

## DIATOMIC RIGID ROTOR CALCULATOR

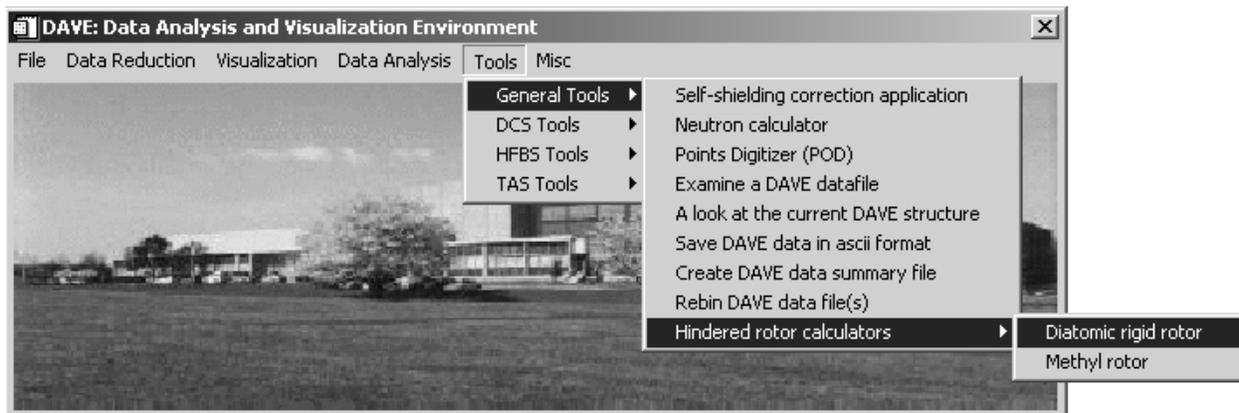
A utility in DAVE under the HINDERED ROTOR CALCULATOR menu item called DIATOMIC RIGID ROTOR allows the user to calculate the eigenvalues and transitions as a function of the hindering barrier height for a diatomic rigid rotor undergoing 2-dimensional rotation. This program solves the single degree-of-freedom Schrödinger equation with a potential that depends on  $\theta$ , the angle that the molecular axis makes with the z-axis. This might correspond to hydrogen adsorbed onto surfaces, for instance. The calculations are performed for the following Hamiltonian using the spherical harmonics, as basis functions:

$$H = \frac{\hat{L}^2}{2I} + \frac{V_2}{2}(1 - \cos 2\theta), \quad (1.1)$$

where  $\hat{L}$  is the angular momentum operator and  $I$  is the moment of inertia. 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→Diatomic rigid rotor. You should see a screen like the one shown in figure 1.

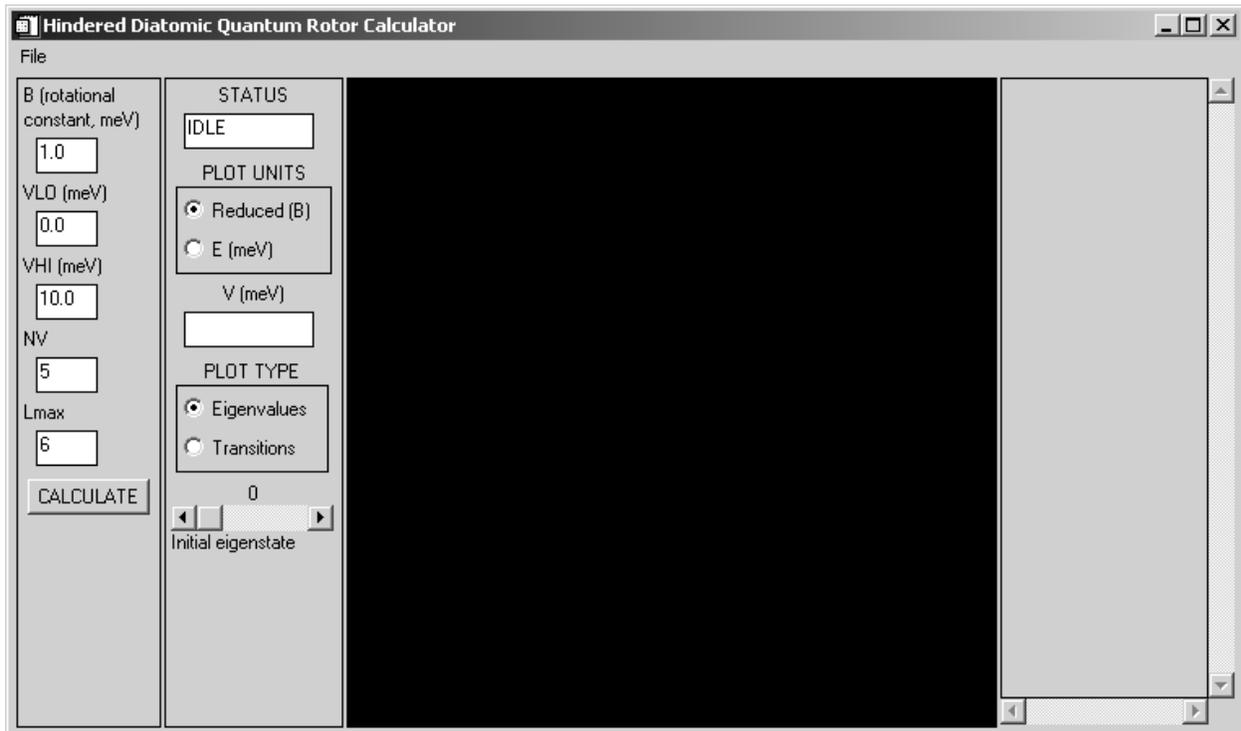


**Figure 1** Opening screen of DAVE showing location of the diatomic rigid rotor calculator.

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

## 1.2 Using DIATOMIC RIGID ROTOR

When initially launched you will see the screen as below where nothing has been calculated yet. There are a number of text fields that you can change for the purposes of your calculation. The rotational constant,  $B$ , is determined by the moment of inertia ( $B = \frac{\hbar^2}{2I}$ ) and is expected to be entered in units of meV. The calculation will proceed over a range of  $VLO$  (meV) to  $VHI$  (meV) on an equally-spaced grid of  $NV$  values. The Hamiltonian is calculated out to a maximum angular momentum quantum number,  $Lmax$ . Note that the larger the value of  $Lmax$ , the longer the calculation will take to complete. To start the calculation, press the button labeled *CALCULATE*. You should see a progress bar appear indicating that the program is performing the computation.



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

After the calculation is complete, you will see the eigenvalues displayed on the screen, as seen in figure 3.

### 1.2.1 The Eigenvalues Display

As an example, figure 3 shows a particular set of input parameters and the result of the calculation. In this case, 25 values of potential barrier between 0 and 30 meV were calculated using a Hamiltonian spanning  $L = 0$  to 5 with a rotational constant of 1 meV. The eigenvalues are shown plotted in reduced units (units of the rotational constant,  $B$ ). As you move the cursor around the plot window, the eigenvalues are listed in the text panel to the right of the plot window. You can type in a precise value of the potential barrier in the text field labeled  $V$  (meV) and hit enter. The resulting eigenvalues will be displayed in the text panel to the right of the plot window.

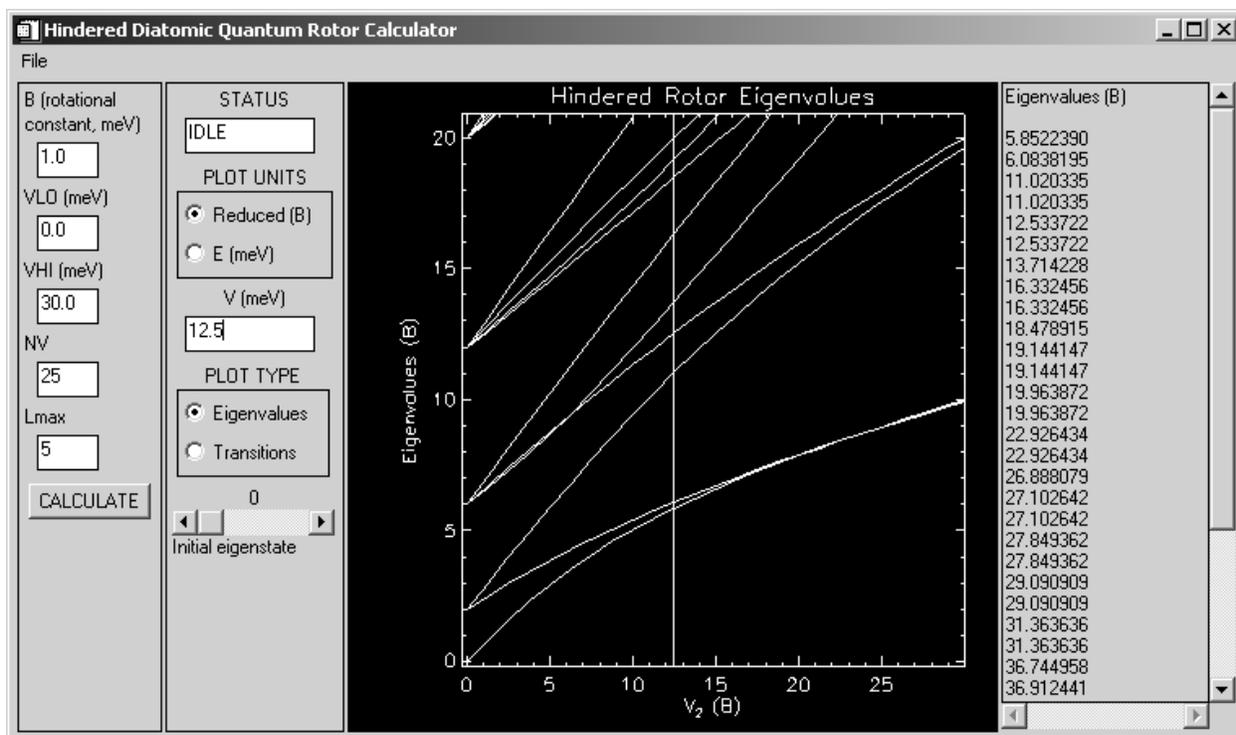
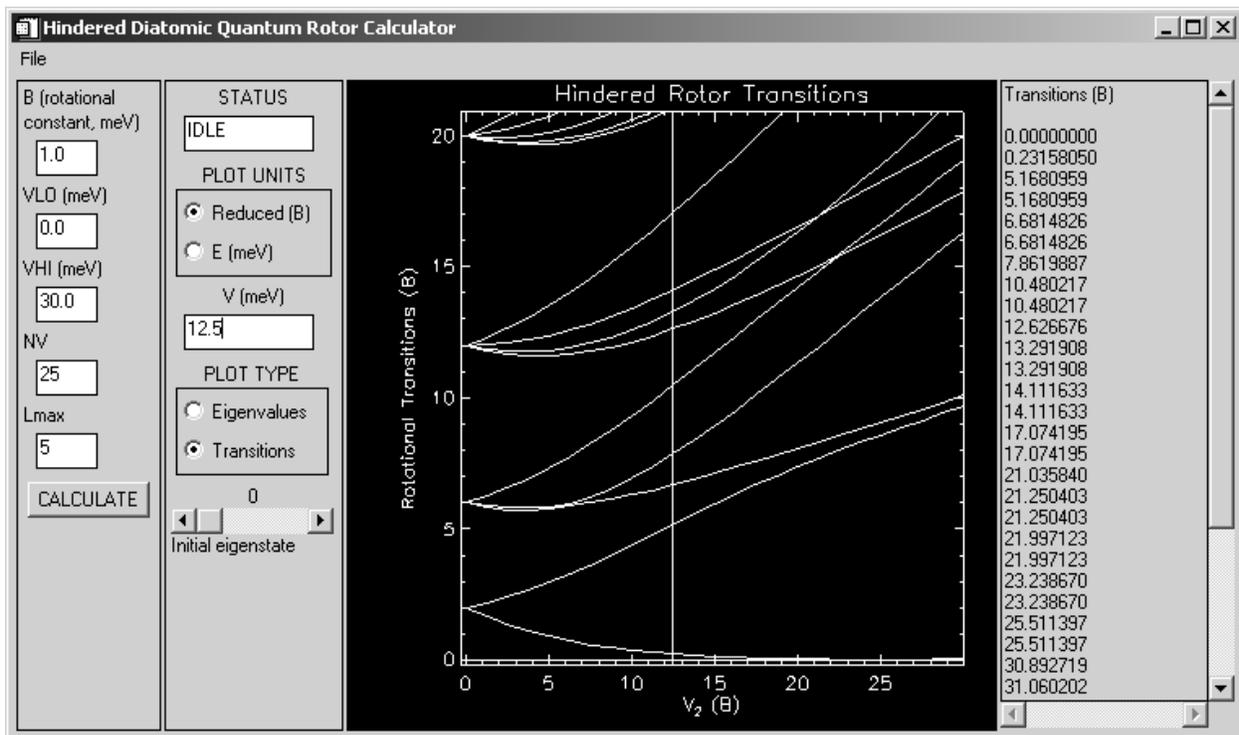


Figure 3 Screen shot of eigenvalues for the hindered rotor applicaton.

Note that the default is to plot the eigenvalues (and also the transitions between eigenstates) in reduced units. You can choose to plot the values in meV by pressing the radio button labeled  $E$ (meV) in the button selection labeled *PLOT UNITS*.

## 1.2.2 The Transitions Display

You can press the radio button labeled *Transitions* in the button selection labeled *PLOT TYPE* to display the transitions between eigenstates as shown in figure 4. These transitions are between the state determined by the slider labeled *Initial eigenstate* and all higher levels. 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 eigenstate*. You can also type in an exact barrier height value in the text field labeled *V (meV)* and hit return. The transitions for this barrier height will appear in the text panel to the right of the display.



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

## Appendix A: Matrix Elements of the Diatomic Rigid Rotor in a 2-Fold Symmetric Potential

This application solves the Schrödinger equation in spherical coordinates for a double-well hindering potential of the form  $V(\theta, \varphi) = \frac{V_2}{2}(1 - \cos 2\theta)$ . The solution is found by diagonalizing the Hamiltonian matrix. The Hamiltonian matrix is found using the spherical harmonics,  $Y_{l,m}(\theta, \varphi)$ , as the basis functions and is shown below.

$$H_{l,m,l',m'} = \left( Bl(l+1) + \frac{2V_2}{3} \right) \delta_{l,l'} \delta_{m,m'} -$$

$$(-1)^{m'} V_2 \left( \frac{16\pi}{45} \right)^{1/2} \left( \frac{5(2l+1)(2l'+1)}{4\pi} \right)^{1/2} \begin{pmatrix} l' & 2 & 1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l' & 2 & 1 \\ -m' & 0 & m \end{pmatrix}$$