  Zero point vibrational energy:      6.198 kcal/mol

  H,Trans:            0.889 kcal/mol
  H,Rot  :            0.592 kcal/mol
  H,pV   :            0.592 kcal/mol
  H,Vib - ZPVE:         0.000 kcal/mol
  S,Trans:          28.080  cal/mol.K
  S,Rot  :           4.475  cal/mol.K
  S,Vib  :           0.000  cal/mol.K
  C,Trans:           4.968  cal/mol.K
  C,Rot  :           1.987  cal/mol.K
  C,Vib  :           0.000  cal/mol.K
  =========================================
  H,Total - ZPVE:      2.074 kcal/mol
  S,Total:          32.555  cal/mol.K
  C,Total (p):       6.955  cal/mol.K
  G,Total:          -7.633 kcal/mol
```

```
      Total Energy        Binding E
    -150.248230Ha       -0.2466022Ha


Standard thermodynamic quantities at   298.15 K  and    1.00 atm


  Zero point vibrational energy:      2.206 kcal/mol


  H,Trans:           0.889 kcal/mol
  H,Rot  :           0.592 kcal/mol
  H,pV   :           0.592 kcal/mol
  H,Vib - ZPVE:         0.003 kcal/mol
  S,Trans:          36.321  cal/mol.K
  S,Rot  :          11.937  cal/mol.K
  S,Vib  :           0.010  cal/mol.K
  C,Trans:           4.968  cal/mol.K
  C,Rot  :           1.987  cal/mol.K
  C,Vib  :           0.064  cal/mol.K
  ==========================================
  H,Total - ZPVE:      2.076 kcal/mol
  S,Total:          48.268  cal/mol.K
  C,Total (p):       7.019  cal/mol.K
  G,Total:          -12.315 kcal/mol
```

If we use H_2O as our example, we find the following values shown below obtained from a DFT calculation using the PBE functional and a double numerical basis set. The experimental value for the enthalpy of reaction is -57.6 kcal/mol. The result of the DFT total energy difference between reactants and products is -57.3 kcal/mol. One must also include the difference ZPVE, which adds 5.83 kcal/mol and the rotational and translational energy, which add -0.74 kcal/mol. The result is -52.2 kcal/mol.

	D_o (Hartrees)	ZPVE (kcal/mol)	$U_{trans,rot}$ (kcal/mol)
H_2O	-76.381619	13.127	2.367
H_2	-1.166147	6.198	2.071
O_2	-150.248230	2.206	2.071
H_2 + 1/2 O_2 → H_2O	-0.091357 (-57.295)	5.826	-0.7395