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PGOPHER: A Program for Simulating Rotational, Vibrational and Electronic Spectra.

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Abstract

The PGOPHER program is a general purpose program for simulating and fitting molecular spectra, particularly the rotational structure. The current version can handle linear molecules, symmetric tops and asymmetric tops and many possible transitions, both allowed and forbidden, including multiphoton and Raman spectra in addition to the common electric dipole absorptions. Many different interactions can be included in the calculation, including those arising from electron and nuclear spin, and external electric and magnetic fields. Multiple states and interactions between them can also be accounted for, limited only by available memory. Fitting of experimental data can be to line positions (in many common formats), intensities or band contours and the parameters determined can be level populations as well as rotational constants. PGOPHER is provided with a powerful and flexible graphical user interface to simplify many of the tasks required in simulating, understanding and fitting molecular spectra, including Fortrat diagrams and energy level plots in addition to overlaying experimental and simulated spectra. The program is open source, and can be compiled with open source tools. This paper provides a formal description of the operation of version 9.1.

Keywords

1 Introduction

Perhaps the key feature of rotationally resolved molecular spectra is the immense amount of information on the molecule and its environment that can be extracted from spectroscopic measurements. The necessary downside is that such informative spectra are necessarily complicated, and extracting the information can be a daunting task. The program described here, PGOPHER, has been developed as a general purpose tool to assist in this task by simulating and fitting rotational, vibrational and electronic molecular spectra. The focus is on an interactive graphical user interface to make simulation and assignment of spectra as easy as the underlying spectroscopy permits, but it is also available in a command line version for use in combination with other programs. Its current form has come about as the result of applying it to many different spectroscopic problems and it has thus become useful in a wide

range of applications. This ranges from simple undergraduate spectroscopy practicals where the rotational constant of CO is determined from a traditional infrared spectrum to complex cases involving multiple interacting rovibronic states[1], including open shell systems and nuclear hyperfine structure. It is not the first molecular spectroscopy program to be published – Pickett's CALPGM suite[2] has become something of a standard and there are several others available including ASYTOP[3], ASYROTWIN[4], SPECVIEW[5] and JB95[6]. PGOPHER aims to cover similar ground, but in a much more general and easy-to-use way.

For many spectroscopic problems much of the required logic used in the handling of basis sets, energy levels and transitions is independent of the molecular type, and the program structure reflects this. An object-oriented approach is used, which allows the molecule-specific part to be restricted to a relatively small part of the program, with much of the program, including the user interface, written in a general way. There are thus separate units of the program for linear molecules, symmetric tops and asymmetric tops which are each outlined below, and these are all concerned with the rotational structure of a particular vibronic state. A fourth unit, which calculates vibrational structure of electronic states ignoring rotation, is also available and is covered in the on-line documentation but not described here as it is a relatively recent addition and has a significantly different structure.

The PGOPHER program has been developed as an open source application, and the source and executables can be freely downloaded from the website[7]; see also [8, 9] for permanently deposited versions of the program with a doi. This paper formally describes the internal structure of the program and the algorithms used; as far as possible the program tries to use standard spectroscopic notation and conventions, but there are necessary details that must be specified. Detailed instructions for running the program, and example files are distributed with the program. The paper is specifically based on version 9.1 of the program[9]; earlier versions are broadly similar, though some features may not be available or are slightly different, as described in the release notes. Most results are quoted without derivation; see standard spectroscopic texts [10-17] for the cases where details are not given.

2 Overall Operation

The underlying structural assumption is that the Hamiltonian is expressed in terms of a series of rotational constants given explicitly for each vibrational state of each electronic state included in the calculation. The generic term vibronic state is used here, as the calculation makes no distinction between the electronic and vibrational parts of the wavefunction. At a minimum the information required for each vibronic state, η, will include the symmetry, an origin for the state (the energy in the absence of rotational terms) and one or more rotational constants. The rotational part of the Hamiltonian is taken to include some small terms that are notionally part of the electronic Hamiltonian, including spin-orbit and spin-spin coupling and any lifting of vibronic degeneracies, such as lambda-doubling. These are conventionally included in the rotational Hamiltonian, and indeed accurate energy level calculations require this.

To allow multiple states to be included, the calculation is set up using a series of objects laid out in a tree structure, as shown in Figure 1. The key object is a "state" object, which specifies the symmetry and constants of a single vibronic state. One or more of these are grouped under "manifold" objects which are in turn grouped under "molecule" objects which are grouped under "species" objects. The intent is that isotopically substituted variants of a molecule are grouped under a species object so that, for example, the intensity of a particular transition involves the product of a relative concentration (specified at the species level) and an abundance (specified at the molecule level). "Transition moment" objects specify the possible transitions between states which are grouped under "Transition moments" objects which specify the connected manifolds. At the top level is a "mixture" object, implying a mixture of several different compounds, each of which has a species object. The "mixture" object also contains a "simulation" object that contains global parameters such as the temperature and line width which govern the overall appearance of the simulation. A minimal set of objects to produce a simulation is shown in Figure 1; any level other than the top level can have multiple objects if required.

```
Mixture                          ⊟·· Sample
    Simulation                       ┊··· Simulation
    Species                      ⊟·· HF
        Molecule                     ⊟·· HF
            Manifold                     ⊟·· X
                State                        ┊··· v=0
        Transition Moments           ⊟·· <X|mu|X>
            Transition Moment                ┊··· <v=0|T(1)|v=0>
```
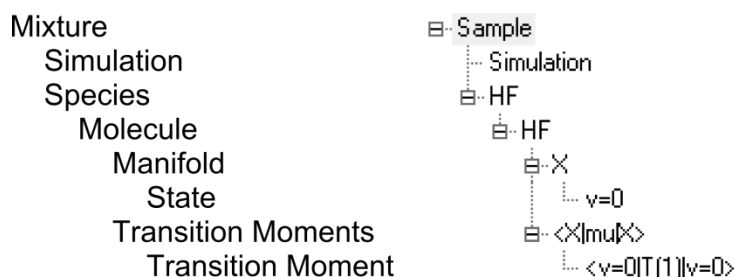
Figure 1 Minimum sample set of objects for a simulation. The left side shows the generic object types, and the right shows a screenshot from the program set up to simulate the pure rotational spectrum of HF. The "v=0" object contains the rotational constants, and <v=0|T(1)|v=0> the (transition) dipole moment.

An important optional possibility is a "perturbation" object, which specifies interactions between vibronic states, and can also be used to add non-standard terms to the Hamiltonian for a vibronic state. The perturbation objects are placed under the manifold containing the states involved and interacting states must therefore be in the same manifold. The concept of a manifold of states in fact arises out of the requirement to handle perturbations, and is used to group interacting states together. In the absence of perturbations the grouping into manifolds is arbitrary, though the calculation is slightly more efficient if the number of states in any given manifold is minimized and states with no interactions with other states are in their own manifold. To give a specific example, in simulating the B-X transition in S_2[18], the ground electronic state shows no perturbations so the calculation can be structured so that each vibrational level of the ground state is in its own manifold. In contrast, the excited B state shows significant interaction with the B" state, and one vibrational level of the B electronic state can interact with more than one vibrational level of the B" state, so calculation of the excited states must be set up as a single manifold

containing several vibrational levels from both the B and B" states. A fragment of the object tree required in this case is shown in Figure 2.
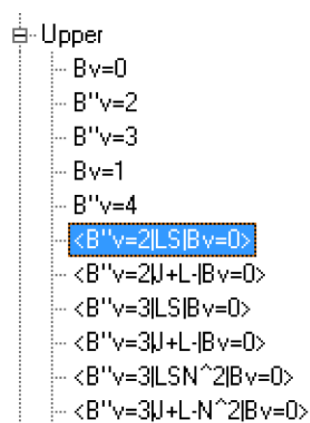

Figure 2 Part of screen shot for simulation of multiple interacting vibronic states in S_2. It includes 5 vibronic states (B…) and 6 perturbations (<B…||B…>) between them.

Other objects are also available for more specialised types of calculation, such as "nucleus" objects under each state which allow hyperfine structure to be simulated. There are no hard limits on the number of any type of object, though the calculation will be slower and take more memory as the number of objects is increased. The limiting step for larger calculations is typically the matrix diagonalization step; to give an indication a model involving ~20 interacting asymmetric top states[19, 20] takes a few seconds on a current desktop machine. PGOPHER makes use of parallel processing where possible; many of the calculations split naturally into independent parts, making this reasonably straightforward to implement. For example, energy levels are typically required for a range of values of total angular momentum, but calculations for a given value of the total angular momentum can be done independently from each other, and thus in parallel.

For instructions on setting up an object tree readers should refer to the documentation supplied with the program. An important consideration is that while most objects will have many possible settings, most of these can be left at the default values. A complicated object tree can be built up easily from a simple one by copying and pasting one or more objects. Given a correctly set up object tree, a variety of spectroscopic calculations can then be performed, most importantly simulating spectra and comparing and fitting them to experiment. Multiple experimental spectra can be overlaid on the simulation, with a separate object tree used to control them. Various supporting tools are also included in the program, such as calibrating spectra against known transitions, assigning transitions, making energy level plots, and other tools for showing details of the calculation. The program can directly handle experimental data and line lists in a wide variety of standard and proprietary formats, including simple text format, JCAMP-DX [21] spectra and HITRAN[22] line lists.

2.1 Energy Levels

The essential structure of the program involves the expansion of the wavefunction for a given rovibrational level, Ψ_i as a linear combination of basis states, $|j\rangle$:

$$\Psi_i = \sum_j c_j^i |j\rangle \tag{1}$$

To calculate the coefficients, the Hamiltonian matrix is set up and diagonalized in this basis. The basis states and Hamiltonian depend on the system, and are discussed individually below, but the basis will typically be expressible in the form $|\eta sJKM\rangle$ where η specifies the vibrational and electronic state (the "state" object) including total electron spin, s is the rovibronic symmetry, J is the total angular momentum, K is its projection along a molecule-fixed axis, and M the projection along a laboratory axis. These basis functions are in turn a specific linear combination of one or two primitive or nonsymmetry-adapted basis functions, $|\eta JKM\rangle$; the exact relationship is discussed in the molecule specific sections below. In the absence of external electric or magnetic fields, there is no energy dependence on the M quantum number and the basis states contributing to any given state of the system will be restricted to states of a single total angular momentum (J) and rovibronic (rotational × vibrational × electronic) symmetry, s. If hyperfine structure is included then the quantum numbers need to be extended to include nuclear spin to give $|\eta sJKIFM\rangle$ for a single nuclear spin, I, and the total angular momentum now becomes F. (Multiple nuclear spins are discussed below.)

The logic above allows a specific Hamiltonian matrix to be set up on specifying the manifold, m, the overall rovibronic symmetry, s, the total angular momentum (J or F), and its projection along a laboratory axis, M. Diagonalizing this matrix will give a set of energy levels which can be uniquely specified by these quantities and an eigenvalue number, i, found by numbering the levels in order of increasing energy. Each of these states will have a set of coefficients, $c_{\eta K}^{msJiM}$, giving the basis set expansion for the state:

$$|msJiM\rangle = \sum_{\eta \in m, K} c_{\eta K}^{msJiM} |\eta sJKM\rangle \tag{2}$$

The sum extends over all vibronic states, η, in the manifold m, and all quantum numbers not otherwise specified, typically K or Ω, but also J and/or N depending on the specific calculation. In the absence of an external field the energies and coefficients are independent of M, so M can be omitted as a label and is not required for calculating the energy levels. The modifications required in the presence of external fields are discussed below in the context of transition moments and energy level shifts in the presence of external static fields.

The treatment of degeneracies requires some comment, in that any linear combination of degenerate states is also a solution of the Schrödinger equation for the system. The numerical diagonalization process (the LAPACK routines[23] DSYEVR or ZHEEVR are used for this) will give the expected duplicate energy values in these circumstances, though

the wavefunction associated with each one is a random combination of the possible wavefunctions, with the only constraint being that the set returned is orthogonal. The final calculated spectrum will be independent of the choice of wavefunction made for the degenerate states, though selected properties may be displayed in different ways. For example the intensities of the individual components of a transition made up of two or more degenerate components may be arbitrary, but the overall intensity is uniquely determined. This particularly affects comparisons with other programs or line-lists from the literature, though the total simulated spectrum should not be affected.

In practice this indeterminacy is found relatively rarely. Formally, the overall rovibronic symmetry can only be degenerate for symmetric tops, and these are handled specially and only one component of the degenerate pair is calculated. This implies no true degeneracy will be encountered, though terms omitted from the Hamiltonian may mean some degeneracies are not lifted. However, the common degeneracies that arise from omitting terms are typically resolved on symmetry grounds. For example, in linear molecules in the absence of lambda doubling, Π states are degenerate but the two components have different parity and will thus be calculated separately. Similarly, the $+K$ and $-K$ levels in a symmetric top either have different rovibronic symmetry or are a pair with overall E symmetry, for which only one component need be calculated. More generally the Hamiltonian matrix is scanned for independent sub-blocks with no matrix elements between them as part of the process of setting it up. (A parameter `SmallE` determines the size of matrix elements that can be discarded.) These sub-blocks are then diagonalized independently; as well as being faster this also avoids spurious mixing between states when the full symmetry of the system has not been used in setting up the calculation.

2.2 Quantum Number Assignment

For the purpose of identifying a state m, J, s, i and M are sufficient for internal processing, but other quantum numbers (such as Ω and N for linear molecules) are typically used to specify states, and PGOPHER provides these. Not only do these additional quantum numbers aid interpretation, but the eigenvalue number, i, is not well defined in the presence of closely spaced states as small changes in parameter values can change the state order. Tracking other aspects of the wavefunction will normally allow stable assignments to be made, though in the presence of strong interactions between states none of the schemes described here are guaranteed to provide consistent quantum numbers. The calculated spectra are independent of the additional quantum numbers applied to the states, and the practical consequence is that fitting transitions involving closely spaced levels may require manual checking to ensure the correct states are picked. (In these circumstance eigenvalue number may be the best label to use.)

To assign other quantum numbers the key requirement is to assign a particular final eigenstate $|msJiM>$ to a particular basis state $|\eta JKM>$, as the basis states are associated with well-defined values for the other quantum numbers. The assignment to a basis state is not

necessarily straight forward. Simply picking the largest coefficient from the basis set expansion, equation (2), is one of the strategies offered (`EigenSearch`=True, `LimitSearch`=False) but will often be problematic. As a specific example consider a linear molecule in a $^3\Pi$ state with rotational constant, $B = 1$ cm^{-1} and spin-orbit coupling constant, $A = 20$ cm^{-1}. Ω is one of the labels on the basis states, and at $J = 5$ picking the dominant basis state and thus assigning Ω is straightforward as the three states are:

$$\Psi_1 = +.938|\Omega{=}0> + .340|\Omega{=}1> + .065|\Omega{=}2> \qquad (3)$$

$$\Psi_2 = -.338|\Omega{=}0> + .856|\Omega{=}1> + .391|\Omega{=}2>$$

$$\Psi_3 = +.077|\Omega{=}0> + .389|\Omega{=}1> + .918|\Omega{=}2>$$

However at $J{=}20$ a simple pick of the largest coefficient would assign both Ψ_2 and Ψ_3 as $\Omega{=}2$:

$$\Psi_1 = +.712|\Omega{=}0> + .636|\Omega{=}1> + .297|\Omega{=}2> \qquad (4)$$

$$\Psi_2 = -.635|\Omega{=}0> + .402|\Omega{=}1> + .659|\Omega{=}2>$$

$$\Psi_3 = +.300|\Omega{=}0> + .658|\Omega{=}1> + .691|\Omega{=}2>$$

This ambiguity is inherent for any basis size larger than 2. In this case the dramatic change in mixing is a classic example of a switch from Hund's case (a) to case (b) with increasing J. If a Hund's case (b) basis was used instead then N would be easy to assign for high J but not for low J, so this does not provide a general solution to the assignment problem. The solution chosen is to preserve the order of the states; for large (positive) values of A the state ordering will be $\Omega{=}2 > \Omega{=}1 > \Omega{=}0$ and this energy ordering is used to assign the quantum numbers, rather than the coefficients. The basis states are thus arranged in an expected energy order, and the lowest eigenstate is assigned to the lowest energy basis state, and so on. This method avoids sudden jumps in quantum number assignments as A is reduced. The same idea of an expected energy ordering can be used for the other molecule types, and is discussed for each molecule type below.

This expected energy ordering will, in general, only apply to subsets of states within the overall basis. For example, if more than one vibronic state is included in the basis then no particular ordering is expected between components of different states. To address this problem the idea of a sub-basis is introduced, defined such that states within a given sub-basis have a clear expected energy ordering, and different vibronic states are assigned to different sub-bases. The mixing between different vibronic states is expected to be small, so methods based on wavefunction coefficients for picking the sub-basis are likely to give sensible results. Assigning a sub-basis to a final eigenstate is achieved by working out the fractional contribution from a given sub-basis from the sum over the sub-basis of the square of the wavefunction coefficients of the eigenstate. This fraction is evaluated for all eigenstates and, if the sub-basis has n members, the eigenstates with the n largest fractions for that sub-basis are assigned to that sub-basis. Within these n states the assignment of basis states is

done by energy ordering. The process is repeated for each sub-basis, excluding eigenstates that have already been assigned. If there are three or more sub-bases then this method can still suffer from the conflicting assignment pattern seen in equation (4), but three-way mixes between sub-bases are relatively rare for the choice of sub-bases described here and these physically correspond to cases where the quantum numbers are likely to be unclear whatever scheme is used.

The correct choice of division between sub-bases also allows quantum numbers to be assigned for closely spaced energy levels that are degenerate in the absence of some interaction, provided each of the near-degenerate levels are assigned to a separate sub-basis. (This is in any case a requirement of the scheme, as assignment by sub-basis would fail if the expected ordering included some degeneracies.) A good example of this is hyperfine structure arising from nuclear spin, for which the natural division is to put levels of different angular momentum excluding nuclear spin (J) in different sub-bases, in addition to any other separations. Physically the interaction with nuclear spin is small, so the J assignment is unlikely to be changed by the addition of nuclear spin terms in the Hamiltonian. This translates to the expectation that mixing between states of different J and thus sub-bases is small, and the method of assignment of eigenstate to sub-basis given here will be reliable. (Indeed, hyperfine matrix elements off-diagonal in J are sometimes omitted from the calculation of hyperfine structure.) This logic is expected to work in general where a sequence of successively smaller sets of terms is added to the Hamiltonian, with each term associated with a new quantum number, and each is associated with a division into separate sub-bases.

2.3 Hyperfine Structure

Hyperfine structure is handled by setting the number of active nuclei at the molecule level, which creates a corresponding set of "nucleus" objects under each state. The number of nuclei does not have a hard limit, though multiple nuclei can lead to rather large calculations. The default coupling scheme given nuclear spins I_1, I_2, … I_n used is:

$$F_1 = J + I_1; \quad F_2 = F_1 + I_2; \quad … \quad F = F_{n-1} + I_n; \tag{5}$$

reducing to $F = J + I$ for a single nucleus. Where pairs of equivalent nuclei are present (such as in H_2 or H_2O) a modified coupling scheme must be used:

$$I_{12} = I_1 + I_2; \quad F = J + I_{12} \tag{6}$$

The `AsNext` setting for a given nucleus indicates the use of this coupling scheme, and the constants for the related nuclei are forced to be identical. Multiple pairs of equivalent nuclei are implemented, though three or more equivalent nuclei are not implemented in the current version. (The `AsNext` setting can also be used for molecules with low symmetry, in which case the alternative coupling scheme (6) is used, but the constants are not forced to be identical.)

The assignment of hyperfine quantum numbers has been mentioned above; in general each different set of hyperfine quantum numbers and J is placed in a different sub-basis. For a single nuclear spin this is reliable, but if more than one nucleus is present some care may be required. If the nuclei are arranged in order of coupling strength, with the nuclei with the largest interactions first (I_1), then the criterion of successively smaller terms will be met, and the quantum numbers are likely to be reliable. Nuclei with similar interaction strength (i.e. similar values for the hyperfine constants) may need to use the $\mathbf{I}_{12} = \mathbf{I}_1 + \mathbf{I}_2$ coupling scheme to avoid strong mixing between sub-bases.

The evaluation of hyperfine matrix elements and assignment of quantum numbers is very similar for all molecule types. This is because the nuclear spin Hamiltonian terms can typically be written as a scalar product of a nuclear spin tensor, $\mathbf{T}^k(I)$, and a rovibronic tensor that is independent of the spin, $\mathbf{T}^k(R)$. k is the rank of the tensors, and it is a standard result of tensor algebra[13] as applied to angular momentum that the matrix element of a scalar product can be expressed as:

$$
\begin{aligned}
&\left\langle \eta' J' K' I' F' M' \middle| \mathbf{T}^k(R) \cdot \mathbf{T}^k(I) \middle| \eta J K I F M \right\rangle \\
&= \delta_{F'F} \delta_{M'M} (-1)^{J+I'+F} \begin{Bmatrix} F & I' & J' \\ k & J & I \end{Bmatrix} \left\langle \eta' J' K' \middle\| \mathbf{T}^k(R) \middle\| \eta J K \right\rangle \left\langle I \middle\| \mathbf{T}^k(I) \middle\| I \right\rangle
\end{aligned}
\tag{7}
$$

This is written assuming a single nuclear spin, I and here $I = I'$. It is the product of three factors, one that is independent of nuclear spin ($\left\langle \eta' J' K' \middle\| \mathbf{T}^k(R) \middle\| \eta J K \right\rangle$), one that depends only on spin ($\left\langle I \middle\| \mathbf{T}^k(I) \middle\| I \right\rangle$) and a Wigner 6-$j$ symbol. If a second nuclear spin is introduced so the coupling scheme is $\mathbf{F}_1 = \mathbf{J} + \mathbf{I}_1$ and $\mathbf{F} = \mathbf{F}_1 + \mathbf{I}_2$ then the above equation still applies if the replacements $J \rightarrow F_1$, $I \rightarrow I_2$ are made and the group of other quantum numbers ηK becomes $\eta J K I_1$. The resulting reduced matrix element of $\mathbf{T}^k(R)$ depends on I_1 and F_1, but as the operator $\mathbf{T}^k(R)$ does not contain nuclear spin, another standard result for reduced matrix elements can be used:

$$
\begin{aligned}
&\left\langle \eta' J' K' I_1 F_1 \middle\| \mathbf{T}^k(R) \middle\| \eta J K I_1 F_1 \right\rangle \\
&= (-1)^{J'+I_2+F_1+k} \sqrt{(2F_1'+1)(2F_1+1)} \begin{Bmatrix} J' & F_1' & I_1 \\ F_1 & J & k \end{Bmatrix} \left\langle \eta' J' K' \middle\| \mathbf{T}^k(R) \middle\| \eta J K \right\rangle
\end{aligned}
\tag{8}
$$

Additional nuclei can be handled the same way, with each introducing an additional 6-j multiplier of the reduced matrix element of $\mathbf{T}^k(R)$ of the same form as in the above equation. Operators involving I_1 are easier to handle as they cannot change F_1 or F:

$$
\left\langle \eta' J' K' I_1 F_1' I_2 F' M' \middle| \mathbf{T}^k(R) \cdot \mathbf{T}^k(I_1) \middle| \eta J K I_1 F_1 I_2 F M \right\rangle = \delta_{F'F} \delta_{F_1' F_1} \left\langle \eta' J' K' I_1 F_1 \middle| \mathbf{T}^k(R) \cdot \mathbf{T}^k(I_1) \middle| \eta J K I_1 F_1 \right\rangle
\tag{9}
$$

Overall this means that only the reduced matrix elements $\langle \eta'J'K'\|\mathbf{T}^k(R)\|\eta JK\rangle$ and $\langle I\|\mathbf{T}^k(I)\|I\rangle$ need be evaluated in a manner specific to the interaction and molecule type, independent of the number of nuclear spins.

The above can also be used for the alternate coupling scheme $\mathbf{I}_{12} = \mathbf{I}_1 + \mathbf{I}_2$; $\mathbf{F} = \mathbf{J} + \mathbf{I}_{12}$ with some modifications. For the operator $\mathbf{T}^k(R) \cdot \mathbf{T}^k(I_1)$ equation (7) can be applied with I replaced by I_{12}, and giving the same reduced matrix element of $\mathbf{T}^k(R)$ and a reduced matrix element involving only nuclear spin that can again be evaluated using standard techniques:

$$
\begin{aligned}
&\langle I_1 I_2 I'_{12}\|\mathbf{T}^k(I_1)\|I_1 I_2 I_{12}\rangle \\
&= (-1)^{I_1+I_2+I_{12}+k}\sqrt{(2I'_{12}+1)(2I_{12}+1)}
\begin{Bmatrix} I_1 & I'_{12} & I_2 \\ I_{12} & I_1 & k \end{Bmatrix}
\langle I_1\|\mathbf{T}^k(I_1)\|I_1\rangle
\end{aligned}
\tag{10}
$$

The operator $\mathbf{T}^k(R)\cdot\mathbf{T}^k(I_2)$ will also be required, and can be evaluated in the same way, yielding an identical expression with I_1 and I_2 exchanged, though I_{12} is replaced by I'_{12} in the initial phase factor. The overall result is again that the same reduced matrix elements $\langle \eta'J'K'\|\mathbf{T}^k(R)\|\eta JK\rangle$ and $\langle I\|\mathbf{T}^k(I)\|I\rangle$ are required, independent of the coupling scheme chosen.

2.4 Transition Moments

Apart from transition energy, the other important ingredient in simulating transitions is the transition intensity, for which the starting point is the transition moment. To allow for the possibility of multiphoton and Raman transitions, it is helpful to write the Hamiltonian for the interaction of a molecule with an external field in the general spherical tensor form:

$$
-\sum_k \mathbf{T}^k(\mu)\cdot\mathbf{T}^k(E) = -\sum_k\sum_p (-1)^p T_p^k(\mu) T_{-p}^k(E)
\tag{11}
$$

Here k is the rank of the tensors involved and p a projection quantum number ($|p| \le k$) specifying the projection of the tensor onto the space-fixed z axis. For the most important electric dipole case $k = 1$ and $\mathbf{T}^1(\mu)$ is the electric dipole moment operator (expressed in a space-fixed frame) and $\mathbf{T}^1(E)$ is the electric field. For magnetic interactions, these become the magnetic dipole and magnetic field, respectively. For more exotic transitions other values of k must be included: 2 for quadrupole transitions, 0 and 2 (typically) for Raman and two-photon transitions or more generally up to n if n photons are involved. The transition moment is then the matrix element of the $T_p^k(\mu)$ term. This depends on the projection of the total angular momentum on the space-fixed z axis, M, though fortunately the dependence on this is independent of the type of molecule and can be evaluated using the Wigner-Eckart theorem:

$$\langle \eta' J' K' M' | T_p^k(\mu) | \eta J K M \rangle = (-1)^{J'-M'} \begin{pmatrix} J' & k & J \\ -M' & p & M \end{pmatrix} \langle \eta' J' K' \| T^k(\mu) \| \eta J K \rangle \tag{12}$$

The reduced matrix element on the right hand side can be evaluated by transforming the tensor operator from space-fixed to body-fixed axis systems using Wigner D matrices:

$$T_p^k(\mu) = \sum_q D_{p,q}^k(\omega)^* T_q^k(\mu) \tag{13}$$

where q labels the projection of the tensor onto the body-fixed axis system. It can be shown[17] that this leads to the following expression for the reduced matrix element:

$$\left\langle \eta' J' K' \left\| \sum_q D_{p,q}^k(\omega)^* T_q^k(\mu) \right\| \eta J K \right\rangle = \sum_q (-1)^{J'-K'} \sqrt{(2J'+1)(2J+1)} \begin{pmatrix} J' & k & J \\ -K' & q & K \end{pmatrix} \langle \eta' | T_q^k(\mu) | \eta \rangle \tag{14}$$

independent of p. In this expression $\langle \eta' | T_q^k(\mu) | \eta \rangle$ corresponds to the transition moment in the body-fixed axis system, and is an integral over electronic and vibrational coordinates only, and is thus a simple numerical property of the two vibronic states involved in the transition. Its value must be specified, along with the origin and rotational constants, as properties of the states involved when setting up the calculation. It is a signed quantity and the relative sign of these transition moments is important if more than one contributes to any given transition.

Combining the above equations yields the transition moment between any two primitive basis states, which are easily transformed to the matrix elements between the symmetry-adapted basis states. To complete the calculation for the transition moment between two final states |*msJiM*> and |*m's'J'i'M'*> requires the coefficients from the matrix diagonalization calculating them:

$$\langle m's'J'i'M' | T_p^k(\mu) | msJiM \rangle = \sum_{\eta'K'\eta K} \left(c_{\eta'K'}^{m's'J'i'M'} \right)^* c_{\eta K}^{msJiM} \langle \eta's'J'K'M' | T_p^k(\mu) | \eta sJKM \rangle \tag{15}$$

2.5 Line Strengths

As the equation above implies, transition moments depend on M, even in the absence of an external field, but fortunately the M dependence disappears when the intensities are summed over M. The intensity of a transition is proportional to the square of the transition moment. In the absence of external fields levels with different M values are degenerate, so the required quantity is the transition moment squared summed over the M values for the upper and lower states. This leads to the definition of the line strength, S in the literature:

$$S(m's'J'i', msJi) = \sum_p \sum_{M',M} \left| \left\langle m's'J'i'M' \middle\| T_p^k(\mu) \middle\| msJiM \right\rangle \right|^2$$

$$= \left| \left\langle m's'J'i' \middle\| T^k(\mu) \middle\| msJi \right\rangle \right|^2 \sum_p \sum_{M',M} \begin{pmatrix} J' & k & J \\ -M' & p & M \end{pmatrix}^2 \qquad (16)$$

$$= \left| \left\langle m's'J'i' \middle\| T^k(\mu) \middle\| msJi \right\rangle \right|^2$$

The second step follows because the M dependence only arises from the Wigner-Eckart theorem as in equation (12) and is independent of all the quantum numbers apart from the total angular momentum and its projection. The final step uses a standard property of Wigner 3-j symbols[24]:

$$\sum_{M',M} \begin{pmatrix} J' & k & J \\ -M' & p & M \end{pmatrix}^2 = \frac{1}{2k+1} \qquad (17)$$

and the fact that a tensor of rank k has $2k+1$ components. The reduced matrix element can be evaluated by adapting equation (15):

$$\left\langle m's'J'i' \middle\| T^k(\mu) \middle\| msJi \right\rangle = \sum_{\eta'K'\eta K} \left(c_{\eta'K'}^{m's'J'i'} \right)^* c_{\eta K}^{msJi} \left\langle \eta's'J'K' \middle\| T^k(\mu) \middle\| \eta sJK \right\rangle \qquad (18)$$

The sum over p in equation (16) corresponds to a sum over possible polarisations of the light; for conventional spectroscopy the unweighted sum above is appropriate. However, to allow PGOPHER to handle relative intensities between different ranks of transitions in multiphoton spectroscopy a slightly modified quantity is used, S^{pol}, defined as the sum over upper and lower M states for a single polarisation, $p = 0$:

$$S^{pol}(m's'J'i', msJi) = \sum_{M',M} \left| \left\langle m's'J'i'M' \middle| T_0^k(\mu) \middle| msJiM \right\rangle \right|^2$$

$$= \left| \left\langle m's'J'i' \middle\| T^k(\mu) \middle\| msJi \right\rangle \right|^2 \sum_{M',M} \begin{pmatrix} J' & k & J \\ -M' & p & M \end{pmatrix}^2 \qquad (19)$$

$$= \frac{1}{2k+1} \left| \left\langle m's'J'i' \middle\| T^k(\mu) \middle\| msJi \right\rangle \right|^2$$

With this definition, the effective line strength for multiphoton transitions involving more than one overall rank, k, can be found by simply summing the S^{pol} values for the individual components, assuming the common case of linearly polarised light. For standard one photon transitions we simply have $S = 3S^{pol}$.

The line strength, S, is related to the Hönl-London factor, though the line strength is a more general quantity. The Hönl-London factor contains only the rotational quantum number dependence of the transition intensity, so for simple systems the Hönl-London factor can be calculated from the above by setting the vibronic transition moment, $\left\langle \eta' \middle| T_q^k(\mu) \middle| \eta \right\rangle$ to one. It

relies on the assumption that the line strength can be separated into the product of rotational and vibronic factors, which in turn requires that there is a single vibronic transition moment contributing to the transition. If there is more than one vibronic transition moment contributing then the line strength will depend on their relative signs and magnitudes, and the Hönl-London factor is a less useful quantity. An additional complication with Hönl-London factors is that there is not a consistent definition in use in the literature, at least for linear molecules. This is explored by Hansson and Watson[25] who show that the definitions differ by factors of 2 or 2J+1. The definitions used here are consistent with those of Hansson and Watson.

2.6 Intensities

Given the line strength for a transition between an upper state, u, and a lower state, l, PGOPHER offers various options (controlled by the `IntensityUnits` setting) for calculating line intensities. As a starting point consider calculating the Einstein A coefficient from a transition dipole moment, $\langle u|\mu|l \rangle$ [12]:

$$A = \frac{8\pi^2}{3\varepsilon_0 c^3 \hbar} \nu_{ul}^3 \left| \langle u|\mu|l \rangle \right|^2 \tag{20}$$

where ν_{ul} is the frequency of the transition. (In this section and the next, all quantities are in SI units unless the units are explicitly stated.) If we replace $|<u|\mu|l>|^2$ with S_{ul} as calculated above this gives the total emission rate from u to l for one state of one molecule on all the degenerate M components of the transition:

$$I_{ul}^{\mathrm{EinsteinASum}} = \frac{8\pi^2}{3\varepsilon_0 c^3 \hbar} \nu_{ul}^3 S_{ul} \tag{21}$$

This is one of the available options (corresponding to `IntensityUnits = EinsteinASum`) but a more useful quantity is the emission rate from a single upper state component summed over the lower state components, which can be obtained by dividing by the upper state degeneracy, g_u:

$$A_{ul} = \frac{8\pi^2}{3\varepsilon_0 c^3 \hbar} \frac{\nu_{ul}^3 S_{ul}}{g_u} \tag{22}$$

This is the A value tabulated in line listings output by PGOPHER, and can be selected for plotting using `IntensityUnits = EinsteinA`. For electric dipole transitions the vibronic transition moments are input in units of Debye (1 Debye = $10^{-21}/c$ C m) and the line strength will therefore be in units of Debye^2. Evaluating the required conversion factors to SI units and fundamental constants using CODATA 2014 values[26] the above equation becomes:

$$\frac{A_{ul}}{s^{-1}} = 3.13618872 \times 10^{-7} \frac{\nu_{ul}^3}{\mathrm{cm}^{-3}} \frac{S_{ul}}{\mathrm{Debye}^2} \frac{1}{g_u} \tag{23}$$

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For magnetic dipole transitions the vibronic transition moments are in units of Bohr magnetons and a slightly modified equation is required:

$$A_{ul} = \frac{8\pi^2\mu_0}{3c^3\hbar}\frac{\nu_{ul}^3 S_{ul}}{g_{upper}} = 2.69735003\times10^{-11}\frac{\nu_{ul}^3}{cm^{-3}}\frac{S_{ul}}{Bohr\,magneton^2}\frac{1}{g_u} \tag{24}$$

Where the magnetic dipole originates from a nucleus, rather than an electron, the nuclear magneton is used for the vibronic transition moment and an additional scaling factor of $(m_p/m_e)^2$ is required in the above equation. Non-dipole transitions will require different scaling factors, but these have not been included in PGOPHER as absolute intensity measurements for such transitions are rare.

The absorption oscillator strength, f_{lu} or simply f, of a transition is an alternative way of defining line strength and is available with IntensityUnits = OscillatorStrength. The relationship is:

$$f_{lu} = \frac{8\pi^2 m_e}{3he^2}\nu_{ul}\frac{S_{ul}}{g_l} \tag{25}$$

using the definition given by Hilborn[27, 28]. The line strength is divided by the lower state degeneracy to give a quantity that is appropriate for a single lower state, summed over all upper states. This is a dimensionless quantity; substituting the fundamental constants gives:

$$f_{lu} = 4.70175463\times10^{-7}\frac{\nu_{ul}}{cm^{-1}}\frac{S_{ul}}{Debye^2}\frac{1}{g_l} \tag{26}$$

The oscillator strength for emission, f_{ul}, is defined to give a quantity appropriate for a single upper state and can be calculated from $f_{ul} = -g_l/g_u\,f_{lu}$ if required.

For line intensities the populations of the states involved in the transition must also be included. A simple starting point is simply to multiply the line strength by the difference in Boltzmann factors for the two states:

$$I_{ul}^{Arbitrary} = S_{ul}^{pol}\left[\exp\left(\frac{-E_l}{k_B T}\right) - \exp\left(\frac{-E_u}{k_B T}\right)\right] \tag{27}$$

This is the calculation for IntensityUnits = Arbitrary. S^{pol} is used here to ensure multiphoton transitions are correct, and the degeneracies of the states do not appear as they are included in S^{pol}. This will give sensible results for relative intensities for a single species, but can give misleading results when comparing related species, such as H_2 and HD. In such cases the partition function, Q, must be included in the calculation:

$$I_{ul}^{Normalized} = \frac{S_{ul}^{pol}}{Q}\left[\exp\left(\frac{-E_l}{k_B T}\right) - \exp\left(\frac{-E_u}{k_B T}\right)\right] \tag{28}$$

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This is the calculation for `IntensityUnits = Normalized`, and is the recommended starting point for all simulations, provided at least some part of the partition function can be calculated. (The partition function is discussed in more detail below.)

For one photon transitions integrated absorption coefficients can be calculated, for which the equation is:

$$\varepsilon_{ul} = \frac{\pi}{3\varepsilon_0 c\hbar} \frac{\nu_{ul} S_{ul}}{Q} \left[\exp\left(\frac{-E_l}{k_B T}\right) - \exp\left(\frac{-E_u}{k_B T}\right) \right] \tag{29}$$

This is the cross section per molecule, with units m^2 Hz/molecule. S is used in this equation, rather than S^{pol}, as it only applies to one photon transitions, and again state degeneracies are included in S rather than in the Boltzmann factors. For intensity units of cm^{-1}/(molecule cm^{-2}), as used by HITRAN[22], including the required fundamental constants and conversion factors equation (29) becomes:

$$\frac{\varepsilon_{ul}}{cm^{-1}/(molecule\ cm^{-2})} = 4.16237903 \times 10^{-19} \frac{\nu_{ul}}{cm^{-1}} \frac{S_{ul}}{Debye^2} \frac{1}{Q} \left[\exp\left(\frac{-E_l}{k_B T}\right) - \exp\left(\frac{-E_u}{k_B T}\right) \right] \tag{30}$$

This is the calculation used for `IntensityUnits = cm2WavenumberperMolecule`. MHz/(molecule nm^2) as used by the JPL catalogue[29] and the CDMS database[30] is also an option (`IntensityUnits = nm2MHzperMolecule`).

A note on the definition of the degeneracies, g, is required, as these can depend on exactly how nuclear spins are accounted for. The standard rotational factor of $2J + 1$ will always be included, changing to $2F + 1$ if hyperfine structure is included in the calculation. The degeneracy will also include any nuclear spin statistical weights given. These weights must include any equivalent spins for correct absolute intensities, but non-equivalent spins are not necessarily required in the calculation. For example in H_2 the 3:1 ratio between ortho and para hydrogen must be set up in the statistical weights to reproduce the alternation in intensity between even and odd J. However, for the HF molecule which has two non-equivalent spin ½ nuclei, the nuclear spin degeneracy of $(2I_1+1)(2I_2+1) = 4$ is independent of J, and can be omitted. Some quantities (Einstein A coefficients, oscillator strengths and absorption coefficients) are unaffected by removing this factor, but the line strength (S and S_{pol}) and partition functions will change. This can be important in certain circumstances, particularly if calculating thermodynamic properties from partition functions. See Fischer et al[31] for a further discussion of this point.

2.7 Population Distribution and Partition Functions

An important aspect of intensity calculations is the population function used, and the partition function arising from it. In simple cases relative populations can be calculated from the Boltzmann factors as used above, and the partition function, Q, required for absolute

populations, can be calculated from a simple sum over the calculated levels, i with energy E_i and degeneracy g_i:

$$Q = \sum_i g_i \exp\left(\frac{-E_i}{kT}\right) \tag{31}$$

but in many cases special treatment is required. For example the formulae presented so far assume a standard equilibrium Boltzmann distribution, but this is not justified in many spectroscopic applications. PGOPHER allows the Boltzmann factors (exp($-E/k_BT$) above) to be replaced by a general expression of variables such as J and state energy via a "custom population function" object or by numerically specifying the population of each state at the manifold level. This can be required for, say, modelling nascent populations following a reaction but PGOPHER also provides several simple adjustments to the standard Boltzmann distribution that are adequate in many circumstances.

The simplest adjustment is for emission spectra; the population distribution for the upper state, f, is typically in equilibrium at some effective temperature and the lower state population can be taken as zero. The net emission rate on a given transition is then the emission rate for a single molecule in the upper state (equation 21 above) scaled by the fraction of molecules in that state:

$$I_{fi}^{\text{HzperMolecule}} = \frac{8\pi^2}{3\varepsilon_0 c^3 \hbar} \frac{v_{fi}^3 S_{fi}}{Q} \exp\left(\frac{-E_f}{k_B T}\right) \tag{32}$$

This is selected by setting `IntensityUnits = HzperMolecule` and setting the `Initial` flag to true on the upper manifold and false on the lower manifold. The `Initial` flag controls whether the manifold is included in population and partition function calculations; the population is taken as zero if `Initial` is false. (It will speed up calculations if this is set to false for the upper manifold of an absorption transition where the energy gap is large compared to k_BT, but this is not essential.)

Also available is the possibility of specifying different temperatures for different degrees of freedom, reflecting the different rates of energy transfer. Separate vibrational and spin temperatures, T_{vib} and T_{spin}, can be specified if required in addition to the main temperature, T, which is essentially a rotational temperature.

A common example of a requirement for a separate vibrational temperature, T_{vib}, is in molecular beam spectra, where rapid rotational cooling means that only very low J states are populated, giving rotational temperatures of a few K, but there will be insufficient collisions to change vibrational states, so the effective vibrational temperature is typically rather higher. The Boltzmann factor for state i is actually taken as:

$$B_i = \exp\left(\frac{-(E_i - E_0)}{k_B T}\right) \exp\left(\frac{-(E_0 - E_B)}{k_B T_{vib}}\right)$$

$$= \exp\left(\frac{-(E_i - E_B)}{k_B T}\right) \quad \text{if } T = T_{vib}$$

(33)

Here E_i is the energy of the state, E_0 is the vibronic state origin and E_B is an energy offset. Note that the selection of E_0 requires that a single vibronic state can be identified for a particular rovibronic state which, as discussed under quantum number assignment, is not guaranteed so specifying a separate T_{vib} where there is significant vibronic mixing may not give consistent results. E_0 is normally the state origin specified in the input file, but for linear molecules, additional code shifts this to the energy of the lowest spin-orbit component, as the origin of the spin-orbit Hamiltonian can be at significantly different energy to that of the lowest component.

The use of an overall energy offset, E_B above, requires some discussion. The origin of the calculated energies depends on the Hamiltonian chosen and how the calculation is set up, and the lowest value of E_i may be significantly different from zero. If the partition function is included in intensity calculations, the final result should be independent of E_B, but the obvious choice of zero will often result in overflow or underflow in intermediate calculations. Ideally E_B would be the energy of the lowest level, but this would require two passes over the energy levels for (in most cases) little gain in accuracy so the lowest value of E_0 is normally used. (The search for the lowest origin considers all manifolds with the `Initial` flag set.) It can also be specified manually via the `AssumedOrigin` setting for a molecule, which may be required at very low temperatures, typically << 1K.

Adjustments to the population calculations are also required when considering nuclear spin states; the textbook example is ortho and para H_2 which interchange very slowly as the probability of a molecular collision changing nuclear spin orientation is very low. As for vibration, a separate temperature, here T_{spin}, can be specified, but different logic is needed to correct the intensity. The requirement is that the ratio between the total population of each spin matches the ratio at the specified spin temperature. More formally, if we define $Q_s(T)$ as the Boltzmann state sum over levels, i, belonging to spin species s at temperature T:

$$Q_s(T) = \sum_{i \in s} g_i \exp\left(\frac{-(E_i - E_0)}{k_B T}\right) \exp\left(\frac{-(E_0 - E_B)}{k_B T_{vib}}\right)$$

(34)

then the equilibrium fraction of a particular spin species at temperature T is:

$$f_s(T) = \frac{Q_s(T)}{\sum_s Q_s(T)} = \frac{Q_s(T)}{Q(T)}$$

(35)

To compute the population with $T_{spin} \neq T$ a spin species abundance, $a_s(T,T_{spin})$ is introduced which scales the population for each level of spin species s to give the required overall ratio of states, which is given by:

$$a_s\left(T,T_{spin}\right) = \frac{f_s\left(T_{spin}\right)Q(T)}{Q_s(T)} \tag{36}$$

so the population of a given level i becomes:

$$P_i\left(T,T_{spin}\right) = a_s\left(T,T_{spin}\right)g_i \exp\left(\frac{-(E_i - E_0)}{k_B T}\right)\exp\left(\frac{-(E_0 - E_B)}{k_B T_{vib}}\right) \tag{37}$$

With this definition the modified partition function sum for a given T and T_{spin}, $Q(T, T_{spin})$ becomes:

$$Q\left(T,T_{spin}\right) = \sum_s a_s\left(T,T_{spin}\right)Q_s(T) = \sum_s f_s\left(T_{spin}\right)Q(T) \tag{38}$$

That this gives the desired result can be confirmed by working out the fraction of states with a given spin species:

$$\frac{a_s\left(T,T_{spin}\right)Q_s(T)}{Q\left(T,T_{spin}\right)} = \frac{f_s\left(T_{spin}\right)Q(T)}{\sum_s f_s\left(T_{spin}\right)Q(T)} = f_s\left(T_{spin}\right) \tag{39}$$

In practice this requires the calculation of the partition function sum at two temperatures: T_{spin} to calculate $f_s(T_{spin})$ and T to calculate $Q(T, T_{spin})$.

Evaluation of the partition function sum can also require special consideration. By default the sum is evaluated in order of increasing J and terminated when the last 8 J values contributed $< 10^{-4}$ to the overall sum. (More than one J value is required for the convergence test as statistical weights from nuclear spins and other symmetry factors often show a strongly oscillating pattern as a function of J.). This sum is not necessarily convergent, as can be seen by considering the standard linear molecule expression for rotational energies:

$$F(J) = BJ(J+1) - DJ^2(J+1)^2 \tag{40}$$

At high enough J this expression will start decreasing and eventually give unphysical negative energies; this is inherent in the power series expansion used and is not restricted to linear molecules. If the partition function sum does not converge before reaching the maximum in this expression then the sum will never converge. Simply limiting the range of J considered may be adequate (setting `AutoQConverge` off will limit the sum to the maximum value of J specified for the simulation) or the molecular parameters may need adjustment to remove the unphysical behaviour at high J.

The other concern is the vibronic states included in the sum. Formally the required sum, for which the term total internal partition sum (TIPS) is sometimes used, should be over all populated states in the molecule. Schematically the sum can be written as:

$$Q_{\text{TIPS}} = \sum_v \sum_J g_{v,J} \exp\left(\frac{-E_{v,J}}{kT}\right) \tag{41}$$

For more complicated systems the sum will have the same form, but the sum over v should be over all vibrational states of all populated electronic states, and the sum over J should be over all the rotational and hyperfine quantum numbers. (See also the discussion above concerning statistical weights.)

If simulating a single vibrational band, say the origin band, the higher vibrational states will not necessarily be set up in the calculation, and will thus not be included in the sum leading to a partition function below the true value. At low temperatures, or if only relative intensities are required, this may be unimportant, but various approaches are available to correct for this. In principle all the required vibrational or electronic states could be included in the calculation, but this could lead to an unnecessarily complicated calculation and, in addition, the required constants may not be known. Two additional approaches to calculating the partition function are provided.

Firstly, a table of values may be supplied giving the partition function as a function of temperature; this is set up by adding an "interpolated partition function" object to a molecule. Values at the required temperature are derived by Lagrange interpolation from the supplied values, as used by the HITRAN database[31]. Some care can be needed in making sure the energy origins used in calculating the Boltzmann factors and the partition function are consistent. An energy zero, E_Q can be specified for the input partition function (which defaults to 0) and then the populations are calculated as:

$$\frac{g_i}{Q_{\text{ext}}} \exp\left(\frac{-\left(E_i - E_Q\right)}{k_B T}\right) \tag{42}$$

As discussed above, the lowest calculated energy is dependent on the details of the Hamiltonian, and will not necessarily be consistent with the energy origin chosen for the external partition function, Q_{ext}. A common choice would be to take the lowest energy as zero, and so an `AutoZero` option is provided (on by default) which multiplies the partition function by $\exp(-E_{\min}/k_B T)$ where $E_{\min}$ is the lowest calculated energy. This population function then becomes

$$\frac{g_i}{Q_{\text{ext}}} \exp\left(\frac{-\left(E_i - E_{\min} - E_Q\right)}{k_B T}\right) \tag{43}$$

which is equivalent to shifting the energy origin to the energy of the lowest state.

A slight modification to this, controlled by the `Multiply` flag, is for the provided function to scale the calculated partition function, rather than replace it. With the right setup, this is equivalent to supplying a vibronic partition function rather than an overall one, as can be seen if we make the approximation that the overall energy, $E_{v,J}$, can be decomposed into a vibrational part, E_v, and a rotational part, E_J. Under these circumstances the overall sum, equation (41) above, can be simplified to a product of two sums:

$$Q_{\text{TIPS}} \approx \left(\sum_v g_v \exp\left(\frac{-E_v}{kT} \right) \right)\left(\sum_J g_J \exp\left(\frac{-E_J}{kT} \right) \right) = Q_{\text{vib}} Q_{\text{rot}} \tag{44}$$

If PGOPHER is set up to only include the lowest vibronic level in the explicitly calculated partition function sum then the second term in the product, essentially the rotational partition function, will be evaluated exactly for the lowest vibronic level, and the first term, essentially the vibrational and electronic partition function, is calculated as one. Supplying Q_{vib} is then equivalent to the common assumption that the partition function can be evaluated as a product. This ignores (among other things) the dependence of rotational constants on vibration, and can be improved by including more states explicitly. In these circumstances the required external values are:

$$Q_{\text{ext}} \approx \frac{\displaystyle\sum_v g_v \exp\left(\frac{-E_v}{kT} \right)}{\displaystyle\sum_{v < v\max} g_v \exp\left(\frac{-E_v}{kT} \right)} \tag{45}$$

where $v_{\max}$ is the highest v included in the explicit calculation.

A second approach is to set up a separate vibrational and electronic energy level calculation in PGOPHER. This is possible with a "vibrational partition function" object, with an additional "molecule" object below it, which allows an independent energy level calculation for the vibronic partition function. The calculation is similar to that described in the previous calculation, evaluating both the sums in equation (45) above. The switchover point from the full to the vibronic only calculation is specified in terms of a switching energy, `ESwitch`. When set up in this way the partition function is still calculated by an explicit sum over states so needs to be checked for convergence as for the full sum as discussed above. This can be a time consuming calculation but is potentially more accurate as anharmonicity and coupling between modes can be included in the calculation while simple approaches do not[31].

2.8 Energy Levels in the Presence of an External Field

The transition moments discussed above are those required when calculating energy levels in the presence of a static external electric or magnetic field. In this case the projection quantum number, M, needs to be explicitly included in the calculation. For the purposes of the calculation, the current implementation requires that the space-fixed axis that defines M is taken as the direction of any external fields. This is equivalent to restricting the external

fields to the $p = 0$ component in spherical tensor notation, which has selection rules $\Delta M = 0$. Equation (2) above then becomes:

$$\left| miM \right\rangle = \sum_{\eta \in m, s, J, K} c^{miM}_{\eta sJK} \left| \eta sJKM \right\rangle \tag{46}$$

As external fields can mix states with different total angular momentum and symmetry, these move from labelling the overall basis set (on the left) to part of the sum on the right. Energy levels are now calculated by setting up a Hamiltonian matrix including all basis states that can contribute to a given value of M. Note that the final states and coefficients now depend on M, though the restriction to $p = 0$ component means that the sum need not be over M. The sum is also restricted to states in the given manifold m, which may require a set-up with all states in the same manifold.

The external field will also mix states of different J (hence the inclusion of J in the sum above) and the basis required here is in principle infinite. In practice a finite range of J will be used, but a range of J to include in the basis for the calculation must be specified and the calculation checked for convergence with respect to increasing the range of J. (A maximum J in the basis 1 or 2 higher than the highest J of interest is often sufficient.) The resulting matrices are likely to be quite large, but this size of calculation is required for exact calculations for molecules subject to fields required for molecular steering and trapping. It would be possible to reduce the computations required at lower fields by calculating Stark and Zeeman shifts using perturbation theory rather than a full diagonalization but this is not currently implemented.

To calculate transition moments in the presence of an external field the direction of the field(s) corresponding to absorbed or emitted radiation must also be specified. If the polarisation of this radiation is not random then the direction is specified by adding one or more "polarization" objects under the simulation object. This is equivalent to specifying the relative values of the tensor describing the external field, $T^1_p(E)$ in the notation above.

3 Molecule Types
The basis set, quantum numbers and Hamiltonian are detailed below for each of the three types of molecules covered here. The Hamiltonian is expressed in terms of angular momentum operators – note the distinction between the quantum number (J), the operator for a component ($\hat{J}_z$) and the vector operator for the angular momentum ($\hat{\mathbf{J}}$). The basis functions all involve rotation matrices to express implicitly the dependence of the rotational wavefunction on the angles between space- and molecule- fixed axis systems; the specific choice made is as described by Brown and Howard[32], which also describes the general method used to evaluate the matrix elements. The choice also dictates that the matrix elements of $\hat{J}_x$ are real and positive in both the space-fixed and molecule-fixed axis systems.

The matrix elements of $\hat{J}_y$ are then necessarily imaginary, but all the standard components of the Hamiltonians given below involve combinations of operators with all real matrix elements, so the default method of calculation is to use real numbers throughout. Imaginary operators typically appear when considering mixing between vibronic states, as (for example) in Coriolis interaction between two vibrational states for which the rotational operator is $\hat{J}_x$, $\hat{J}_y$ or $\hat{J}_z$. For this reason PGOPHER allows the entire wavefunction calculation to be done using complex arithmetic, controlled by the `AllowComplex` flag. If this flag is on the calculation is still carried out with real arithmetic unless imaginary operators are detected.

`AllowComplex` defaults to off, as multiplying imaginary matrix elements by $-i$ often makes little or no difference to the calculation. There are two considerations that lead to this small difference: Firstly, for some point groups all the matrix elements connecting two vibronic states are imaginary, in which case multiplying the imaginary matrix elements by $-i$ simply corresponds to a different choice of phase for the wavefunctions. Alternatively, imaginary matrix elements typically involve small mixing between states, for which the standard second order perturbation theory formula would give good results, and this formula is independent of the phase of the matrix elements.

In the sections below, standard "spectroscopic" units are used, in that in an energy expression such as

$$F(J) = BJ(J+1) - DJ^2(J+1)^2 \tag{47}$$

F, B and D all have the same energy equivalent units, with the factors of $h/2\pi$ from the angular momentum operators included in the rotational constants. (Constants can be input in any of the common spectroscopic units (cm^{-1}, MHz, eV or K) and the calculations are done in the same units.)

3.1 Linear Molecules

For each vibronic state, η, the standard components of the term symbol must be specified including the overall electron spin, S and the vibronic symmetry (Σ^+, Σ^-, Π, … and g or u if the molecule has a centre of symmetry). The vibronic symmetry implicitly gives the projection of the angular momentum excluding spin, $\mathbf{N} = \mathbf{J} - \mathbf{S}$ on the molecular (z) axis. This latter is in general $K = \Lambda + l$, the sum of an electronic orbital component, Λ, and a vibrational component, l. For simplicity Λ is used for this in PGOPHER and below, but it should be understood as K and the difference between vibrational and electronic angular momentum only manifests in the values of the parameters required. The other vibrational quantum numbers are not required for the calculation, but might be used in choosing the name for each state.

A Hund's case (a) basis is used, so the standard basis will contain the $2S + 1$ values of Ω, the projection of J on the z axis. Allowing for both possible signs of Λ this gives $2(2S+1)$ primitive basis functions $|\eta J \Lambda \Omega\rangle$ where $\Lambda \neq 0$. The overall (rovibronic) symmetry properties

must also be specified; a key symmetry is the overall parity of the wavefunction, + or −. It is often more convenient to use *e* and *f* labels to specify parity [33], as the parity typically alternates with *J*. These labels are defined such that:

e levels have parity +$(-1)^J$ (*J* integral) or +$(-1)^{J-\frac{1}{2}}$ (*J* half-integral)

f levels have parity −$(-1)^J$ (*J* integral) or − $(-1)^{J-\frac{1}{2}}$ (*J* half-integral)

Either parity or *e/f* labels can be used for display as selected by the `JAdjustSym` setting; on input either is accepted. The parity can be determined [34] from the effect of reflection in the *xz* molecular plane, σ_v. The primitive basis functions $|\eta J\Lambda\Omega\rangle = |\eta\Lambda\rangle|S\Sigma\rangle|J\Omega M\rangle$ are chosen to have the following symmetries[14]:

$$\sigma_v|\eta\Lambda\rangle = (-1)^{\Lambda+s}|\eta-\Lambda\rangle \tag{48}$$

where *s* is 1 for Σ^- states and 0 otherwise.

$$\sigma_v|S\Sigma\rangle = (-1)^{S-\Sigma}|S-\Sigma\rangle \tag{49}$$

were Σ (= $\Omega-\Lambda$) is the projection of *S* along the molecular axis and

$$\sigma_v|J\Omega M\rangle = (-1)^{J-\Omega}|J-\Omega M\rangle \tag{50}$$

To give basis functions with well-defined symmetry, symmetric and antisymmetric combinations of the primitive basis functions are taken:

$$|\eta J \pm \Omega\rangle = \begin{cases} \frac{1}{\sqrt{2}}\left\{|\eta J\Lambda\Omega\rangle \pm |\eta J-\Lambda-\Omega\rangle\right\} & \text{if } \Omega \neq 0 \text{ or } \Lambda \neq 0 \\ |\eta J\Lambda\Omega\rangle & \text{if } \Lambda = \Omega = 0 \end{cases} \tag{51}$$

In this equation Λ is taken as ≥ 0 and the range of Ω is $|\Lambda|+S$ to $|\Lambda|-S$. The basis state is then specified by η (implying $|\Lambda|$), *J*, an optional sign (+ or −) and Ω, and has parity $\pm(-1)^{J-S+s}$.

While a Hund's case (a) basis is used, the basis is complete (in Ω) so the calculations are exact even if the molecule is case (b). There are various possible approaches to other Hund's cases; for case (c) a separate vibronic state (η) for each value of Ω can be appropriate, which is possible via the `OmegaSelect` setting and/or the choice of Λ and *S* for each state. For Ω integer, $\Lambda = \Omega$ and *S* = 0 is the most straightforward choice. The values of Λ and *S* used are to a certain extent arbitrary for Hund's case (c), though they will affect the definition of the molecular parameters.

To assign Ω values to eigenstates the sub-basis mechanism described above is used, which requires an expected energy ordering for different Ω values for a given *J*. In spectroscopic terms, this translates to knowing whether the electronic state is normal or inverted. In principle this is just given by the sign of the spin-orbit coupling constant, *A*, but a different test is needed if $\Lambda = 0$ to account for spin-spin terms or if *A* = 0, so the test used in practice is to compare the diagonal matrix elements of the Hamiltonian for the states with

$\Omega = |\Lambda|+S$ and $\Omega = |\Lambda|-S$ for the smallest possible J (= $|\Lambda|+S$) for which all Ω components are present. If $\Lambda = 0$ the states with $J = \Omega = S$ and $J = S$, $\Omega = 0$ are compared. The choice of smallest J maximizes the contributions from the spin-orbit and spin-spin terms, though other terms can be important if the states compared are very close in energy. (This is where $A \approx 2B$ in the absence of other terms.) To allow for cases where this fails (possible in case of strong mixing between electronic states) the `OmegaOrder` setting allows the test for normal or inverted to be overridden.

The energy ordering scheme is also used to assign the other quantum numbers commonly used for linear molecules. For small values of A, the energy will be approximately $BN(N+1)$ so for a given J, where the possible values of the N quantum number are $J-S$ to $J+S$, the expected ordering is $N = J-S$, $N = J-S-1$, ... This also applies to the other label used for linear molecule spin states, the spin component number, typically written as F_1, F_2, F_3..., for which the expected energy ordering is $F_1 < F_2 < F_3$ ... The assignment of N and F_n is potentially more reliable than Ω as the expected energy ordering is independent of the molecular constants. For all of these quantum numbers the energy ordering scheme used for assignment means the values assigned are stable even if, as will commonly be the case, one or more of them is a poor quantum number.

The lowest J levels, with $J < |\Lambda|+S$, require special consideration as there are some missing values of the quantum numbers. The expected energy ordering is unchanged and the values of Ω and N to omit are straightforward, given the requirements $J \geq |\Omega|$, $N \geq |\Lambda|$ and $J \geq |N-S|$. However, the choice of spin component number to omit is less straightforward, and a slightly non-standard choice is made. If the F_1 level is taken as the level with $J = N + S$ then this should be omitted for the lowest J. This choice can lead to some unphysical switches in branch labels such as ${}^r R_1(J)$, which are conventionally done in terms of spin component number. The choice of omitted spin component is therefore made by considering the normal/inverted test described above, and for non-inverted states F_1 is kept and the higher spin components discarded. This is equivalent to deriving the spin component number from Ω, rather than N, and only makes a difference for the lowest J levels of non-inverted states. A specific example is the $X^2\Pi$ state of NO; the scheme used here will assign all the strong R branch transitions in the fundamental band of NO in the infrared to ${}^r R_1(J)$ while the alternative choice would assign the first member as ${}^r R_2(\frac{1}{2})$. In practice the choices described above typically correspond to the normal choice in the literature. The only known common case where this does not hold is for the lowest level in the $X^3\Sigma^-_g$ state of O_2 which has $J=0$, $N=1$ and e symmetry and which PGOPHER will label with F_1 by default but F_3 is also used in the literature. (The higher energy levels are not affected.) The alternative labelling scheme can be forced for O_2 by setting `OmegaOrder` to `Inverted`.

The Hamiltonian used is, as far as possible, consistent with the bulk of the literature. The rotational operator is taken as the standard power series expansion in the angular momentum excluding spin, **N**:

$$H_{\text{rot}} = B\hat{\mathbf{N}}^2 - D\hat{\mathbf{N}}^4 + H\hat{\mathbf{N}}^6 + L\hat{\mathbf{N}}^8 + M\hat{\mathbf{N}}^{10} + P\hat{\mathbf{N}}^{12} \tag{52}$$

To evaluate matrix elements of H_{rot}, the standard substitution $\hat{\mathbf{N}}^2 = (\hat{\mathbf{J}} - \hat{\mathbf{S}})^2$ is made, and the matrix elements of $\hat{\mathbf{J}}$ and $\hat{\mathbf{S}}$ are well known for a Hund's case (a) basis[32]. Matrix elements of $\hat{\mathbf{N}}^{2n}$ are evaluated by setting up the matrix of $\hat{\mathbf{N}}^2$, and then taking powers of the matrix. As discussed by Brown et al[35], strictly $\hat{\mathbf{N}}$ in the above should be replaced by the rotational angular momentum of the nuclear framework, $\hat{\mathbf{R}} = \hat{\mathbf{J}} - \hat{\mathbf{S}} - \hat{\mathbf{L}}$. The form involving $\hat{\mathbf{N}}$ is more common, but the form with $\hat{\mathbf{R}}$ can be used by setting the `RSquaredH` flag to true. This replaces even powers of $\hat{\mathbf{N}}$ with $\hat{\mathbf{R}}$ throughout, including the operators below. The difference in practice is small, with the main effect a shift of the origin of $B\Lambda^2$ in the energy levels. The definition of the origin of a particular vibronic state in any case needs careful checking when using literature values; the choice here corresponds to the energy with all terms (apart from the origin) zero, which can be significantly different from the energy of the lowest level and the choice made in some papers.

The fine structure terms required for $S > 0$ are based on IUPAC recommendations[36]. In the list below, $[\ldots]_+$ indicates an anti-commutator:

$$\hat{O},\hat{Q}\big._+ = \hat{O}\hat{Q} + \hat{Q}\hat{O} \tag{53}$$

The spin-orbit terms are:

$$\hat{H}_{\text{SO}} = A\hat{L}_z\hat{S}_z + \frac{A_D}{2}\big[\hat{N}^2, \hat{L}_z\hat{S}_z\big]_+ + \eta\hat{L}_z\hat{S}_z\big(\hat{S}_z^2 - \tfrac{1}{5}(3\hat{S}^2 - 1)\big) \tag{54}$$

As discussed by Brown et al[37] the term in η is only required for $S > 1$. For $S > \tfrac{1}{2}$ spin-spin terms are also required:

$$\begin{aligned}
\hat{H}_{\text{SS}} &= \tfrac{2}{3}\lambda\big(3\hat{S}_z^2 - \hat{S}^2\big) + \tfrac{1}{2}\lambda_D\big[\tfrac{2}{3}\big(3\hat{S}_z^2 - \hat{S}^2\big), \hat{N}^2\big]_+ + \tfrac{1}{2}\lambda_H\big[\tfrac{2}{3}\big(3\hat{S}_z^2 - \hat{S}^2\big), \hat{N}^4\big]_+ \\
&\quad + \tfrac{1}{12}\theta\big(35\hat{S}_z^4 - 30\hat{S}^2\hat{S}_z^2 + 25\hat{S}_z^2 - 6\hat{S}^2 + 3\hat{S}^4\big)
\end{aligned} \tag{55}$$

The term in θ is only required[35] for $S > 3/2$. The spin rotation interaction has the form:

$$\begin{aligned}
\hat{H}_{\text{SR}} &= \gamma\hat{\mathbf{N}}\cdot\hat{\mathbf{S}} + \tfrac{1}{2}\gamma_D\big[\hat{\mathbf{N}}\cdot\hat{\mathbf{S}}, \hat{\mathbf{N}}^2\big]_+ + \tfrac{1}{2}\gamma_H\big[\hat{\mathbf{N}}\cdot\hat{\mathbf{S}}, \hat{\mathbf{N}}^4\big]_+ + \tfrac{1}{2}\gamma_L\big[\hat{\mathbf{N}}\cdot\hat{\mathbf{S}}, \hat{\mathbf{N}}^6\big]_+ \\
&\quad - \sqrt{70/3}\,\gamma_S T_0^2\big\{T^1(\hat{\mathbf{J}}), T^3(\hat{\mathbf{S}})\big\}
\end{aligned} \tag{56}$$

The term in γ_S is only required[38] for $S > 1$ and Brown and Milton[39] have given the only non-zero matrix element:

$$\begin{aligned}
&\langle\eta\Lambda S\Sigma \pm 1 J\Omega \pm 1|\hat{H}_{\text{SR}}^{(3)}|\eta\Lambda S\Sigma J\Omega\rangle \\
&= -\tfrac{1}{2}\gamma_S[S(S+1) - 5\Sigma(\Sigma \pm 1) - 2]\sqrt{J(J+1) - \Omega(\Omega \pm 1)}\sqrt{S(S+1)\Sigma(\Sigma \pm 1)}
\end{aligned} \tag{57}$$

Λ-type doubling is implemented for Π states:

$$\hat{H}_{\mathrm{LD}} = \tfrac{1}{2}o\left(\hat{S}_+^2 e^{-2i\phi} + \hat{S}_-^2 e^{+2i\phi}\right) - \tfrac{1}{2}p\left(\hat{N}_+\hat{S}_+ e^{-2i\phi} + \hat{N}_-\hat{S}_- e^{-2i\phi}\right) + \tfrac{1}{2}q\left(\hat{N}_+^2 e^{-2i\phi} + \hat{N}_-^2 e^{-2i\phi}\right)$$
$$+ \tfrac{1}{4}\left[\hat{S}_+^2 e^{-2i\phi} + \hat{S}_-^2 e^{+2i\phi}, o_D\hat{\mathbf{N}}^2 + o_H\hat{\mathbf{N}}^4 + o_L\hat{\mathbf{N}}^6\right]_+$$
$$- \tfrac{1}{4}\left[\hat{N}_+\hat{S}_+ e^{-2i\phi} + \hat{N}_-\hat{S}_- e^{-2i\phi}, p_D\hat{\mathbf{N}}^2 + p_H\hat{\mathbf{N}}^4 + p_L\hat{\mathbf{N}}^6\right]_+$$
$$+ \tfrac{1}{4}\left[\hat{N}_+^2 e^{-2i\phi} + \hat{N}_-^2 e^{-2i\phi}, q_D\hat{\mathbf{N}}^2 + q_H\hat{\mathbf{N}}^4 + q_L\hat{\mathbf{N}}^6\right] \tag{58}$$

The terms in $e^{\pm 2i\phi}$ ensure that the Λ-doubling operators only connect the two halves of a Π state:

$$\left\langle \eta'\Lambda = \pm 1 \middle| e^{\pm 2i\phi} \middle| \eta\Lambda = \mp 1 \right\rangle = +1 \tag{59}$$

For Λ doubling the term in q applies to any Π state, p requires $S > 0$ and o requires $S > \tfrac{1}{2}$. Λ doubling for Δ and higher Λ states can be implemented using the more general perturbation mechanism, and this can also be used for higher powers of $\hat{\mathbf{N}}^2$ that are not specifically included in the above. This is covered in some detail on the online documentation.

The definition of the vibronic transition moments requires some care. The general form, $\left\langle \eta' \middle| T_q^k(\mu) \middle| \eta \right\rangle$ above, hides some detail as there will in general be two symmetry-related matrix elements:

$$\left\langle \eta'\Lambda'S'\Sigma' \middle| T_q^k(\mu) \middle| \eta\Lambda S\Sigma \right\rangle = (-1)^{S'-S+s'-s} \left\langle \eta'-\Lambda'S'-\Sigma' \middle| T_{-q}^k(\mu) \middle| \eta-\Lambda S-\Sigma \right\rangle \tag{60}$$

The relationship between the two comes from applying the σ_v operator to all components of the transition moment and using equations (48) and (49), combined with the selection rule $\Omega' - \Omega = q = \Lambda' + \Sigma' - \Lambda - \Sigma$. (An additional $(-1)^k$ is required for magnetic dipole transitions.) The value input to the program is the transition moment satisfying $\Omega' - \Omega = q$ with the transition moment with the opposite sign of q calculated from the above. For $q = 0$ this does not uniquely specify the transition moment, so the transition moment with $\Lambda' > 0$ is specified, or $\Sigma' > 0$ if $\Lambda' = 0$. This is only important if more than one transition moment contributes to a given transition when interference between the transition moments is possible, in which case the relative signs make a difference.

3.2 Symmetric Tops

For each vibronic state, η, the overall electron spin, S, and vibronic symmetry must be specified. As for linear molecules, the make-up of the overall vibronic symmetry in terms of vibrational and electronic parts does not affect the form of the Hamiltonian used, though it will affect the magnitudes of the parameters. Unlike the linear case, the angular momentum excluding spin, $\mathbf{N} = \mathbf{J} - \mathbf{S}$, is normally a good quantum number, so the primitive basis states are specified by J, N and the projection of $\mathbf{N}$ along the highest order symmetry axis, K, giving $(2S+1)(2J+1)$ functions for a given J. If required, the values of $|K|$ included in the basis can be reduced from the standard range of 0 to N by specifying a minimum or maximum K. This can be essential to avoid divergence in calculations where only a limited range of K is known. For vibronic states that are degenerate (E symmetry) the size of the basis is typically doubled, and

the component of the vibronic state is specified by an l quantum number with values ±1. This is similar to Λ in the linear case, in that it can contain both vibrational and electronic parts but it is not strictly an angular momentum quantum number.

The primitive basis states need some adaptation to give basis states of well-defined rovibronic symmetry, as discussed by Hegelund et al[40]; see also section 12.4 of Bunker and Jensen[10]. Non-degenerate rovibronic basis states are typically symmetric or antisymmetric combinations of the primitive basis states:

$$\left| \eta J N \pm K l \right\rangle = \frac{1}{\sqrt{2}} \left\{ \left| \eta J N K l \right\rangle \pm \left| \eta J N - K - l \right\rangle \right\} \tag{61}$$

with the obvious exception of $K = l = 0$ where there is only one primitive basis state. Degenerate rovibronic states occur as pairs of primitive basis states, $|\eta JNKl\rangle$ and $|\eta JN{-}K{-}l\rangle$, with no matrix elements between them. In these cases the overall Hamiltonian matrix factors into two identical blocks, so it is only necessary to calculate one of the blocks and thus use one of the pair of degenerate primitive basis states. The only proviso is that matrix elements within the block must not be discarded, which is done by selecting the state with a positive value of the quantum number ϕ (as used in reference [40]) or g (reference [10]). For most point groups there are no matrix elements off-diagonal in this quantum number, even in the presence of the field, though special action is required for D_{2nd} groups. (An extra factor of two is in principle introduced into the overall degeneracy of these states though in practice this vanishes when combined with the calculation of the nuclear spin statistical weights.) Overall, the basis states are specified by η, J, N (if $S > 0$), K, l (for degenerate vibronic states) and a sign for non-degenerate rovibronic states if $K \neq 0$.

The quantum numbers for the final eigenstates are given in terms of $|K|$ and, for degenerate vibronic states, the sign of Kl, which is most in line with standard usage. The sign of Kl is designed to be consistent with the definition of Hoy and Mills[41]. The sub-basis mechanism can be used to assign these quantum numbers. For non-degenerate states this is straightforward, with a single sub-basis being made up of states with all K for a given J, N and rovibronic symmetry. A particular value of $|K|$ will only appear once in any given sub-basis, and the expected ordering follows from classifying the molecule as prolate or oblate from the rotational constants. Degenerate states are more complicated, as the essential K dependence of the energy for an oblate rigid rotor becomes $(C{-}B)K^2 - 2C\zeta Kl$. (Read A for C for a prolate rotor.) For a given sign of Kl the ordering depends on $|K|$ as before, but the ordering of the $Kl < 0$ and $Kl > 0$ sets is not well defined. They are therefore put into separate sub-bases. Special consideration is required for $K = 0$ as the sub-basis it belongs to depends on the relative sign of $C{-}B$ and ζ. For an oblate top ($C{-}B < 0$) with $\zeta > 0$, the $K = 0$ level will be the highest energy of the $Kl > 0$ set so is put in the same sub-basis, but the other set if $\zeta < 0$ or prolate. Given mixing between states of different $|K|$ is typically small for symmetric tops, the sub-basis mechanism is important only when $S \neq 0$ and the default is not to use it but

rather to look for the basis state with the largest coefficient to assign K and l. (This is controlled by the `LimitSearch` setting for the manifold.)

The overall rovibronic symmetry is also part of the specification of the final eigenstates, and is required in principle to completely specify the state. For example, for molecules with C_{3v} symmetry, levels of non-degenerate vibronic states with $K = 3n$ are split by a small amount, with the levels having A_1 and A_2 symmetry. This splitting is sufficiently small so that it is often ignored, though it can be significant for degenerate vibronic states, particularly for $K = 1$. Transitions involving such states will typically show in PGOPHER simulations as a pair of transitions with the same frequency while some other sources may show them as a single line. These non-degenerate states typically show patterns of levels that alternate with J; for the C_{3v} example the A_1 level is alternatively above and below the A_2 level with increasing J. To assist in these cases an alternative way is provided of specifying the rovibronic symmetry, analogous to the e/f notation used in linear molecules. A_1 and A_2 become A_+ and A_- for even J, and vice versa for odd J. Similar notation is occasionally found in the literature – see Tarrago and Nhu[42] and the HITRAN database[43]. The same logic applies to any point groups with A_1/A_2 or B_1/B_2 pairs of symmetries; E symmetry levels are left unchanged as they do not show an alternation with symmetry. The use on output is controlled by the `JAdjustSym` setting; on input either is accepted.

The rotational Hamiltonian is standard for symmetric tops [11]:

$$
\begin{aligned}
H_{\mathrm{rot}} = {}& B\hat{\mathbf{N}}^2 + (C - B)\hat{N}_z^2 + \left(-2C\zeta + \eta_J\hat{\mathbf{N}}^2 + \eta_K\hat{N}_z^2\right)\hat{l}_z\hat{N}_z \\
& - D_J\hat{\mathbf{N}}^4 - D_{JK}\hat{\mathbf{N}}^2\hat{N}_z^2 - D_K\hat{N}_z^4 \\
& + H_J\hat{\mathbf{N}}^6 + H_{JK}\hat{\mathbf{N}}^4\hat{N}_z^2 + H_{JK}\hat{\mathbf{N}}^2\hat{N}_z^4 + H_K\hat{N}_z^6 \\
& + L_J\hat{\mathbf{N}}^8 + L_{JJK}\hat{\mathbf{N}}^6\hat{N}_z^2 + L_{JK}\hat{\mathbf{N}}^4\hat{N}_z^4 + L_{KKJ}\hat{\mathbf{N}}^2\hat{N}_z^6 + L_K\hat{N}_z^8
\end{aligned}
\tag{62}
$$

Note that ζ is dimensionless. For prolate tops, replace C by A. This only has diagonal matrix elements, which follow by replacing $\hat{\mathbf{N}}^2$ by $N(N+1)$, $\hat{N}_z$ by K and $\hat{l}_z$ by l. Various l-doubling terms are also available, which apply to vibronic states of E symmetry:

$$
\begin{aligned}
\hat{H}_{\mathrm{ID}} = {}& \tfrac{1}{2}\left(q_+ + D_{qJ}\hat{\mathbf{N}}^2\right)\left(\hat{N}_+^2\hat{l}_+^2 + \hat{N}_+^2\hat{l}_+^2\right) + \tfrac{1}{2}\left[\hat{N}_+^2\hat{l}_+^2 + \hat{N}_+^2\hat{l}_+^2, D_{qK}\hat{N}_z^2\right]_+ \\
& + \tfrac{1}{2}q_-\left(\hat{N}_+^2\hat{l}_-^2 + \hat{N}_-^2\hat{l}_+^2\right) \\
& + \left(r + D_{rJ}\hat{\mathbf{N}}^2\right)\left[\hat{N}_+\hat{l}_-^2 + \hat{N}_-\hat{l}_+^2, \hat{N}_z\right]_+ + D_{rK}\left[\left[\hat{N}_+\hat{l}_-^2 + \hat{N}_-\hat{l}_+^2, \hat{N}_z\right]_+, \hat{N}_z^2\right]_+
\end{aligned}
\tag{63}
$$

The $\hat{l}_\pm^2$ operator is taken to have the following non-zero matrix elements:

$$
\langle l \pm 1 | \hat{l}_+^2 | l \mp 1 \rangle = 1
\tag{64}
$$

The q_+ term and associated centrifugal distortion terms, D_{qJ} and D_{qK} are potentially present for all symmetric tops, but there are symmetry restrictions for the other terms. These are

discussed by Cartwright and Mills[44]; note that their constants ($q_t^{(+)}$, $q_t^{(-)}$ and r_t) are defined to include the vibrational dependence as for example :

$$q_+ = \tfrac{1}{2}\rho\sqrt{(v_t+1)^2 - l_t^2}\, q_t^{(+)} \tag{65}$$

Here ρ defines the sign convention for the constant, and Cartwright and Mills[44] suggest the use of $\rho = -1$. Care needs to be taken with the sign of the l doubling; it is perhaps best specified in terms of the ordering of selected levels, such as the $K = l = \pm1$ levels in C$_{3v}$. With the definition above, a positive value of q_+ will put the A$_1$ levels above A$_2$ levels for odd J, or the A$_+$ levels below the A$_-$ levels using the notation introduced above.

The spin-rotation terms (needed if $S > 0$) are based on the asymmetric top S-reduction form described below:

$$\begin{aligned}
\hat{H}_{sr} &= \tfrac{1}{2}\varepsilon_{bb}\left(\hat{N}_+\hat{S}_- + \hat{N}_-\hat{S}_+\right) + \varepsilon_{cc}\hat{N}_z\hat{S}_z \\
&\quad + D_N^s\hat{\mathbf{N}}^2\hat{\mathbf{N}}\cdot\hat{\mathbf{S}} + \tfrac{1}{2}D_{NK}^s\left(\hat{\mathbf{N}}^2\hat{N}_z\hat{S}_z + \hat{N}_z\hat{S}_z\hat{\mathbf{N}}^2\right) + D_{KN}^s\hat{\mathbf{N}}\cdot\hat{\mathbf{S}}\hat{N}_z^2
\end{aligned} \tag{66}$$

and electron spin-orbit and spin-spin terms are:

$$\hat{H}_{ss} = \alpha\left(3\hat{S}_z^2 - \hat{\mathbf{S}}^2\right) + \tfrac{1}{2}\beta\left(\hat{S}_+^2 + \hat{S}_-^2\right) + a_{eff}\hat{l}_z\hat{S}_z \tag{67}$$

As for the linear case, centrifugal distortion and other terms not included among the standard parameters above can be implemented by perturbations.

As for linear molecules, there can be two possible vibronic transition moments related by symmetry for perpendicular bands. Specifically the value of one vibronic transition moment, $\left\langle \eta' \middle| T_q^k(\mu) \middle| \eta \right\rangle$, is input to the program which gives transitions with $K' = K + q$. The transition moment with the opposite sign of q is then calculated by symmetry.

3.3 Asymmetric Tops

For asymmetric tops a symmetric top primitive basis is used, $|\eta JNK\rangle$, involving the same η, J, N, S and K quantum numbers described in the previous section. The complication of degenerate vibronic states is not possible for asymmetric tops so the l quantum number is not required, but the choice of the axis used to define K is now not obvious. Here we use the molecule-fixed z axis as the quantization axis for K, but this can be mapped to any of the three principal inertial axes, a, b or c. A choice must also be made for the x and y axes, giving six possible choices, normally referred to as the representation and specified using the notation devised by King *et al*[45] shown in Table 1.

Table 1 Definition of the Representation for the axis system for asymmetric tops

	Representation					
	Ir	IIr	IIIr	Il	IIl	IIIl
z	a	b	c	a	b	c
x	b	c	a	c	a	b
y	c	a	b	b	c	a

Which of the six representations is used must be specified as part of the process of setting up the calculation. It is important to be aware of which representation is used, as many of the parameters below are specified in terms of operators in the x, y and z axis system rather than the a, b and c system used to specify the rotational constants A, B and C. For example, the centrifugal distortion term $D_K \hat{N}_z^4$ is defined in terms of the $\hat{N}_z$ operator and thus the z axis. Likewise the $\delta_J \left(\hat{N}_+^4 + \hat{N}_-^4 \right)$ term is defined in term of the $\hat{N}_\pm = \hat{N}_x \pm i\hat{N}_y$ operator, and thus the x and y axes. Changing the representation thus changes the definition of the constants, and converting constants is not straightforward.

To give basis states of well-defined symmetry, symmetric and antisymmetric combinations of the primitive basis states are taken:

$$\left| \eta J N \pm K \right\rangle = \frac{1}{\sqrt{2}} \left\{ \left| \eta J N K \right\rangle \pm \left| \eta J N - K \right\rangle \right\} \tag{68}$$

and the basis states are then completely specified by η, J, N, K and a sign (+ or −) for $K \neq 0$. These are the standard Wang combinations, for which the notation E+, E−, O+ and O− is used, where E and O refer to even and odd K and the sign is the sign in the above. Unlike the symmetric top case the symmetry is not required as part of the basis specification. If the PhaseAdjust setting is on, the functions above are multiplied by an additional phase factor given in Table 2, which will remove the need for imaginary matrix elements in some circumstances where odd powers of $\hat{N}_y$ are used.

Table 2 Phase factors applied when the PhaseAdjust setting is on.

	K even, +	K even, −	K odd, +	K odd, −
	E+	E−	O+	O−
N even	1	−i	i	−1
N odd	i	−1	1	−i

The overall rovibrational symmetry is specified in terms of irreducible representations of the point group. For this to be possible, the correspondence between the principal inertial axes and the elements of the point group must be specified, via the C2zAxis and C2xAxis settings. In C$_{2v}$ the C2zAxis setting specifies the z' axis of the point group (the C$_2$ axis) and the C2xAxis setting specifies the x' axis of the point group which is normally chosen to be

the out of plane axis in planar molecules. Primes are used here to emphasize that the conventional axes for the point group (x', y' and z') can be different from the axes that define the axis representation (Table 1). For example, in C_{2v} the point group would typically take z along the C_2 axis, but there is no necessity to choose this axis to define K in the basis. The meaning of `C2zAxis` and `C2xAxis` depend on the point groups; see Table 3 for details.

Table 3 Symmetry properties for asymmetric tops

	`C2zAxis`	`C2xAxis`	J adjusted symmetry labels
C_1	$-^a$	-	A always
C_i	$-^a$	-	A_g/A_u
C_2	$C_2(z')$	-	E/O, +/− or E+O−/E−O+
C_s	$\sigma(x'y')^b$	-	E/O, +/− or E+O−/E−O+
D_2	$C_2(z')$	$\sigma(y'z')^b$	E+/O−/E−/O+
C_{2v}	$C_2(z')$	x'	E+/O−/E−/O+
C_{2h}	$C_2(z')$	-	Eg/Og/Eu/Ou, +g/−g/+u/−u or E+O−g/E−O+g/E+O−u/E−O+u
D_{2h}	$C_2(z')$	$C_2(x')$	E+g/O−g/E−g/O+g/E+u/O−u/E−u/O+u

^a All rotational states of a given vibronic state have the same symmetry; J adjusted symmetry is the same as the standard rovibronic symmetry.

^b Axis is perpendicular to specified plane of symmetry.

While the individual Wang combination basis functions will have a specific rovibrational symmetry, the relationship depends on N, the point group, the representation, the `C2zAxis` and `C2xAxis` settings and the vibronic symmetry. To factor out the N dependence (as for e and f in linear molecules) notation based on the Wang labels, E+/E−/O+/O− is used, if the `JAdjustSym` setting in on. The assignment of these labels is based on the symmetries of totally symmetric vibronic states so, for example, the E+ label is used for any state which has the same overall rovibronic symmetry as even K symmetric combinations for a totally symmetric vibronic state. For point groups other than C_{2v} some adjustment to this notation is needed; for molecules with a centre of symmetry a g or u label is added from the rovibronic symmetry. For the lower symmetry groups some of the labels must be combined, as some rovibronic symmetries correspond to more than one Wang combination. The variations are summarised in Table 3.

An additional symmetry notation used in asymmetric tops is *ee/eo/oe/oo* where the first and second letters specify the whether the K_a or K_c quantum numbers are even or odd respectively. These can be mapped to the symmetries specified above, and are used in specifying the statistical weights – the weights are given for levels with *ee*, *eo*, *oe* and *oo* symmetry for totally symmetric vibronic levels, and the weights are adjusted as required for other vibronic symmetries. The mapping between all three symmetry notations depends on many factors, and there are too many possibilities to tabulate here, but PGOPHER will print a

symmetry table for each vibronic state if requested. Two sample tables are presented in Figure 3.

```
Symmetry Table for A1 C2v PseudoC2v:False Ir C2zaxis:a C2xaxis:c
 A1 0 ee E+ Ka+Kc=N    (Even N) E- Ka+Kc=N+1 (Odd N)
 A2 1 eo E- Ka+Kc=N+1 (Even N) E+ Ka+Kc=N    (Odd N)
 B1 2 oo O+ Ka+Kc=N    (Even N) O- Ka+Kc=N+1 (Odd N)
 B2 3 oe O- Ka+Kc=N+1 (Even N) O+ Ka+Kc=N    (Odd N)

J adjusted Symmetry Table
 E+: Even N: A1 0  ee E+ Ka+Kc=N    Odd N: A2 1  eo E+ Ka+Kc=N
 E-: Even N: A2 1  eo E- Ka+Kc=N+1  Odd N: A1 0  ee E- Ka+Kc=N+1
 O+: Even N: B1 2  oo O+ Ka+Kc=N    Odd N: B2 3  oe O+ Ka+Kc=N
 O-: Even N: B2 3  oe O- Ka+Kc=N+1  Odd N: B1 2  oo O- Ka+Kc=N+1

Symmetry Table for B1 C2v PseudoC2v:False Ir C2zaxis:a C2xaxis:c
 A1 0 oo O+ Ka+Kc=N    (Even N) O- Ka+Kc=N+1 (Odd N)
 A2 1 oe O- Ka+Kc=N+1 (Even N) O+ Ka+Kc=N    (Odd N)
 B1 2 ee E+ Ka+Kc=N    (Even N) E- Ka+Kc=N+1 (Odd N)
 B2 3 eo E- Ka+Kc=N+1 (Even N) E+ Ka+Kc=N    (Odd N)

J adjusted Symmetry Table
 E+: Even N: A1 0  oo O+ Ka+Kc=N    Odd N: A2 1  oe O+ Ka+Kc=N
 E-: Even N: A2 1  oe O- Ka+Kc=N+1  Odd N: A1 0  oo O- Ka+Kc=N+1
 O+: Even N: B1 2  ee E+ Ka+Kc=N    Odd N: B2 3  eo E+ Ka+Kc=N
 O-: Even N: B2 3  eo E- Ka+Kc=N+1  Odd N: B1 2  ee E- Ka+Kc=N+1
```

Figure 3 Sample symmetry table printout for vibronic states of A_1 (first half) and B_1 symmetry in C_{2v}.

There can be circumstances in which it is appropriate to use a higher effective symmetry than the molecule possesses, because the important terms in the Hamiltonian involve even powers of the rotational Hamiltonian, giving an effective C_2 symmetry around each axis, isomorphic to D_2 and C_{2v}. The `PseudoC2v` setting is available to indicate this situation. This forces the use of C_{2v} symmetry (or D_{2h} symmetry if the molecule has a centre of symmetry) in calculations, potentially speeding then up by a factor of 16. Alternatively the higher effective symmetry can be set, in which case the `FakeSym` setting may be required to disable some logic that would otherwise limit possible transitions. (For an example of an exclusion, compare a molecule with C_{2v} symmetry, which can only have a dipole moment along one axis, to a molecule with C_1 symmetry, which can have a dipole moment along any axis.)

The conventional rotational quantum numbers for asymmetric tops are K_a and K_c, corresponding to $|K|$ along the a and c axes in the prolate and oblate limits respectively. While K_a and K_c are not good quantum numbers away from these limits, the sub-basis mechanism can be used to assign them, as there is a clear expected energy ordering with levels increasing in energy with K_a and decreasing with K_c. The ordering is thus $J_{KaKc} = J_{0,J}, J_{1,J}, J_{1,J-1}, \dots, J_{J,1}, J_{J,0}$. For the sub-basis mechanism, each of the Wang combination types are put in a separate sub-basis as mixing between these is likely to be small because of the effective C_{2v} or D_2 symmetry of the important terms in the Hamiltonian discussed above. The symmetry

mapping mentioned above determines the set of K_a and K_c quantum numbers included in each sub-basis, and the expected energy ordering then gives the assignment within the sub-basis. The basis is specified in terms of single K value; for the Ir or Il representation where $K = K_a$, the K_c value associated with the basis is determined by symmetry, and similarly for IIIr or IIIl, where $K = K_c$. For IIr or IIl where $K = K_b$, the mapping to K_a and K_c is not as straightforward; the possible values of K_b are also limited by symmetry and the choice made is that if $B \geq (A+C)/2$ then the K_a and K quantum numbers are taken in the same order and if $B < (A+C)/2$ then the K_c and K quantum numbers are taken in the same order. This does not affect the final K_a and K_c assignment as the energy ordering logic is not changed, but can affect some details of the wavefunction display.

The rigid rotor Hamiltonian can be specified in two ways, either the standard form:

$$\hat{H}_{\text{rot}} = A\hat{J}_a^2 + B\hat{J}_b^2 + C\hat{J}_c^2 \tag{69}$$

or an alternate form:

$$\hat{H}_{\text{alt}} = A\hat{J}_z^2 + \overline{B}\left(\hat{\mathbf{J}}^2 - \hat{J}_z^2\right) + \tfrac{1}{4}\delta\left(\hat{J}_+^2 + \hat{J}_-^2\right) \tag{70}$$

The alternate form can give better determined parameters if two of the rotational constants are very similar, and low resolution spectra may be insensitive to δ. A common application of this is a near-prolate top where $B \approx C$ and, for a Ir or Il representation:

$$\overline{B} = \tfrac{1}{2}(B+C) \tag{71}$$

$$\delta = B - C \tag{72}$$

(In practice the alternate form is always used for evaluating matrix elements, with appropriate values substituted for A, $\overline{B}$ and δ.)

The centrifugal distortion terms can use either the A-reduced or S-reduced forms proposed by Watson[46], controlled by the `SReduction` flag. It is important to specify the form used, along with the axis representation in any calculation as the definition of the constants depends on both of these. The specific forms used are:

A-Reduction:

$$\begin{aligned}
\hat{H}_{\text{A}} = {}&-\Delta_J\hat{\mathbf{N}}^4 - \Delta_{JK}\hat{\mathbf{N}}^2\hat{N}_z^2 - \Delta_K\hat{N}_z^4 - \tfrac{1}{2}\left[\delta_J\hat{\mathbf{N}}^2 + \delta_K\hat{N}_z^2, \hat{N}_+^2 + \hat{N}_-^2\right]_+ \\
&+ \Phi_J\hat{\mathbf{N}}^6 + \Phi_{JK}\hat{\mathbf{N}}^4\hat{N}_z^2 + \Phi_{KJ}\hat{\mathbf{N}}^2\hat{N}_z^4 + \Phi_K\hat{N}_z^6 \\
&+ \tfrac{1}{2}\left[\phi_J\hat{\mathbf{N}}^4 + \phi_{JK}\hat{\mathbf{N}}^2\hat{N}_z^2 + \phi_K\hat{N}_z^4, \hat{N}_+^2 + \hat{N}_-^2\right]_+ \\
&+ L_J\hat{\mathbf{N}}^8 + L_{JJK}\hat{\mathbf{N}}^6\hat{N}_z^2 + L_{JK}\hat{\mathbf{N}}^4\hat{N}_z^4 + L_{KKJ}\hat{\mathbf{N}}^2\hat{N}_z^6 + L_K\hat{N}_z^8 \\
&+ \tfrac{1}{2}\left[l_J\hat{\mathbf{N}}^6 + l_{JK}\hat{\mathbf{N}}^4\hat{N}_z^2 + l_{KJ}\hat{\mathbf{N}}^2\hat{N}_z^4 + l_K\hat{N}_z^6, \hat{N}_+^2 + \hat{N}_-^2\right]_+
\end{aligned} \tag{73}$$

S-Reduction:

$$\hat{H}_S = -D_J \hat{\mathbf{N}}^4 - D_{JK} \hat{\mathbf{N}}^2 \hat{N}_z^2 - D_K \hat{N}_z^4 + d_1 \hat{\mathbf{N}}^2 \left(\hat{N}_+^2 + \hat{N}_-^2 \right) + d_2 \left(\hat{N}_+^4 + \hat{N}_-^4 \right)$$
$$+ H_J \hat{\mathbf{N}}^6 + H_{JK} \hat{\mathbf{N}}^4 \hat{N}_z^2 + H_{KJ} \hat{\mathbf{N}}^2 \hat{N}_z^4 + H_K \hat{N}_z^6$$
$$+ h_1 \hat{\mathbf{N}}^4 \left(\hat{N}_+^2 + \hat{N}_-^2 \right) + h_2 \hat{\mathbf{N}}^2 \left(\hat{N}_+^4 + \hat{N}_-^4 \right) + h_3 \left(\hat{N}_+^6 + \hat{N}_-^6 \right) \tag{74}$$
$$+ L_J \hat{\mathbf{N}}^8 + L_{JJK} \hat{\mathbf{N}}^6 \hat{N}_z^2 + L_{JK} \hat{\mathbf{N}}^4 \hat{N}_z^4 + L_{KKJ} \hat{\mathbf{N}}^2 \hat{N}_z^6 + L_K \hat{N}_z^8$$
$$+ l_J \hat{\mathbf{N}}^6 \left(\hat{N}_+^2 + \hat{N}_-^2 \right) + l_{JK} \hat{\mathbf{N}}^2 \left(\hat{N}_+^4 + \hat{N}_-^4 \right) + l_{KJ} \hat{\mathbf{N}}^2 \left(\hat{N}_+^6 + \hat{N}_-^6 \right) + l_K \left(\hat{N}_+^8 + \hat{N}_-^8 \right)$$

(See the on-line documentation for the names used by PGOPHER).

The electron spin rotation Hamiltonian, present if S > 0 is:

$$\hat{H}_{SR} = \varepsilon_{aa} \hat{N}_a \hat{S}_a + \varepsilon_{bb} \hat{N}_b \hat{S}_b + \varepsilon_{cc} \hat{N}_c \hat{S}_c$$
$$+ \tfrac{1}{2} \bar{\varepsilon}_{ab} \left(\hat{N}_a \hat{S}_b + \hat{S}_b \hat{N}_a + \hat{N}_b \hat{S}_a + \hat{S}_a \hat{N}_b \right)$$
$$+ \tfrac{1}{2} \bar{\varepsilon}_{ac} \left(\hat{N}_a \hat{S}_c + \hat{S}_c \hat{N}_a + \hat{N}_c \hat{S}_a + \hat{S}_a \hat{N}_c \right) \tag{75}$$
$$+ \tfrac{1}{2} \bar{\varepsilon}_{bc} \left(\hat{N}_b \hat{S}_c + \hat{S}_c \hat{N}_b + \hat{N}_c \hat{S}_b + \hat{S}_b \hat{N}_c \right)$$

where $\bar{\varepsilon}_{ab} = \tfrac{1}{2} (\varepsilon_{ab} + \varepsilon_{ba})$, $\bar{\varepsilon}_{ac} = \tfrac{1}{2} (\varepsilon_{ac} + \varepsilon_{ca})$ and $\bar{\varepsilon}_{bc} = \tfrac{1}{2} (\varepsilon_{bc} + \varepsilon_{cb})$. The form above is required as $\hat{N}_p$ and $\hat{S}_q$ only commute if $p = q$. This is discussed by Brown and Sears[47] who also derived the centrifugal distortion of this interaction, which depends on the reduction:

A-Reduction:

$$H_{SRA} = \Delta_N^s \hat{\mathbf{N}}^2 \hat{\mathbf{N}} \cdot \hat{\mathbf{S}} + \tfrac{1}{2} \Delta_{NK}^s \left(\hat{\mathbf{N}}^2 \hat{N}_z \hat{S}_z + \hat{N}_z \hat{S}_z \hat{\mathbf{N}}^2 \right) + \Delta_{KN}^s \hat{\mathbf{N}} \cdot \hat{\mathbf{S}} \hat{N}_z^2 + \Delta_K^s \hat{N}_z^3 \hat{S}_z$$
$$+ \delta_N^s \hat{\mathbf{N}} \cdot \hat{\mathbf{S}} \left(\hat{N}_+^2 + \hat{N}_-^2 \right) + \tfrac{1}{2} \delta_K^s \left\{ \left(\hat{N}_+^2 + \hat{N}_-^2 \right) \hat{N}_z \hat{S}_z + \hat{N}_z \hat{S}_z \left(\hat{N}_+^2 + \hat{N}_-^2 \right) \right\} \tag{76}$$

S-Reduction:

$$\hat{H}_{SRS} = D_N^s \hat{\mathbf{N}}^2 \hat{\mathbf{N}} \cdot \hat{\mathbf{S}} + \tfrac{1}{2} D_{NK}^s \left(\hat{\mathbf{N}}^2 \hat{N}_z \hat{S}_z + \hat{N}_z \hat{S}_z \hat{\mathbf{N}}^2 \right) + D_{KN}^s \hat{\mathbf{N}} \cdot \hat{\mathbf{S}} \hat{N}_z^2 + D_K^s \hat{N}_z^3 \hat{S}_z$$
$$+ d_1^s \hat{\mathbf{N}} \cdot \hat{\mathbf{S}} \left(\hat{N}_+^2 + \hat{N}_-^2 \right) + d_2^s \left(\hat{N}_+^3 \hat{S}_+ + \hat{N}_-^3 \hat{S}_- \right) \tag{77}$$

The S-reduction names are used in PGOPHER. For S ≥ 1 the electron spin-spin interaction is also required[13]:

$$\hat{H}_{ss} = \alpha \left(3 \hat{S}_z^2 - \hat{\mathbf{S}}^2 \right) + \beta \left(\hat{S}_x^2 - \hat{S}_y^2 \right) = \alpha \left(3 \hat{S}_z^2 - \hat{\mathbf{S}}^2 \right) + \tfrac{1}{2} \beta \left(\hat{S}_+^2 + \hat{S}_-^2 \right) \tag{78}$$

Unlike the linear and symmetric top cases, the lower symmetry forces the requirement to specify separate values for spherical tensor vibronic transition moments, $\langle \eta' | T_q^k(\mu) | \eta \rangle$ and $\langle \eta' | T_{-q}^k(\mu) | \eta \rangle$. A slightly non-standard notation is used here; if $T(k,q)$ and $T(k,-q)$ are the two input values (taking $q > 0$), then for matrix elements with $K' = K + q$ the vibronic part of the transition matrix element is taken as $T(k,q) + T(k,-q)$. For matrix elements with $K' = K - q$, the vibronic part is taken as $T(k,q) - T(k,-q)$. With this definition the effective

operators associated with T(k,q) and T(k,–q) have different symmetries in the more symmetric point groups, such as C₂ᵥ, so only one value need be specified for a given vibronic transition. For one photon transitions the transition dipole moment can also be given in the more common format of *x, y* and z components; these correspond to T(1,–1), T(1,+1), and T(1,0) in this notation, though with a slightly different phase choice.

3.4 Matrix elements and adding additional terms to the Hamiltonian

The specific Hamiltonians described above are only sufficient where interactions between different vibronic states can be ignored, but this is often insufficient, especially for high resolution studies or states above the vibronic ground state. PGOPHER is specifically designed to make adding additional terms to the Hamiltonian straightforward; these are added as additional objects (one per additional term) under a manifold object, and can be used to add terms for a single state omitted from the standard Hamiltonians described above, or to add interactions between different vibronic states. Each individual perturbation is specified in terms of angular momentum operators. The documentation with the program details the possible operators, which include most possible combinations of angular momentum operators for each molecular type. The possible combinations are sufficiently general that each of the operators in the standard Hamiltonians above can be expressed as a perturbation.

The same basic implementation can be used for both vibrational and electronic interactions. For example interactions between vibrational states within the ground electronic state of HCHO have been modelled[19] in terms of operators including $\hat{J}_b, \hat{J}_b\hat{J}_c$ and $\hat{\mathbf{J}}^2\hat{J}_b$. Similarly, interactions between the B and B" electronic states in S₂ have been modelled[18] in terms of a *J* independent spin-orbit operators and a *J* dependent $\hat{J}_{\pm}\hat{L}_{\mp}$ uncoupling interaction.

The same approach can also be used to add terms beyond the standard ones considered above. For example, the standard symmetric top Hamiltonian, equation (62) above, implements centrifugal distortion terms with powers of **N** up to 8. Arbitrary higher powers can be added as required using perturbation objects; the next order terms might include $\hat{\mathbf{N}}^{10}$ and $\hat{\mathbf{N}}^8\hat{N}_z^2$ for example.

The perturbation mechanism is also used to implement an additional facility, to assist in verifying the precise Hamiltonian used. (The reason for including this in the perturbation section is that all the standard Hamiltonians can be converted to a sum of perturbation objects). A basic symbolic algebra package is included in the program and is used to work out and display expressions for the matrix elements used for each parameter as part of the header for each fit or line list. This is often important as, while PGOPHER is designed to conform to common usage, non-standard Hamiltonians are not unusual in the literature. This is particularly the case for interactions between vibronic states, for which a standard has not really evolved, but also applies to more common terms. Comparing matrix elements of

different Hamiltonians is an effective way of identifying the exact calculation performed as part of published work. A worked example of this is given is the program documentation for the $A^5\Pi - X^5\Sigma$ transition of CrO where the literature analysis[38] chose to specify the origin of the Ω components individually, rather than use A, η, λ and θ. PGOPHER is sufficiently flexible to be able to handle either formulation.

5 Fitting Spectra

In general the dependence of the calculated values, y_i, $i = 1..n$ on the parameters of the simulation, p_j, $j = 1..m$, is non-linear, but for fitting purposes it is assumed that the dependence is linear over small ranges of the parameters, so it is possible to approximate the dependence of the calculated values for a given vector of parameter values, $\mathbf{p}$, as:

$$y_i(\mathbf{p} + \Delta\mathbf{p}) = y_i(\mathbf{p}) + \sum_{j=1}^{m} \frac{\partial y_i}{\partial p_j} \Delta p_j \quad \text{or in matrix form: } \mathbf{y(p+\Delta p)} = \mathbf{y(p)} + \mathbf{a}\ \mathbf{\Delta p} \qquad (79)$$

where $\mathbf{\Delta p}$ is the vector of changes in the parameters, $\mathbf{a}$ is the $m \times n$ matrix of partial derivatives and $\mathbf{y(p)}$ the vector of values calculated with parameters $\mathbf{p}$. If the effective observed values are taken as the difference between the true observations, $\mathbf{O}$, and the values calculated from the current parameter set, $\mathbf{y(p)}$ then the standard methods of linear least squares fitting[48] can then be used to estimate the changes in the parameters, $\mathbf{\Delta p}$, that minimises the sum of residuals squared, $|\mathbf{O} - \mathbf{y(p+\Delta p)}|^2$:

$$\mathbf{\Delta p} = (\mathbf{a}^T\mathbf{a})^{-1}\mathbf{a}^T\ (\mathbf{O} - \mathbf{y(p)}) \qquad (80)$$

In practice the non-linear nature of the problem means this process must be repeated until converged, as discussed below.

The evaluation of $(\mathbf{a}^T\mathbf{a})^{-1}\mathbf{a}$ requires care, as it can be sensitive to numerical problems. The method used here to avoid such problems involves singular value decomposition, where the matrix $\mathbf{a}$ is decomposed into a product of three matrices:

$$\mathbf{a} = \mathbf{U\Sigma V}^T \qquad (81)$$

where $\mathbf{U}$ and $\mathbf{V}$ are square orthogonal matrices of sizes $m \times m$ and $n \times n$ respectively and $\mathbf{\Sigma}$ is a diagonal matrix of size $m \times n$. This is equivalent to using a transformed set of parameters, $\mathbf{p}' = \mathbf{V}^T\mathbf{p}$ with no correlation between the parameters, and the changes to the transformed parameters being given by $\mathbf{\Sigma}^{-1}\mathbf{U}^T(\mathbf{O} - \mathbf{y(p)})$. (As $\mathbf{\Sigma}$ is not a square matrix, $\mathbf{\Sigma}^{-1}$ is not a true inverse, but is found by inverting the diagonal elements.) As well as being numerically more stable, the singular values Σ_i (the diagonal elements of $\mathbf{\Sigma}$) can be used to indicate parameters, or combinations of parameters, that are not determined by the data. This is discussed by Lees[49]; note that the discussion in that paper is in terms of the normal matrix, $\mathbf{B} = \mathbf{a}^T\mathbf{a}$ and its eigenvalues λ_i, but this is equivalent to the singular value decomposition used here given that $\mathbf{a}^T\mathbf{a} = (\mathbf{U\Sigma V}^T)^T\ \mathbf{U\Sigma V}^T = \mathbf{V\Sigma}^T\mathbf{\Sigma V}^T$ from which it can be seen that $\Sigma_i = \lambda_i^{1/2}$.

The singular values are the inverse of the standard deviations of the transformed parameters, $\mathbf{p}'$, so a small singular value implies a poorly determined parameter. To make this an absolute indicator, independent of the units or other scaling factors of the parameters, the scaled parameters suggested by Lees[49], p^*_i are adopted:

$$p^*_i = c_i \, p_i \text{ where } \frac{1}{c_i^2} = \sum_{j=1}^{n} \frac{\partial y_j}{\partial p_i} \tag{82}$$

With this transformation, each column of the derivative matrix, $\mathbf{a}$, is a unit vector and the singular values are in the range $0...m$. With this scaling, singular values approaching the machine precision imply completely undetermined parameters and the fit will make essentially random changes to the parameters. These changes can be easily avoided by setting the inverses of very small elements of $\mathbf{\Sigma}$ to zero. This means combinations of parameters that are very poorly determined are not changed. An obvious example would be floating the origin of both the upper and lower state in a transition, where the only the difference between the parameters is well determined. The process described here will leave the sum unchanged, and display that as the problem combination, but nevertheless make equal and opposite changes to the parameters and thus improve the simulation. Less obvious examples can arise quite often in the process of putting a fit together, especially where a partial assignment means there is limited data in the fit. The threshold for elimination is the `SVDThresh` setting, for which empirical testing suggested the default value of 10^{-6} as able to catch many common problems. If any transformed parameters are discarded, the corresponding combination of original parameters is printed out to allow identification of the problem.

An alternative decomposition of $\mathbf{a}$, QR factorization, is also available, which provides similar advantages as regards numerical stability[50] but without the automatic constraints on undetermined parameters. It is used if `SVDThresh` is set negative.

The above assumes equal weight should be given to each observation, but this can be varied by specifying the accuracy of each observation in the form of an estimated standard deviation. Formally these estimates have the same units as the observation, though in fact only the relative values affect the outcome of the fit. It is also possible to specify correlation coefficients between observations; this is not normally required but can be essential for correct statistics in fitting to differences between observations[51]. Internally both are accounted for by transforming observations so they have standard deviation one and uncorrelated with other observations and then using the unweighted fit process. If correlations are present the transformation requires taking linear combinations of observations, though weighting only requires a simple scaling.

The program is designed for interactive fitting, where a plausible initial set of parameters is set up to simulate the available observation, some parameters are selected to be floated, a single fit cycle is performed and the results then inspected. A typical work flow might involve starting by setting only the major parameters for a molecule, perhaps the origin

and rotational constants. The interactive nature of the program makes it straightforward to find sensible values by trial and error, or checking estimates derived from the literature. A single fit cycle is then performed, with some of these parameters floated; if not successful an "undo fit" button is available to step the parameters back one or more fit cycles. Once a given fit is successful, it can be refined by some combination of adding more observations, floating more parameters and adding more parameters to the model, and repeating the testing. For example, the importance of centrifugal distortion terms can be tested by floating successively higher order terms and if the resulting parameters are not determined, undoing the fit and fixing the parameter to zero. This naturally overlaps with an interactive assignment process where a few lines of low J are initially identified and the assignments extended to increasingly higher values of J.

As fits are non-linear, the fit cycles need to be repeated until convergence is reached. There is no formal convergence test in the program; the fit is simply repeated until the values are as stable as required. The work flow described above, which results in increasingly larger numbers of parameters being floated, typically needs only a few cycles at each step, as parameters from the previous step will be reasonably well determined. The rapid convergence also removes the need for refinements to the fitting process such as adapting the step sizes or directions. This scheme also reduces the likelihood of reaching a false minimum in the residual error, another common problem with non-linear fits. The possibility cannot be completely excluded, but the interactive nature of the program does provide for easy checks on other factors, such as inspecting plots of observed-calculated values or calculated intensities that can indicate poor fits. It also makes it straightforward to repeat the fit from several different starting points.

Several possible styles of least squares fitting are implemented; in addition to the traditional spectroscopic fits to line positions, it is also possible to fit to line intensities, energy levels or common differences in any combination. Alternatively a contour fit directly to an observed spectrum can be used, which does not require line assignment and can be essential where lines are only partly resolved. While the lack of requirement for an assignment might be superficially attractive, a contour fit will typically require more care for successful outcome. Firstly, this is because the starting parameters are more important; the method described below for determining derivatives will only work for a single isolated line if the simulated line position is within a line width of the observed transition. In practice this translates into a requirement that a reasonable number of the strongest lines are close to the observations, or that the overall initial band contour is qualitatively correct. An additional problem with contour fits is that a false minimum in residuals is more likely; an obvious "easy" fit is to increase the linewidth in the simulation to wash out all the structure, and more subtle problems are also possible. The interactive nature of the program does, however, allow such problems to be spotted easily. An effective method of working on partially resolved structure is to start with a standard line position fit, and then refine with a contour fit as this gives a good starting position for the contour fit.

Given the variety of possible styles of fitting, it is a requirement that any of the parameters controlling a given simulation can be floated and thus determined as part of the fitting process. As well as the standard molecular parameters such as rotational constants, other variables such as temperature, linewidth and even the population of individual levels can also be determined by fitting. To allow for this generality, the derivatives of the observations with respect to the fitted parameters are evaluated numerically. This involves repeating the full simulation for each parameter, p_j displaced from its initial value by an increment δp_j, and the estimate of the derivative of observation i, y_i is:

$$\frac{\partial y_i}{\partial p_j} \approx \frac{y_i(p_j + \delta p_j) - y_i(p_j)}{\delta p_j} \qquad (83)$$

For speed, only a single displacement is done for each parameter. By default the displacement $\delta p_i = 10^{-4} p_i$ (or an arbitrary 10^{-3} if $p_i = 0$) but this can be set individually for each parameter if required. In straightforward cases the fit is insensitive to the size of the displacement but if the fit is rather non-linear, or parameters differ by many orders of magnitude, this can require some adjustment. Some interactive tools are provided for this; the first of these is a "check derivatives" command, which repeats the derivative calculations with all the increments scaled by a chosen value. The largest difference between the two estimates of the derivatives is then displayed for each parameter, expressed as a fraction of the largest derivative with respect to that parameter. This will reveal parameters for which the increment may require adjustment; well-behaved parameters will typically give fractional errors $< 10^{-5}$ whereas fractional errors $> 10^{-3}$ will often cause problems with the fits. Empirically it is found that a good value for the increment is the standard deviation of the parameter, or some fraction of it. If the increment is too small then machine precision will limit the accuracy to which the derivative can be calculated, but if it is too large then non-linearities in the function will also limit the accuracy. The standard deviation is likely to be a reasonable compromise, as it must necessarily make a significant change in the calculated values and if the calculation is non-linear over the range of the standard deviation the fitting process is anyway likely to be suspect. A command is therefore available to set the increments of selected parameters to a chosen fraction of the standard deviation of the parameter from the previous fit.

At the end of each fit cycle, the root mean square error in the fit is given, in terms of an unweighted sum:

$$\sigma_u = \sqrt{\frac{\sum_{i=1}^{n}(O_i - y_i)^2}{n - m}} \qquad (84)$$

and also a weighted sum, σ_f, which is essentially the above equation with the observed − calculated value, $O_i - y_i$, replaced by $(O_i - y_i)/\sigma_i$, where σ_i is the standard deviation of observation i. (The true form is more complicated if correlations between observations have been included.). The parameter values before and after the fit are reported, together with

the standard deviation of the parameter (calculated from σ$_f$) and the correlation coefficients between the parameters. Also given is the sensitivity, S_j, of each parameter as defined by Watson[52], which gives guidance as to the number of significant figures that should be quoted for any given parameter. This is defined as the change in a parameter that increases the overall error in the fit by a factor of no more than $0.1/m$. For fits with strong correlations between parameters this can be rather smaller than the standard deviation, implying that many more significant figures must be quoted than suggested by the standard deviation to ensure that the calculated values can be reproduced from a given set of parameters. See Le Roy[53] for a discussion of this point, and a sequential rounding and refitting procedure that can be performed to reduce the unphysical precision required in published parameters. This can be done manually if required with PGOPHER; the requirement to do so will be indicated by the summary of the parameter displayed using the common convention with the standard deviation expressed in units of the least significant digit, as in 2.345(56) meaning 2.345±0.056. The number of figures displayed in the parameter and standard deviation is determined from the sensitivity, and is increased if required from the default of 2 in the standard deviation if the sensitivity is less than 1/10th of the standard deviation.

Several other enhancements to the fitting process are described in the on-line documentation. Line lists from other sources can be included in the fitting process with different weights as appropriate, such as combining data from microwave and infra-red sources. The program will take a variety of different formats including HITRAN[22] and Pickett's CALPGM suite[2]. It is also possible to specify constraints between parameters using general algebraic expressions, or fit to an introduced variable (see "variables" in the on-line documentation) with other parameters set from this variable.

In reporting the results of fits, the log file is intended to be a complete description of the fit, suitable for inclusion as supplementary data with a paper. As well as the standard information about residuals and errors, it also includes the correlation matrix and, as discussed above, algebraic expressions for the matrix elements used. It is also possible to produce a line list with predicted uncertainties based on the estimated errors in parameters and the correlations between them. (The `ShowEstUnc` flag controls this.)

6 Conclusions

The program presented is sufficiently general purpose that it will handle most requirements for simulating and fitting rotational structure in molecular spectra. The most significant omissions in the current version are spherical top molecules, and a general way for handling internal rotation. The structure of the program allows the former to be added fairly easily, but internal rotation is a more difficult problem. Where internal rotation effects are small the spectroscopic effects can be modelled by adding a few additional terms to the Hamiltonian via the perturbation objects described above, but larger effects will require additions to the program.

In addition to the general purpose nature of the program, a key feature is the interactive set of tools for assigning, fitting and understanding spectra. These all follow the traditional spectroscopic method of assigning spectra, based on trial and error and informed by expert knowledge. There are alternative approaches to assignment that have been developed recently such as genetic algorithms[54] and the systematic search over many possible assignments used in the AUTOFIT program[55]. The core of both of these requires repeated related simulations, much as already implemented in PGOPHER for least squares fitting, and addition of these methods is being considered for future versions of the program.

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