

2.3 Rotations

The rotational partition function and associated thermodynamic quantities for linear species are given in Equations (1) and (2). The rotational partition function for a single atom is equal to one, $Q_{e,r} = 1$, hence its contribution to the thermodynamic quantities is zero.

$$Q_{e,r} = \frac{8\pi^2 I k_B T}{\sigma_{ext} h^2} \quad (1)$$

$$\begin{aligned} S &= k_b \left[\ln(Q_{e,r}) + 1 \right] \\ c_p &= k_b \\ \Delta H &= k_b T \end{aligned} \quad (2)$$

2.3 Computing Harmonic Oscillator Potential Coefficients

The coefficients $A_{m,i}$ and $B_{m,i}$ are solved using the method of least squares. The system of equations that is solved is expressed in Equation (3). The first N lines correspond to the user-supplied hindered rotor potential, V_i , as a function of the value of the dihedral angle, $\phi_{i,j}$. The last line sets the derivative of the potential equal to zero at a dihedral angle of 0° .

$$\begin{array}{c} V(\phi_{i,0}) \\ \vdots \\ V(\phi_{i,N}) \\ 0 \end{array} = \begin{bmatrix} 1 & \cos(\phi_{i,0}) & \cdots & \cos(5\phi_{i,0}) & \sin(\phi_{i,0}) & \cdots & \sin(5\phi_{i,0}) \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 1 & \cos(\phi_{i,N}) & \cdots & \cos(5\phi_{i,N}) & \sin(\phi_{i,N}) & \cdots & \sin(5\phi_{i,N}) \\ 0 & 0 & \cdots & 0 & 1 & \cdots & 5 \end{bmatrix} \quad (3)$$

2.5 Tunneling Corrections

The Cantherm software offers three options for tunneling corrections: Wigner, symmetric Eckart, and asymmetric Eckart. The Wigner and symmetric Eckart options only require the user to enter the species information for the reactants and the transition state; the asymmetric Eckart option also requires the species information for the products.

The form of the Wigner tunneling correction¹ is shown in Equation (4), where ν_{TS} is the imaginary frequency of the transition state in cm^{-1} , k_b is the Boltzmann constant, h is the Planck constant, and T is the absolute temperature.

$$\kappa(T) = 1 + \frac{1}{24} \left(\frac{h |\nu_{TS}|}{k_b T} \right)^2 = 1 + \frac{1}{24} \left(\frac{1.44 |\nu_{TS}|}{T} \right)^2 \quad (4)$$

¹ J.O. Hirschfelder and E. Wigner, "Some Quantum-Mechanical Considerations in the Theory of Reactions Involving an Activation Energy", J. Chem. Phys. (1939) **7** 616-628

The form of the Eckart tunneling correction^{2,3} is shown in Equation (5), where ΔV_I is the difference in thermal energy between the transition state and the reactants and $\kappa(E)$ is defined in Equation (6).

$$\kappa(T) = e^{\Delta V_I / k_b T} \int_0^\infty e^{-E / k_b T} \kappa(E) d(E / k_b T) \quad (5)$$

$$\kappa(E) = 1 - \frac{\cosh(2\pi a - 2\pi b) + \cosh(2\pi d)}{\cosh(2\pi a + 2\pi b) + \cosh(2\pi d)} \quad (6)$$

The expressions $2\pi a$, $2\pi b$, and $2\pi d$ are defined in Equations (7)-(9). The expression for $2\pi b$ as presented by Johnston and Heicklen has been corrected, as suggested by Garrett and Truhlar⁴. The dimensionless parameter α_1 is defined in Equation (10); the definition of α_2 is similar with ΔV_2 , the difference in thermal energy between the transition state and the products, replacing ΔV_I . ξ is the dimensionless energy, normalized by ΔV_I .

$$2\pi a = \frac{2\sqrt{\alpha_1 \xi}}{1/\sqrt{\alpha_1} + 1/\sqrt{\alpha_2}} \quad (7)$$

$$2\pi b = \frac{2\sqrt{[(\xi - 1)\alpha_1 + \alpha_2]}}{1/\sqrt{\alpha_1} + 1/\sqrt{\alpha_2}} \quad (8)$$

$$2\pi d = 2\sqrt{|\alpha_1 \alpha_2 - 4\pi^2 / 16|} \quad (9)$$

$$\alpha_1 = 2\pi(\Delta V_I) / h\nu_{TS} \quad (10)$$

The integral in Equation (5) is evaluated numerically using the Clenshaw-Curtis method; this was performed in python, using the `integrate.quad()` module in the SciPy library. If each of the $2\pi a$, $2\pi b$, and $2\pi d$ variables is less than 200, the $\kappa(E)$ expression is evaluated as written in Equation (6). If not, each of the `cosh()` arguments is evaluated. If none of the arguments are greater than ten, the $\kappa(E)$ expression presented in Equation (11) is evaluated.

$$\kappa(E) = 1 - \frac{e^{2\pi a - 2\pi b - 2\pi d} + e^{-2\pi a + 2\pi b - 2\pi d} + 1 + e^{-2*2\pi d}}{e^{2\pi a + 2\pi b - 2\pi d} + e^{-2\pi a - 2\pi b - 2\pi d} + 1 + e^{-2*2\pi d}} \quad (11)$$

This expression is obtained by expressing `cosh()` in terms of exponentials and then multiplying the numerator and denominator by $\exp(-2\pi d)$. If at least one of the `cosh()` arguments is greater than ten, then the $\kappa(E)$ expression presented in Equation (12) is evaluated instead.

$$\kappa(E) = 1 - e^{-2*2\pi a} - e^{-2*2\pi b} - e^{-2\pi a - 2\pi b + 2\pi d} - e^{-2\pi a - 2\pi b - 2\pi d} \quad (12)$$

² C. Eckart, "The penetration of a potential barrier by electrons", Phys. Rev. (1930) **35** 1303-1309

³ H.S. Johnston and J. Heicklen, "Tunneling Corrections for Unsymmetrical Eckart Potential Energy Barriers", J. Phys. Chem. (1962) **66** 532-533

⁴ B.C. Garrett and D.G. Truhlar, "Semiclassical Tunneling Calculations", J. Phys. Chem. (1979) **83** 2921-2926

This expression is obtained by assuming all terms in the denominator of Equation (11) are negligible except for the $\exp(2\pi a + 2\pi b - 2\pi d)$ term. Dividing this remaining term into each term in the numerator yields the equation presented.

The limits of numeric integration are determined by evaluating the integrand from zero to one-thousand, in ten-thousand increments. The maximum of the integrand is computed and the $(E/k_bT)_{\min}$ and $(E/k_bT)_{\max}$ are the smallest and largest (E/k_bT) values whose integrand is at least $1/1000^{\text{th}}$ the maximum. These are the values passed to the `integrate.quad()` module to compute the tunneling correction.

The Eckart tunneling correction function has been tested against the results presented by Johnston and Heicklen. This function replicates the results presented in Table I, with the following exceptions:

- $\alpha_1 = 0.5$; $\alpha_2 = 0.5, 1, 2, 4$; $u^* = 2, 3, 4, 5, 6, 8, 10, 12, 16$
- $\alpha_1 = 1$; $\alpha_2 = 1, 2$; $u^* = 2, 3, 4, 5, 6, 8, 10, 12, 16$

$u^* = h\nu_{TS}/k_bT$; the definitions of α_1 and α_2 are the same as before. The function was adapted to numerically integrate using the trapezoidal rule and Simpson's rule, and the same results as using the Clenshaw-Curtis method were obtained. For debugging purposes, the function was modified from using element-by-element division to using matrix division; many of the aforementioned discrepancies were now replicated. In the case of the noted discrepancies, we believe the correct numbers to be those presented in Table 1.

Table 1: Computed Eckart tunneling corrections as a function of α_1 (left-most column), α_2 (second column from left), and u^* (top row). The definitions of α_1 , α_2 and u^* are in the text. The values presented differ from those presented by Johnston and Heicklen; see text for discussion.

α_1	α_2	2	3	4	5	6	8	10	12	16
0.5	0.5	0.338	0.259	0.214	0.186	0.168	0.147	0.137	0.133	0.135
	1	0.490	0.408	0.359	0.328	0.308	0.287	0.282	0.286	0.315
	2	0.700	0.644	0.611	0.593	0.584	0.587	0.608	0.645	0.755
	4	0.954	0.963	0.983	1.011	1.046	1.135	1.247	1.382	1.731
1	1	0.743	0.703	0.688	0.689	0.705	0.767	0.870	1.016	1.469
	2	1.085	1.167	1.271	1.398	1.548	1.929	2.443	3.130	5.263

3. Input File

For each molecule specified in the input file, the following fields must be present:

- Structure: A molecule can be specified as either **NONLINEAR**, **LINEAR**, or **ATOM**. This field is necessary in order to apply the appropriate rotational partition function
- Geometry: The geometry of the molecule must be specified. One way to do so is to pass the location of the Gaussian output file, *e.g.*

GEOM File Gaussian-geometry.log,

to Cantherm. The second is to copy and paste the geometry from the .log file. Search for "Input orientation" in the .log file and copy and paste the geometry information into the input file. An example geometry, for water, is shown below. The number on the line immediately after the GEOM keyword specifies how many atoms are present in the molecule.

```
GEOM
3
1      8      0    -0.021483  0.000000  -0.015182
2      1      0     0.026269  0.000000   0.945620
3      1      0     0.900149  0.000000  -0.290892
```

- Force constant matrix: The force constant matrix must also be specified. The location of the Gaussian output file that contains the force constant matrix in Cartesian coordinates, *e.g.*

FORCEC File Gaussian-frequency.log

or the frequencies in wavenumber (cm^{-1}), *e.g.* the three frequencies for water,

```
FREQ
3
1638.4678      3809.9312
3906.9015
```

may be passed to Cantherm. If specifying the frequencies, the first line immediately following the FREQ keyword specifies the number of frequencies. Note: When running a frequency job in Gaussian, the keyword `iop(7/33=1)` must be supplied to ensure the force constant matrix in Cartesian coordinates is stored in the .log file.

- Energy: The 0K energy, and the level of theory at which this energy was calculated, must be specified. The 0K energy is read in from a Gaussian output file, *e.g.*

ENERGY File Gaussian-geom.log CBS-QB3

or specified manually, *e.g.*

ENERGY -76.337491 CBS-QB3

The only levels of theory currently recognized by Cantherm are CBS-QB3 and G3.

- External symmetry: The external symmetry of the molecule must be specified, *i.e.* EXTSYM 2
- Electronic spin multiplicity: The electronic spin multiplicity of the molecule must be specified, *i.e.* NELEC 1
- Hindered Rotors: The number of hindered rotors must be specified. One way to supply Cantherm with all necessary information is as follows: ROTORS 1 listOfPivotAtoms.txt, in which the .txt file contains the following:

L1: 1 2 3

L2: 3 1 2 3 4 5

In the example above, the hindered rotor information is contained in the second line. The first number is the symmetry of the hindered rotor potential. The next two numbers correspond to the two pivot atoms, atom1 and atom2. The identity of these atoms can be determined by viewing a molecule in Gaussian, right-clicking, and then selecting “Labels”. The remaining numbers, after atom2, correspond to the atom IDs which should be associated with the pivot atom atom2’s segment of the molecule. These IDs are important when computing the moment of inertia $I^{(2,3)}$.

The next line in the input file deals with the hindered rotor potentials:

POTENTIAL separable file hinderedrotor-1.txt; *POTENTIAL* is a keyword for the input file, *separable* assumes all of the hindered rotors are uncoupled, *file* informs Cantherm to look for the potential in the file named *hinderedrotor-1.txt*. The .txt file can be generated from Gaussian; after opening the results of a SCAN job, select “Results” → “Scan”. In the graph that pops up, right-click and select “Save Data...”

- Bond additivity corrections: The number of particular bonds may be specified by the user; the order is: C-H, C-C, C=C, C≡C, O-H, C-O, and C=O

4. Example Files

Two example files are provided. The first calculates the reaction rate expression for the dehydration reaction: s-Butanol = 1-Butene + H₂O, using an asymmetric Eckart tunneling correction. The second calculates the thermochemistry of s-Butanol.