Solving the 1D Schrodinger Equation for a Hindered Rotor

Start with the one-dimensional, time-independent Schrodinger equation:

$$-\frac{h^2}{8\pi^2 I_j}\frac{d^2\Psi(\phi)}{d\phi^2}+V_j(\phi)\Psi(\phi)=E\Psi(\phi)$$

In the equation, h is the Planck constant, I_j is the reduced moment of inertia of the j^{th} hindered rotor, V_j is the potential energy scan of the j^{th} hindered rotor, ϕ is the dihedral angle and Ψ is the wavefunction.

We solve the Schrodinger equation by assuming the wavefunction takes the form:

$$\Psi(\phi)=\sum_{m'=-m}^{m} c_{m'}\frac{e^{im'\phi}}{\sqrt{2\pi}}$$

$c_{m'}$ are constant coefficients multiplying the basis functions, i is the imaginary number where $i^2 = -1$, and m' spans from $-m$ to m. The value of m implemented in CanTherm is 200. The second derivative of the wavefunction with respect to the dihedral angle is:

$$\frac{d^2\Psi}{d\phi^2}=\sum_{m'=-m}^{m}-(m')^2 c_{m'}\frac{e^{im'\phi}}{\sqrt{2\pi}}$$

We solve the eigenvalue problem by multiplying the Schrodinger equation by $e^{-in\phi}/\sqrt{2\pi}$ and integrating over ϕ from 0 to 2π:

$$\int_0^{2\pi}\left\{-\frac{h^2}{8\pi^2 I_j}\left[\sum_{m'=-m}^{m}-(m')^2 c_{m'}\frac{e^{i(m'-n)\phi}}{2\pi}\right]+V_j(\phi)\left[\sum_{m'=-m}^{m}c_{m'}\frac{e^{i(m'-n)\phi}}{2\pi}\right]\right\}d\phi=$$

$$\int_0^{2\pi}E\left[\sum_{m'=-m}^{m}c_{m'}\frac{e^{i(m'-n)\phi}}{2\pi}\right]d\phi$$

In CanTherm, the potential $V(\phi)$ is fit to a Fourier series:

$$V(\phi)=A+\sum_{k=1}^{5}a_k\cos(k\phi)+b_k\sin(k\phi)$$

Expressing sine and cosine in terms of our basis functions:

$$\cos(k\phi)=\frac{1}{2}\left(e^{ik\phi}+e^{-ik\phi}\right)$$

$$\sin(k\phi)=\frac{1}{2i}\left(e^{ik\phi}-e^{-ik\phi}\right)$$

The potential takes on the form:

$$V(\phi)=A+\sum_{k=1}^{5}\frac{a_k}{2}\left(e^{ik\phi}+e^{-ik\phi}\right)+\frac{b_k}{2i}\left(e^{ik\phi}-e^{-ik\phi}\right)=A+\frac{1}{2}\sum_{k=1}^{5}(a_k-ib_k)e^{ik\phi}+(a_k+ib_k)e^{-ik\phi}$$

Since our basis functions are orthonormal

$$\int_0^{2\pi} \frac{e^{-in\phi}}{\sqrt{2\pi}} \frac{e^{im\phi}}{\sqrt{2\pi}} d\phi = \delta_{n,m} \;\; where \;\; \delta_{n,m} = \begin{cases} 1 & if \;\; n = m \\ 0 & if \;\; n \neq m \end{cases}$$

We can easily express the first (kinetic energy) term of the Schrodinger equation as:

$$\int_0^{2\pi} \left\{ -\frac{h^2}{8\pi^2 I_j} \left[\sum_{m'=-m}^{m} -(m')^2 c_{m'} \frac{e^{i(m'-n)\phi}}{2\pi} \right] \right\} d\phi = \frac{h^2}{8\pi^2 I_j} \sum_{m'=-m}^{m} (m')^2 c_{m'} \delta_{n,m'}$$

In matrix form, where the first row corresponds to *n=-m'* and the last to *n=m'*:

$$\begin{bmatrix} \frac{h^2(-m)^2}{8\pi^2 I_j} & 0 & \cdots & 0 \\ 0 & \frac{h^2(-m+1)^2}{8\pi^2 I_j} & \ddots & 0 \\ \vdots & \ddots & \ddots & \vdots \\ 0 & 0 & \cdots & \frac{h^2(m)^2}{8\pi^2 I_j} \end{bmatrix} \begin{bmatrix} c_{-m'} \\ \vdots \\ c_0 \\ \vdots \\ c_{m'} \end{bmatrix}$$

The second (potential energy) term is handled using the following relationship:

$$\int_0^{2\pi} e^{ik\phi} \frac{e^{-in\phi}}{\sqrt{2\pi}} \frac{e^{im\phi}}{\sqrt{2\pi}} d\phi = \delta_{k,n-m} \;\; where \;\; \delta_{k,n-m} = \begin{cases} 1 & if \;\; k = n-m \\ 0 & if \;\; k \neq n-m \end{cases}$$

The integrand of the potential term becomes:

$$\left[A + \frac{1}{2} \sum_{k=1}^{5} (a_k - ib_k) e^{ik\phi} + (a_k + ib_k) e^{-ik\phi} \right] \left[\sum_{m'=-m}^{m} c_{m'} \frac{e^{i(m'-n)\phi}}{2\pi} \right] =$$

$$A \sum_{m'=-m}^{m} c_{m'} \frac{e^{i(m'-n)\phi}}{2\pi} + \frac{1}{2} \sum_{k=1}^{5} (a_k - ib_k) \sum_{m'=-m}^{m} c_{m'} \frac{e^{i(m'-n+k)\phi}}{2\pi} + \frac{1}{2} \sum_{k=1}^{5} (a_k + ib_k) \sum_{m'=-m}^{m} c_{m'} \frac{e^{i(m'-n-k)\phi}}{2\pi}$$

Integrating over the dihedral angle from 0 to 2π:

$$\int_0^{2\pi} \left\{ A \sum_{m'=-m}^{m} c_{m'} \frac{e^{i(m'-n)\phi}}{2\pi} + \frac{1}{2} \sum_{k=1}^{5} (a_k - ib_k) \sum_{m'=-m}^{m} c_{m'} \frac{e^{i(m'-n+k)\phi}}{2\pi} + \frac{1}{2} \sum_{k=1}^{5} (a_k + ib_k) \sum_{m'=-m}^{m} c_{m'} \frac{e^{i(m'-n-k)\phi}}{2\pi} \right\} d\phi =$$

$$A \sum_{m'=-m}^{m} c_{m'} \delta_{n,m'} + \frac{1}{2} \sum_{k=1}^{5} (a_k - ib_k) \sum_{m'=-m}^{m} c_{m'} \delta_{k,n-m'} + \frac{1}{2} \sum_{k=1}^{5} (a_k + ib_k) \sum_{m'=-m}^{m} c_{m'} \delta_{k,m'-n} =$$

$$\sum_{m'=-m}^{m} \left[A c_{m'} \delta_{n,m'} + \frac{1}{2} \sum_{k=1}^{5} \left((a_k - ib_k) c_{m'} \delta_{k,n-m'} + (a_k + ib_k) c_{m'} \delta_{k,m'-n} \right) \right]$$

The first term, in matrix form, looks similar to the kinetic energy contribution: The "A" term is along the diagonal, with all off-diagonal terms equal to zero. The second term populates the five immediate off-diagonal terms below the diagonal, while the third term populates the five immediate off-diagonal terms above the diagonal:

$$\frac{1}{2}\begin{bmatrix} 0 & \cdots & 0 & a_5 - ib_5 & \cdots & a_1 - ib_1 & 2A & a_1 + ib_1 & \cdots & a_5 + ib_5 & 0 & \cdots & 0 \end{bmatrix}\begin{bmatrix} c_{-m'} \\ \vdots \\ c_0 \\ \vdots \\ c_{m'} \end{bmatrix}$$

Summing the kinetic and potential energy terms results in the matrix of interest, *i.e.* the matrix whose eigenvalues correspond to the energy levels of the system. Each row in the matrix follows this pattern, where n varies from $-m$ to m:

$$\frac{1}{2}\left[0 \quad \cdots \quad 0 \quad a_5 - ib_5 \quad \cdots \quad a_1 - ib_1 \quad 2A + \frac{h^2(n)^2}{4\pi^2 I_j} \quad a_1 + ib_1 \quad \cdots \quad a_5 + ib_5 \quad 0 \quad \cdots \quad 0 \right]$$

The eigenvalues of this (2m+1) x (2m+1) matrix are computed and substituted into the partition function for a hindered rotor, where E_l is the l^{th} eigenvalue:

$$q = \sum_{l=1}^{2m+1} e^{-E_l / k_b T}$$

The partition funciton's contributions to the thermodynamic quantities are:

$$H(T) - H(0) = \frac{\sum_l E_l e^{-E_l / k_b T}}{\sum_l e^{-E_l / k_b T}}$$

$$S = k_b \ln\left(\frac{1}{\sigma_{rotor}} \sum_l e^{-E_l / k_b T} \right) + \frac{\sum_l E_l e^{-E_l / k_b T}}{T \sum_l e^{-E_l / k_b T}}$$

$$c_P = \frac{\left(\sum_l E_l^2 e^{-E_l / k_b T} \right)\left(\sum_l e^{-E_l / k_b T} \right) - \left(\sum_l E_l e^{-E_l / k_b T} \right)^2}{k_b T^2 \left(\sum_l e^{-E_l / k_b T} \right)^2}$$

k_b is the Boltzmann constant, T is the absolute temperature, and σ_{rotor} is the symmetry number of the hindered rotor.

Free Rotor Partition Function

When the barrier to rotation is << $k_b T$, a more accurate approximation of the vibrational mode is a free rotor. The partition function for a free rotor is:

$$q_{free} = \frac{\sqrt{8\pi^3 I_j k_b T}}{\sigma_{rotor} h}$$

The free rotor's contributions to the thermodynamic quantities are:

$$H(T) - H(0) = \frac{1}{2} k_b T$$

$$S = R \ln\left(\frac{e^{0.5}\sqrt{8\pi^3 I_j k_b T}}{\sigma_{rotor} h} \right)$$

$$c_p = \frac{1}{2} k_b$$

(Coming soon in CanTherm): For every hindered rotor specified by the user, and for each temperature listed in the input file, CanTherm automatically determines whether the rotor should be treated as hindered or free; the rotor is treated as free rotation if $k_b T$ is greater than X times the largest barrier height (X to be determined).