1-D RIGID ROTOR CALCULATOR

A utility in DAVE under the HINDERED ROTOR CALCULATOR menu item called METHYL ROTOR allows the user to calculate the eigenvalues and transitions for a rigid rotor undergoing 1-dimensional rotation. This program solves the single degree-of-freedom Schrödinger equation with an m-fold symmetric hindering potential as specified by the user. Originally written for methyl rotations in which m=3, this program was later generalized for arbitrary m. Now the calculations are performed for the following Hamiltonian using the free-rotor basis functions:

$$H = -\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\phi^2} + V(\phi), \qquad\qquad (1.1)$$

where $V(\phi) = \frac{V_m}{2}(1 - \cos m\phi) + \frac{V_n}{2}(1 - \cos(n\phi + \alpha))$. Details of the numerical calculation can be found in the Appendix.

1.1   Getting started

First, launch DAVE and select the Tools→General Tools→Hindered rotor calculators→Methyl rotor. You should see a screen like the one shown in figure 1.
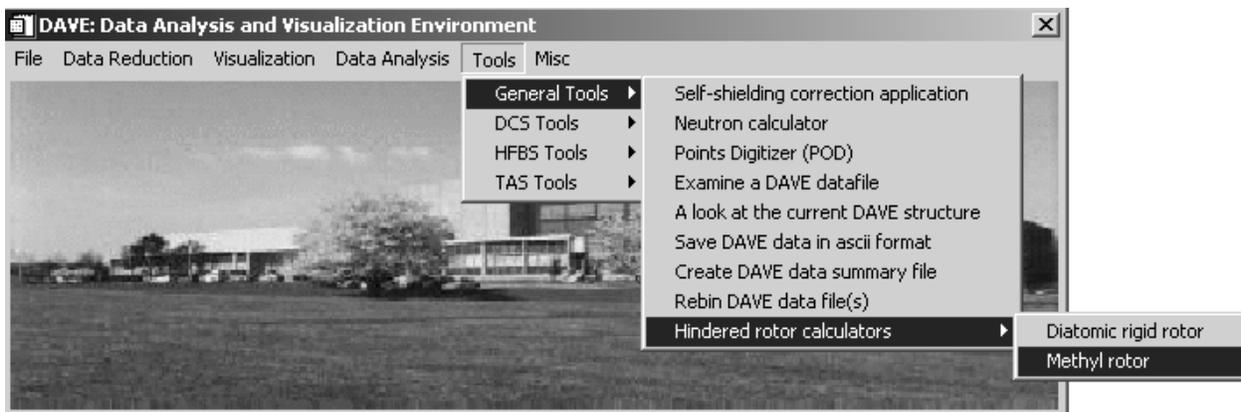

Figure 1   Opening screen of DAVE showing location of methyl rotation calculator.

Launch the program. You will see the application's main screen as shown in figure 2.

1.2   Using METHYL ROTOR

When initially launched you will see one tab of three application screens. You can navigate around these by pressing one of the three buttons at the top of the screen. You can tell which application component you are in by which button is de-sensitized. This first tab is labeled *input parameters* and all physical quantities relevant to the calculation are entered here. The calculation is also invoked here. In this screen you can enter the rotational constant (in meV), the symmetry of the hindering potential, the upper limit on the barrier height, the size of the Hamiltonian matrix, and the number of barrier values between 0 and the upper limit specified above to include in the calculation.
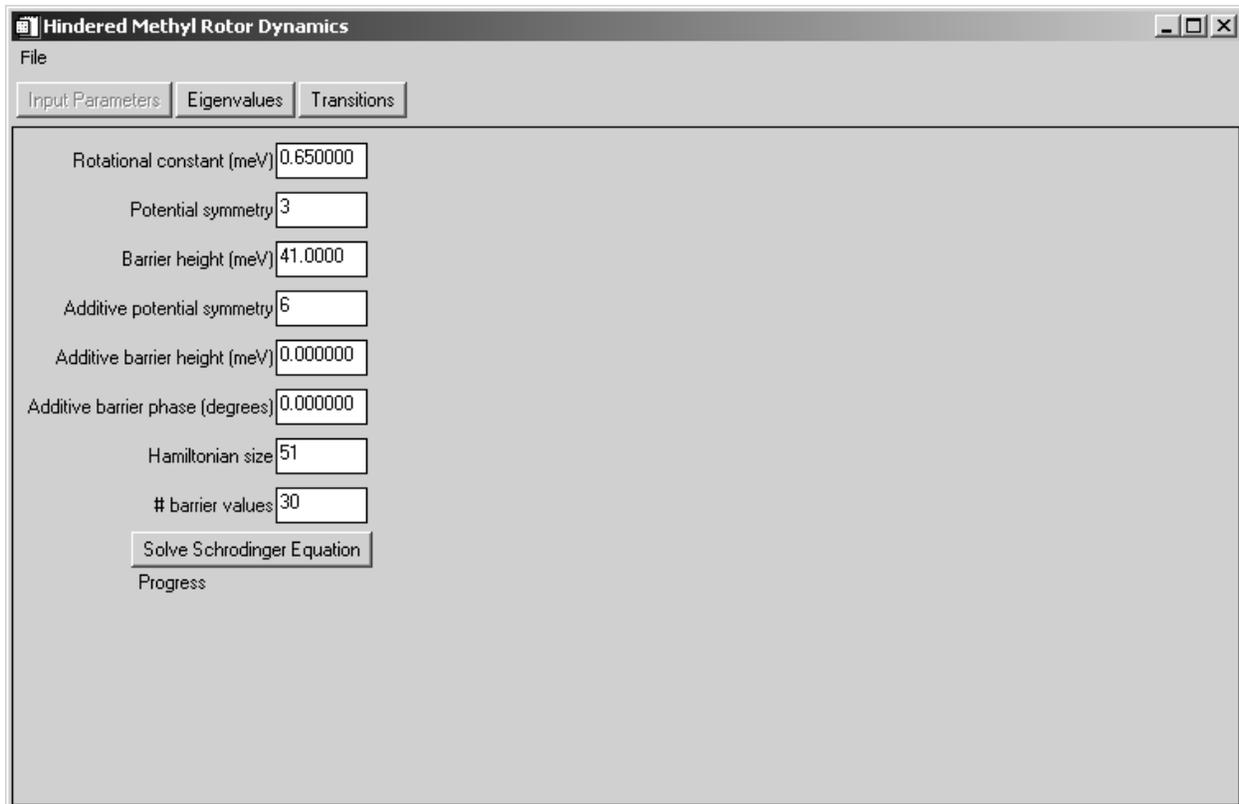

Figure 2 Screen shot of input parameters screen for the hindered rotor applicaton.

When you have entered the relevant input parameters, you can press the button labeled *Solve Schrodinger Equation*. The progress of the calculation will appear just below the button. When the progress reads 'Finished' you may proceed to either of the next two screens to view the results.

1.2.1   The Eigenvalues Screen

The eigenvalues are displayed in a window on the Eigenvalues screen as a function of barrier height as shown in figure 3. You can use the mouse to zoom into the data in the standard way (hold left mouse button and drag to zoom, click right mouse to zoom out). As you move the cursor around the screen you will see that the eigenvalues are displayed in a text panel to the right of the plot window. Also, the value in the text field labeled *V3 (meV)* is continuously updated as you move the cursor about the screen. These values are the intercept of the vertical line with the curves. You can obtain the eigenvalues for a particular value of barrier height by typing it in the text field labeled *V3 (meV)* and hitting enter. A vertical line will appear indicating your selection and the values in the text panel to the right of the plot window will show the eigenvalues.
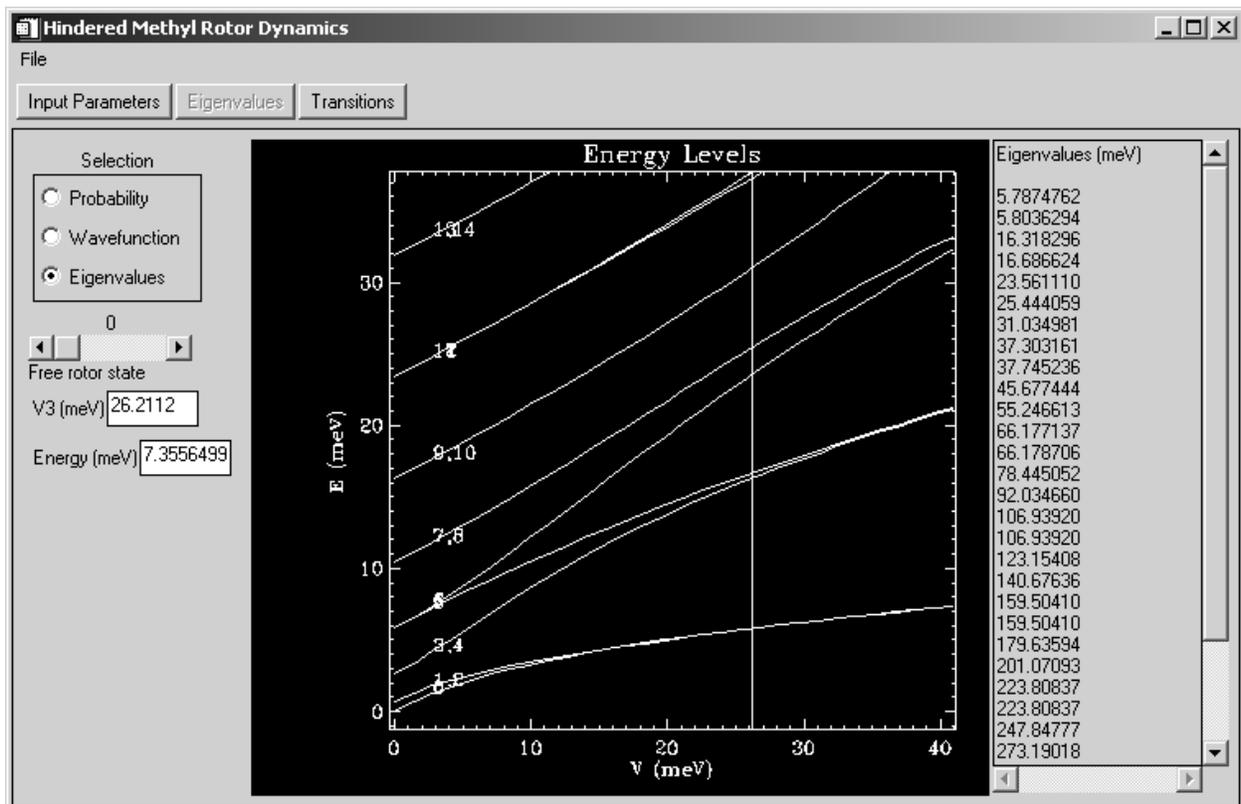

Figure 3 Screen shot of eigenvalues screen for the hindered rotor applicaton.

You can also display the probability density and the wavefunctions by selecting one of the radio buttons labeled *Probability* or *Wavefunction*.   The particular eigenstate displayed depends on the position of the slider labeled *Free rotor state*.

1.2.2   The Transitions Screen

Pressing the button labeled Transitions takes you to the screen that displays the rotational transitions (between the eigenstates) and also displays an animated rendering of the transitions.
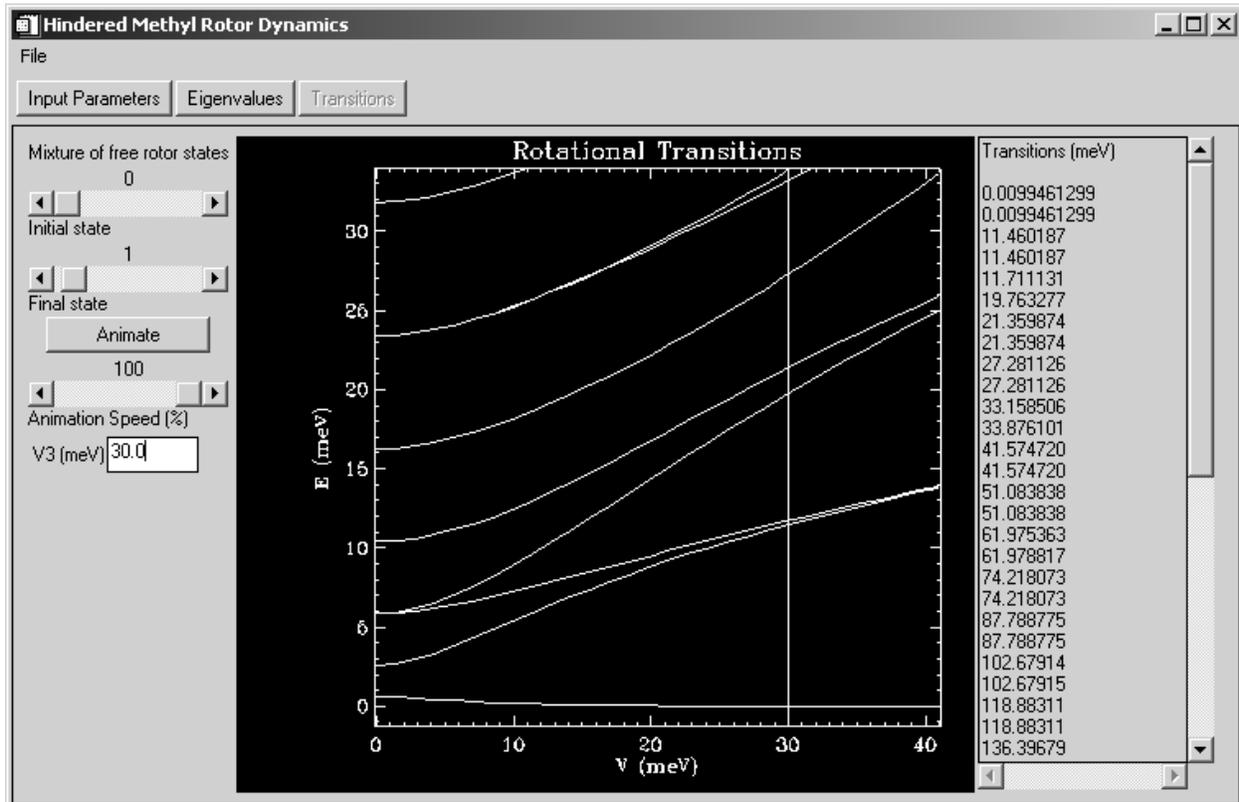

Figure 4 Screen shot of transitions screen for the hindered rotor applicaton.

Initially you will see transitions between the ground state and all higher eigenstates displayed as a function of barrier height. You can change the initial state from the ground state to any higher state using the slider control labeled *Initial state*. You can also type in an exact barrier height value in the text field labeled *V3 (meV)* and hit return. The transitions for this barrier height will appear in the text panel to the right of the display.

Finally, you may press the button labeled Animate to show the time-dependence of the probability for a mixture of the *Initial state* and *Final state*. You may use the slider controls labeled as such to view tunneling and libration, for instance. The animation speed can be controlled with the slider labeled *Animation Speed*.

Appendix A: Matrix Elements of the 1-D Rigid Rotor in a p-Fold Potential

The Hamiltonian for the rigid rotor in a p-fold symmetric potential is given by

$$H = -\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\phi^2} + V(\phi) \tag{A1}$$

where

$$V(\phi) = \frac{V_p}{2}(1 - \cos p\phi) + \frac{V_r}{2}(1 - \cos(r\phi + \alpha)). \tag{A2}$$

The matrix elements can be calculated using the free-rotor basis eigenfunctions

$$\psi_n(\phi) = \frac{1}{\sqrt{2\pi}}\exp(in\phi), \quad n = 0, \pm1, \pm2, \ldots \tag{A3}$$

The Hamiltonian (A1) can be decomposed into two parts, $H_{mn} = H^0_{mn} + V_{mn}$, where the elements H^0_{mn} are related to the zero-potential energy levels as

$$H^0_{mn} = \frac{n^2\hbar^2}{2I}\delta_{mn}, \tag{A4}$$

which can be found via the eigenvalue equation for the free rotor Schrödinger equation

$$-\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\phi^2}\psi_n(\phi) = E_n\psi_n(\phi), \tag{A5}$$

with the eigenfunctions given by (A3) and solving for E_n. The elements of the potential matrix, V_{mn}, are found by calculating the following integral:

$$V_{mn} = \int_0^{2\pi} d\phi\, \psi^*_m(\phi)V(\phi)\psi_n(\phi). \tag{A6}$$

Explicit calculation of (A6) and including the zero-potential energy matrix elements (A4) results in the final expression for the matrix elements of the total Hamiltonian:

$$H_{mn} = \frac{\hbar^2 n^2}{2I}\delta_{mn} + \frac{V_p}{4}\left\{2\delta_{n,m} - \delta_{n-m+p,0} - \delta_{n-m-p,0}\right\}$$
$$+ \frac{V_r}{4}\left\{2\delta_{n,m} - e^{i\alpha}\delta_{n-m+r,0} - e^{-i\alpha}\delta_{n-m-r,0}\right\},$$

(A7)

where $\delta_{n,k}$ is the kronecker delta, $\delta_{n,k} = \begin{cases} 1, & n = k \\ 0, & n \neq k \end{cases}$ and $n, m = 0, \pm 1, \pm 2, \ldots$.