## Rotations

For a general, non-linear polyatomic molecule the rotational partition function is:

We denote the rotational temperature as, such that the above equation becomes:

The entropy of rotations is:

The energy of rotations is:

That is for each degree of rotational freedom.

## Vibrations

Vibrations are treated in the harmonic oscillator approximation, where the energy levels are given by  
for each of the normal modes. The partition function (for a single normal mode) is therefore:

Which is a [geometric progression](http://en.wikipedia.org/wiki/Geometric_progression). We will define the characteristic vibrational temperature as, now the sum of the series can be written as:  
Since there are vibrations, the overall partition functions is:   
the vibrational energy is:  
the Helmholtz free energy:  
 and the entropy is:

some approximation

In the conventional approach for calculation of thermochemical properties of molecules, for a molecule, the internal energy and entropy  
where the molecule is assumed to be a rigid rotor, free to rotate and translate in all 3 degrees of freedom. The vibrational terms are evaluated assuming an approximately quadratic energy potential surface and using a quantum harmonic oscillator model (what about the normal modes?). The energy and entropy of vibrations are a sum of the individual contribution of each of the normal modes:

In this approximation, each normal mode has some contribution (ρ) from the cluster property (Pcluster) and complementary contribution (1- ρ) from the molecular property (Pmolecular), such that the contribution of any normal mode to the thermodynamic properties of the system (PNMode) is described as:

For each fragment, the projection of the normal modes on the x Cartesian axis is:

Such that

The fractional motion along x, for a given is:

In a similar fashion, we define the projection of each fragment of the rotation along the principle axis of rotation:

Such that the fractional rotation along, for a given is:

The fractional motion parameters: and define how much the fragment is effectively free

References

Wikipedia: [Calculation of thermodynamics quantities in the canonical ensemble](http://en.wikipedia.org/w/index.php?title=Partition_function_%28statistical_mechanics%29&oldid=624949972)