Coupled Methyl Rotor Calculator

Summary features of the *Coupled Methyl Rotor Calculator*

Provides numerical solutions to the coupled rotor Hamiltonian:

$$H = -B\left(\frac{\partial^2}{\partial\phi_1^2} + \frac{\partial^2}{\partial\phi_2^2}\right) + \frac{V_{31}}{2}\left(1 - \cos 3\phi_1\right) + \frac{V_{32}}{2}\left(1 - \cos(3\phi_2 + \alpha)\right) - \frac{W_3}{2}\left(1 - \cos(3\phi_1 - 3\phi_2)\right)$$

- Completely user-specified model:
    - *B*: rotational constant (meV)
    - V_{31}: barrier height (meV) for rotor #1
    - V_{32}: barrier height (meV) for rotor #2
    - W_3: coupling strength (meV) between rotor #1 and rotor #2
    - α: phase (degrees) between two rotors
    - *N*: number of indices for each rotor $\rightarrow$ Hamiltonian size = $N^2 \times N^2$
- User can specify the size of the Hamiltonian depending on the desired accuracy in the calculation
- Convenient estimation of the time required to perform a calculation *before* doing the calculation
- Save and restore your results
- Displays the eigenvalues of the Hamiltonian
- Displays the transitions between eigenstates
- Numerical construction of the Hamiltonian has been fully vectorized for optimal calculation speed in IDL

Introduction

A set of relatively simple molecular solids, composed of—among other components—methyl groups, can display quantum rotational dynamics that are made manifest as discrete tunneling and librational peaks in their inelastic neutron scattering spectra. Although many of these systems exhibit motion that can be described in terms of a simple single particle model (SPM) in which the particle is subject to a $\cos 3\phi$ potential that hinders reorientation, other molecular solids exhibit motion that also includes a coupling term between two rotors that depends on the relative orientation of one rotor to the other. In these cases, the dynamics are significantly more complicated and the energy levels found in the simple SPM are further split depending upon the strength of the coupling. This application in DAVE allows the user to calculate the energy levels and the transitions between these states for two methyl rotors subject to a three-fold barrier potential and a cosine-coupling term.

The User Interface

The user interface (UI) for the application is shown in figure 1. The key elements of the UI are annotated with explanations of their significance in operating the program.
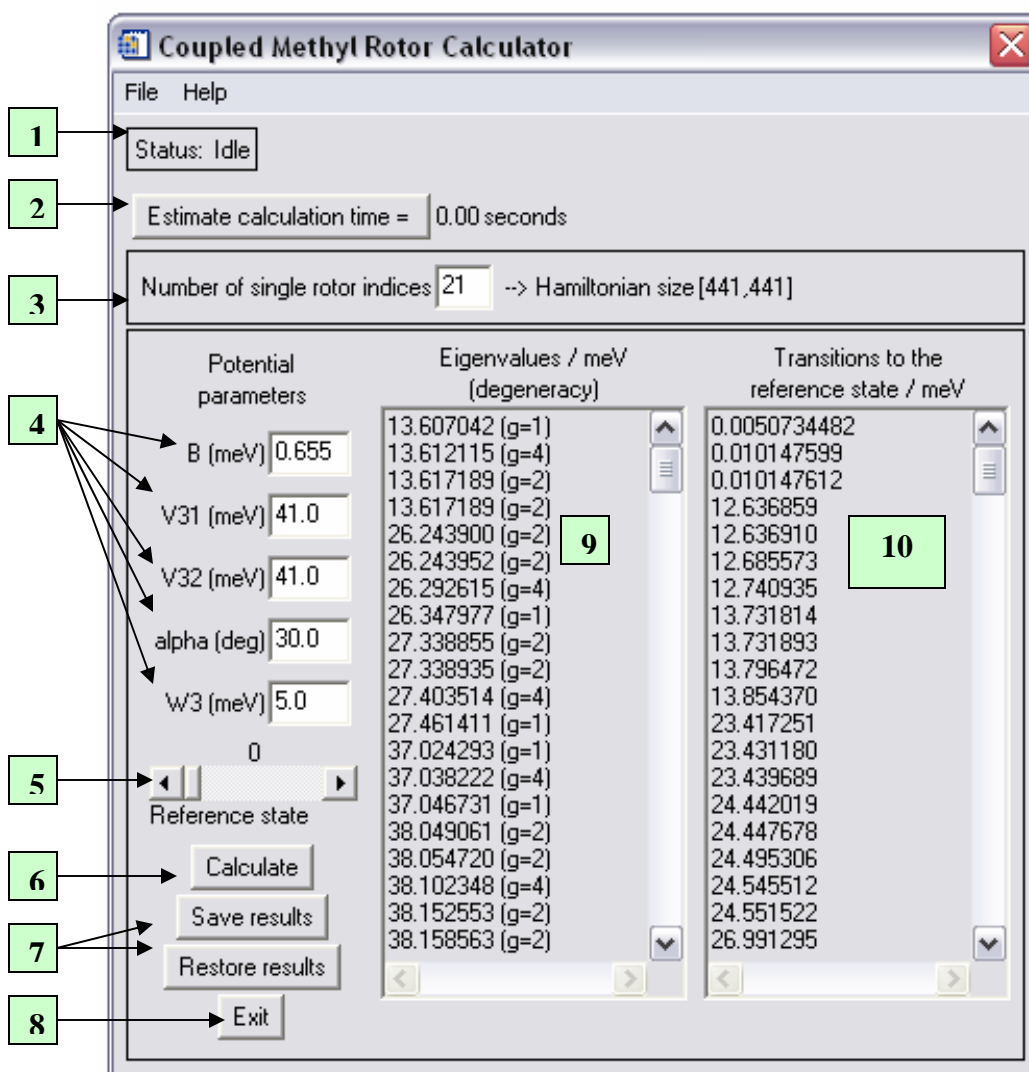
Figure 1 The user interface for the coupled rotor application.

1. *Status line* provides information on the current state of the calculation. For instance, during a calculation, it will display *Constructing the Hamiltonian* followed by *Diagonalizing the Hamiltonian*. When the calculation is complete, the status will be *Idle*.
2. *Estimate calculation time* will, when pressed, provide an estimate in seconds of how long it will take to construct and diagonalize the Hamiltonian. When the program is first launched, the Hamiltonian is constructed and diagonalized for a small number of different (small) sized Hamiltonians. The program determines how long it takes to perform these calculations as a function of N, the Hamiltonian size, and then fits a power-law, saving the fit parameters. This power law is then used at run-time to provide an estimate of the calculation time with the Hamiltonian size as the only input.

3. *Number of single rotor indices* is a user-specified parameter that indicates how many terms to retain in the expansion of the Hamiltonian in the basis set composed of product states of the single rotor basis states. For example, if the user specifies $N=21$ (as in fig. 1) then the Hamiltonian size will be $21^2 \times 21^2$ (441×441). This corresponds to a basis of $\langle \phi_1, \phi_2 | n, m \rangle = \dfrac{1}{2\pi} \exp(in\phi_1) \exp(im\phi_2)$ for $n, m = 0, \pm1, \pm2, \dots \pm10$. When the user presses **ENTER** after typing in a new value for N in this text box, the Hamiltonian size is immediately updated to indicate the new size. Accuracy of the eigenvalues is improved for large values of N. However increasing N also increases the time to perform the calculation.

4. *Potential parameters* are a series of values that the user changes by typing in new values. Note that these parameters have no effect on the calculation time. Note that pressing **ENTER** after typing in the numbers into these fields does not initiate the calculation.

5. *Reference state* slider controls which of the eigenstates is used to calculate the transitions between eigenstates. For instance, in figure 1 the slider is set to state 0. The transitions displayed in 10 are those between the zeroth eigenstate and the first, second, third, etc.

6. *Calculate* allows the user to control when the calculation is performed. Since these calculations can be time-consuming, conscious effort was made to limit execution of the calculation to only a single user event. The calculation consists of constructing the Hamiltonian and diagonalizing it to obtain the eigenvalues.

7. *Save/Restore results* permits the users to save and restore the results of their calculations. Upon restoration of a particular result, the entire UI is updated with the restored values. This feature is particularly helpful when the user wishes to save/restore the results of a lengthy calculation.

8. *Exit* closes the application.

9. *Eigenvalues (meV)* displays the eigenvalues beginning with the value specified by the reference state slider. The degeneracy of the eigenstate is given in parentheses next to the eigenvalue.

10. *Transitions to the reference state* displays the transitions between the eigenvalue specified by the reference state slider and all higher eigenvalues.

Example usage

Let's consider the case where we seek the low-lying transitions for the following parameter values: B = 0.655 meV (this is the generally accepted value for a methyl group), $V_{31} = V_{32} = 14.2$ meV, $W_3 = 9.3$ meV, $\alpha = 0^o$. We want to make sure that the calculation is accurate enough to obtain reliable estimates for the E_{01}, E_{12}, and E_{23} transitions. The indices for these transitions simply denote the eigenvalue index and do not purport to represent any relationship to the split librational ground state. Grouping the eigenvalues by identical values yields something more meaningful though it will not be discussed further here.

Our strategy is to start with a relatively small number of indices, 11, which yields a 121×121 Hamiltonian. We will then increase the size of the Hamiltonian and see how many terms need to be included until the transition values stop changing.

When I ran this program, the time estimate for this calculation for the 121×121 Hamiltonian was 0.13 seconds. The results are shown in the following table.

E_{01}	0.158 meV
E_{12}	0.189 meV
E_{23}	0.012 meV

I next increased the number of indices to 21, resulting in a 441×441 Hamiltonian. The time estimate for this calculation increased to 4.5 seconds. The results are shown in the following table.

E_{01}	0.223 meV
E_{12}	0.235 meV
E_{23}	0.009 meV

I next increased the number of indices to 31, resulting in a 961×961 Hamiltonian. The time estimate for this calculation increased to 41.8 seconds. The results are shown in the following table.

E_{01}	0.223 meV
E_{12}	0.235 meV
E_{23}	0.009 meV

The values are not changing anymore so, for the precision needed here, we have obtained the required accuracy with the 441×441 Hamiltonian and need not increase the Hamiltonian size further.

Calculation of the matrix elements (optional)
The numerical implementation of the Hamiltonian is obtained through calculation of the matrix elements $\langle n', m' | H | n, m \rangle$ in which the individual elements are determined in the free rotor basis:

$$\langle \phi_1, \phi_2 | n, m \rangle = \frac{1}{2\pi} e^{in\phi_1} e^{im\phi_2}, \quad n, m = 0, \pm 1 \pm 2, \ldots$$

For the sake of clarity in the calculation of the matrix elements, the Hamiltonian is decomposed into the following parts:

$$H = -B\left(\frac{\partial^2}{\partial \phi_1^2} + \frac{\partial^2}{\partial \phi_2^2} \right) + \frac{V_{31}}{2}(1 - \cos 3\phi_1) + \frac{V_{32}}{2}(1 - \cos(3\phi_2 + \alpha)) - \frac{W_3}{2}(1 - \cos(3\phi_1 - 3\phi_2))$$

$$= H_{FR} + V_{31}(\phi_1) + V_{32}(\phi_2) + W_3(\phi_1, \phi_2),$$

where H_{FR} is the free rotor Hamiltonian, $V_{31}(\phi_1)$ is the hindering potential for the first rotor, $V_{32}(\phi_2)$ is the potential for the second rotor, and $W_3(\phi_1, \phi_2)$ represents the coupling between the two rotors.

The matrix elements due to the free rotor part of the Hamiltonian are straightforward to calculate:

$$\langle n',m'|H_{FR}|n,m\rangle = \int_0^{2\pi}d\phi_1\int_0^{2\pi}d\phi_2\langle n',m'|\phi_1,\phi_2\rangle\left[-B\left(\frac{\partial^2}{\partial\phi_1^2}+\frac{\partial^2}{\partial\phi_2^2}\right)\right]\langle\phi_1,\phi_2|n,m\rangle$$

$$= \left(n^2+m^2\right)B\delta_{n',n}\delta_{m',m}$$

The hindering potential yields the following matrix elements for the first rotor in this basis:

$$\langle n',m'|V_{31}(\phi_1)|n,m\rangle = \int_0^{2\pi}d\phi_1\int_0^{2\pi}d\phi_2\langle n',m'|\phi_1,\phi_2\rangle\left[\frac{V_{31}}{2}\left(1-\frac{1}{2}\left(e^{i3\phi_1}+e^{-i3\phi_1}\right)\right)\right]\langle\phi_1,\phi_2|n,m\rangle$$

$$= \frac{V_{31}}{2}\delta_{n',n}\delta_{m',m}-\frac{V_{31}}{4}\delta_{m',m}\int_0^{2\pi}d\phi_1\langle n'|\phi_1\rangle\left(e^{i3\phi_1}+e^{-i3\phi_1}\right)\langle\phi_1|n\rangle$$

$$= \frac{V_{31}}{2}\delta_{n',n}\delta_{m',m}-\frac{V_{31}}{4}\delta_{m',m}\left[\delta_{n-n'+3,0}+\delta_{n-n'-3,0}\right]$$

$$= \frac{V_{31}}{4}\delta_{m',m}\left[2\delta_{n',n}-\delta_{n-n'+3,0}-\delta_{n-n'-3,0}\right]$$

There is an additional phase factor in the hindering potential for the second rotor which yields a slightly different form for the matrix elements:

$$\langle n',m'|V_{32}(\phi_2)|n,m\rangle = \int_0^{2\pi}d\phi_1\int_0^{2\pi}d\phi_2\langle n',m'|\phi_1,\phi_2\rangle\left[\frac{V_{31}}{2}\left(1-\frac{1}{2}\left(e^{i3\phi_2}e^{i\alpha}+e^{-i3\phi_2}e^{-i\alpha}\right)\right)\right]\langle\phi_1,\phi_2|n,m\rangle$$

$$= \frac{V_{32}}{2}\delta_{n',n}\delta_{m',m}-\frac{V_{32}}{4}\delta_{n,n'}\int_0^{2\pi}d\phi_2\langle m'|\phi_2\rangle\left(e^{i3\phi_2}e^{i\alpha}+e^{-i3\phi_2}e^{-i\alpha}\right)\langle\phi_2|m\rangle$$

$$= \frac{V_{32}}{4}\delta_{n',n}\left[2\delta_{m',m}-\delta_{m-m'+3,0}e^{i\alpha}-\delta_{m-m'-3,0}e^{-i\alpha}\right]$$

$$= \frac{V_{32}}{4}\delta_{n',n}\left[2\delta_{m',m}-\left(\delta_{m-m'+3,0}+\delta_{m-m'-3,0}\right)\cos\alpha\right]+$$

$$i\frac{V_{32}}{4}\delta_{n',n}\left[\delta_{m-m'-3,0}-\delta_{m-m'+3,0}\right]\sin\alpha$$

Finally the coupling term is calculated as follows:

$$\langle n',m'|W_3(\phi_1,\phi_2)|n,m\rangle = \int_0^{2\pi}d\phi_1\int_0^{2\pi}d\phi_2\langle n',m'|\phi_1,\phi_2\rangle\left[\frac{W_3}{2}(1-\cos(3\phi_1+3\phi_2))\right]\langle\phi_1,\phi_2|n,m\rangle$$

$$= \frac{W_3}{2}\delta_{n',n}\delta_{m',m} -$$

$$\frac{W_3}{4}\int_0^{2\pi}d\phi_1\int_0^{2\pi}d\phi_2\langle n',m'|\phi_1,\phi_2\rangle\left[e^{i3\phi_1}e^{i3\phi_2}+e^{-i3\phi_1}e^{-i3\phi_2}\right]\langle\phi_1,\phi_2|n,m\rangle$$

$$= \frac{W_3}{2}\delta_{n',n}\delta_{m',m}-\frac{W_3}{4}\left(\delta_{n-n'+3,0}\delta_{m-m'-3,0}+\delta_{n-n'-3,0}\delta_{m-m'+3,0}\right)$$

$$= \frac{W_3}{4}\left[2\delta_{n',n}\delta_{m',m}-\delta_{n-n'+3,0}\delta_{m-m'-3,0}-\delta_{n-n'-3,0}\delta_{m-m'+3,0}\right]$$

Putting these terms all together in a single comprehensive expression yields:

$$\langle n',m'|H|n,m\rangle = \left(n^2+m^2\right)B\delta_{n',n}\delta_{m',m}$$

$$+\frac{V_{31}}{4}\delta_{m',m}\left[2\delta_{n',n}-\delta_{n-n'+3,0}-\delta_{n-n'-3,0}\right]$$

$$+\frac{V_{32}}{4}\delta_{n',n}\left[2\delta_{m',m}-\left(\delta_{m-m'+3,0}+\delta_{m-m'-3,0}\right)\cos\alpha\right]$$

$$+i\frac{V_{32}}{4}\delta_{n',n}\left[\delta_{m-m'-3,0}-\delta_{m-m'+3,0}\right]\sin\alpha$$

$$-\frac{W_3}{4}\left[2\delta_{n',n}\delta_{m',m}-\delta_{n-n'+3,0}\delta_{m-m'-3,0}-\delta_{n-n'-3,0}\delta_{m-m'+3,0}\right]$$

About the program:
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