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

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

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

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

Issues with Standard Approach

- If a vibrational mode is very anharmonic and/or low-frequency, the harmonic oscillabor approximation for the partition function may not be appropriate
- For van der Waals complexes, there can be several very low-frequency modes. These will dominate the vibrational entropy, and may cause large errors. Grimme [*Chem. Eur. J.* **18**, 9955 (2012)] proposed using a smooth scaling between the harmonic oscillator treatment and a rotational treatment for these modes.
- See also Barone and co-workers [*J. Chem. Theory Comput.* **12**, 1011 (2016)]

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.
- For most programs, info for $H^{298\mathrm{K}}$, $S^{298\mathrm{K}}$, and $G^{298\mathrm{K}}$ is printed out by default for any second derivative calculation
- *WARNING: When most programs print 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.

Example for H_2O HF/6-31G*

```
Entropy, S
  Electronic S       0.000 [cal/(mol K)] (multiplicity = 1)
  Translational S   34.608 [cal/(mol K)] (mol. weight = 18.0106 [u], P = 101325.00 [Pa])
  Rotational S      10.376 [cal/(mol K)] (symmetry no. = 2)
  Vibrational S      0.003 [cal/(mol K)]
Total S             44.987 [cal/(mol K)]
Correction S         0.000 [cal/(mol K)]
```

Example for H_2O HF/6-31G*

```
Enthalpy, H_trans = E_trans + k_B * T
  Electronic H       0.000 [kcal/mol]   0.000 [kJ/mol]  0.00000000 [Eh]
  Translational H    1.481 [kcal/mol]   6.197 [kJ/mol]  0.00236046 [Eh]
  Rotational H       0.889 [kcal/mol]   3.718 [kJ/mol]  0.00141628 [Eh]
  Vibrational H     14.419 [kcal/mol]  60.329 [kJ/mol]  0.02297799 [Eh]
Correction H        16.789 [kcal/mol]  70.245 [kJ/mol]  0.02675473 [Eh]
Total H, Enthalpy at  298.15 [K]                      -75.98396593 [Eh]

Gibbs free energy, G = H - T * S
  Electronic G       0.000 [kcal/mol]   0.000 [kJ/mol]  0.00000000 [Eh]
  Translational G   -8.837 [kcal/mol] -36.975 [kJ/mol] -0.01408304 [Eh]
  Rotational G      -2.205 [kcal/mol]  -9.225 [kJ/mol] -0.00351356 [Eh]
  Vibrational G     14.418 [kcal/mol]  60.325 [kJ/mol]  0.02297662 [Eh]
Correction G         3.376 [kcal/mol]  14.125 [kJ/mol]  0.00538001 [Eh]
Total G, Free enthalpy at  298.15 [K]                 -76.00534064 [Eh]
```

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:

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

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