Computing Thermodynamic Quantities

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How do we compute thermodynamic properties from quantum chemistry?

- Thermodyanic properties are valid for a *large number* of molecules, not individual molecules
- *Statistical mechanics* provides the bridge between quantum mechanics of individual molecules and thermodynamic properties
- Use quantum mechanics to compute molecular partition functions, obtain thermodynamic properties from the partition functions in the usual way

Statistical Mechanics

$$
\begin{aligned}
q &= \sum_{i}^{states} e^{-\epsilon_i/k_b T} \\
q &= \sum_{i}^{levels} g_i e^{-\epsilon_i/k_b T} \\
Q &= q^N \quad \text{(different particles)} \\
Q &= \frac{q^N}{N!} \quad \text{(identical particles)}
\end{aligned}
$$

$$
\begin{aligned}
H = U + PV &= k_b T^2 \left(\frac{\partial lnQ}{\partial T}\right)_V + k_b TV \left(\frac{\partial lnQ}{\partial V}\right)_T \\
S = \frac{U - A}{T} &= k_b T \left(\frac{\partial lnQ}{\partial T}\right)_V + k_b lnQ \\
G = H - TS &= k_b TV \left(\frac{\partial lnQ}{\partial T}\right)_V - k_b T lnQ
\end{aligned}
$$

Standard Partition Functions

Typically, the molecular partition function is written as a product of partition functions for translation, rotation, vibration, and electronic degrees of freedom

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

- Electronic partition function is usually 1; only relevant if excited electronic states are populated to a measurable extent (low-lying states and/or high temperatures)
- Translational partition function simple and just depends on mass and temperature

- Rotational partition function simple (although may require symmetry factors); just need geometry and temperature
- Vibrational partition function uses harmonic oscillator approximation; need vibrational frequencies and temperature

Thermodynamic Properties From Partition Functions

- Once we have the molecular partition function, use standard statistical mechanics to obtain thermodynamic properties such as S, H, etc.
- Major correction to enthalpy is vibrational. At 0K, the enthalpy is just E_e + ZPVE. At higher temperatures, other terms also contribute.
- Info for H^{298K} and S^{298K} is printed out by Q-Chem by default for any second derivative calculation
- *WARNING: When Q-Chem prints the "total enthalpy," it means the total enthalpy* correction *to* E_e. You must add this "total enthalpy" to E_e to get the real total enthalpy.

```
#####################################################
#  Entering drvman.exe on Fri Dec 15 14:51:30 2000  #
#####################################################

 Calculating MO derivatives via CPHF
   1        10           2      0.009892    0.007094
   2        12           0      0.000000    0.000000    Roots Converged
 Calculating analytic Hessian of the SCF energy
 Polarizability Matrix (a.u.)
            1           2           3
    1  −5.5054487  −0.0000000  −0.0000000
    2  −0.0000000  −0.0400454  −0.0000000
    3  −0.0000000  −0.0000000  −2.5654448

 Direct stationary perturbation theory relativistic correction:

 rels  =       0.031221304489
 relv  =      −0.096844180832
 rel2e =       0.023322614724
 E_rel =      −0.042300261619

 Hessian of the SCF Energy
            1           2           3           4           5           6
    1   0.8044023   0.0000000  −0.0000000  −0.4022012  −0.0000000  −0.3374251
    2   0.0000000  −0.0001352   0.0000000  −0.0000000   0.0000676  −0.0000000
    3  −0.0000000   0.0000000   0.6352335  −0.2165519  −0.0000000  −0.3176168
    4  −0.4022012  −0.0000000  −0.2165519   0.4391751   0.0000000   0.2769885
    5  −0.0000000   0.0000676  −0.0000000   0.0000000  −0.0000838   0.0000000
    6  −0.3374251  −0.0000000  −0.3176168   0.2769885   0.0000000   0.3002754
    7  −0.4022012  −0.0000000   0.2165519  −0.0369740  −0.0000000   0.0604366
    8   0.0000000   0.0000676  −0.0000000  −0.0000000   0.0000162   0.0000000
    9   0.3374251  −0.0000000  −0.3176168  −0.0604366  −0.0000000   0.0173414
            7           8           9
    1  −0.4022012   0.0000000   0.3374251
    2  −0.0000000   0.0000676  −0.0000000
    3   0.2165519  −0.0000000  −0.3176168
    4  −0.0369740  −0.0000000  −0.0604366
    5  −0.0000000   0.0000162  −0.0000000
    6   0.0604366   0.0000000   0.0173414
    7   0.4391751   0.0000000  −0.2769885
    8   0.0000000  −0.0000838   0.0000000
    9  −0.2769885   0.0000000   0.3002754
 Gradient time:  CPU 0.59 s  wall 1.00 s

#####################################################
#  Entering vibman.exe on Fri Dec 15 14:51:31 2000  #
#####################################################

 ***********************************************************************
 **                                                                   **
 **                       VIBRATIONAL ANALYSIS                        **
 **                       --------------------                        **
 **                                                                   **
 **        VIBRATIONAL FREQUENCIES (CM**−1) AND NORMAL MODES          **
 **                  INFRARED INTENSITIES (KM/MOL)                    **
 **                                                                   **
 ***********************************************************************


 Frequency:      2169.95                4141.60                4392.63
 IR Active:          YES                    YES                    YES
 IR Intens:        7.245                 44.303                 29.972
 Raman Active:       YES                    YES                    YES
               X      Y      Z        X      Y      Z        X      Y      Z
 O          0.000  0.000 −0.069    0.000  0.000  0.052   −0.068  0.000  0.000
 H         −0.448  0.000  0.545   −0.570  0.000 −0.416    0.540  0.000  0.453
 H          0.448  0.000  0.545    0.570  0.000 −0.416    0.540  0.000 −0.453

 STANDARD THERMODYNAMIC QUANTITIES AT   298.18 K  AND     1.00 ATM
```

```
   This Molecule has  0 Imaginary Frequencies
   Zero point vibrational energy:       15.302 kcal/mol

   Atom    1 Element O  Has Mass   15.99491
   Atom    2 Element H  Has Mass    1.00783
   Atom    3 Element H  Has Mass    1.00783
   Molecular Mass:    18.010570 amu
   Principal axes and moments of inertia in atomic units:
                           1         2         3
    Eigenvalues --      2.58381   4.13508   6.71889
          X             1.00000   0.00000   0.00000
          Y             0.00000   0.00000   1.00000
          Z             0.00000   1.00000   0.00000
   Rotational Symmetry Number is   2
   The Molecule is an Asymmetric Top
   Translational Enthalpy:        0.889 kcal/mol
   Rotational Enthalpy:           0.889 kcal/mol
   Vibrational Enthalpy:         15.303 kcal/mol
   gas constant (RT):             0.593 kcal/mol
   Translational Entropy:        34.609  cal/mol.K
   Rotational Entropy:           10.672  cal/mol.K
   Vibrational Entropy:           0.001  cal/mol.K

   Total Enthalpy:               17.673 kcal/mol
   Total Entropy:                45.281  cal/mol.K
Archival summary:
1\1\cicero.chemistry.gatech.edu\FREQ\HF\STO−3G\O1H2\sherrill\15Dec2000\0\\#,FREQ
,HF,STO−3G,\\Water\\0,1\O\H,1,0.989276\H,1,0.989276,2,100.02\\HF=−74.9659011\\@

        *************************************************************
        *                                                           *
        *  Thank you very much for using Q−Chem.  Have a nice day.  *
        *                                                           *
        *************************************************************

 Total job wall time:  3.00 s
***************************************************************

Q−Chem finished
cicero.chemistry.gatech.edu on Fri Dec 15 14:51:32 EST 2000.

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```

We Don't Compute ΔH_f Directly

- The enthalpies we compute are *absolute* enthalpies, **not** heats of formation ΔH_f
- In quantum chemistry, enthalpies H are relative to infinitely separated electrons and nuclei
- ΔH_f is relative to the elements in their standard states (e.g., graphite for carbon atom)
- This distinction doesn't matter if we just need *differences* in enthalpies:

$$\begin{aligned}\Delta H_{rxn} &= \Delta H_f(\text{product}) - \Delta H_f(\text{reactant}) \\ &= H(\text{product}) - H(\text{reactant})\end{aligned}$$

A Common Mistake...

- The difference between E_e and H can be significant (up to many kcal/mol), even at 0K, and even more at higher temperatures
- This difference largely cancels out in many reactions, but not always; the difference can easily be several tenths to a few kcal/mol
- For high accuracy, it is not acceptable to ignore the difference between enthalpy and bare electronic energies