DOCUMENTATION for SPFIT and SPCAT

These programs use subroutines in SPINV.C to calculate energies and intensities for asymmetric rotors and linear molecules with up to 99 vibrational states and up to 9 spins. No distinction is made between electronic states and vibrational states, or between electronic and nuclear spins. SPFIT is used for fitting transitions and term values, with no requirement that the transitions obey any particular selection rules. SPFIT takes input files with extensions *par* and *lin*, copies the *par* file to a *bak* file, creates new text output files with extensions *par, fit, var*. The *par* and *var* files follow essentially the same format and contain fitting parameters and optionally correlation information. The *fit* file contains the results of the fit. SPCAT is used for predicting line positions and strengths. It takes the *var* file as input along with an *int* file that specifies limits for the calculation and contains the transition dipoles. The main output files for SPCAT use extensions *out* and *cat*, which are for general information and for the catalog output format, respectively. The *cat* file follows the format of the JPL catalog, but does not have experimental data flagged. Auxiliary output files with extensions *egy* and *str* can also be requested. The *egy* file can contain energies, derivatives with respect to the parameters, eigenvalues, and the undiagonalized Hamiltonian. The *str* file contains a list of all transition dipole moments. The file names for SPFIT and SPCAT can be specified as command line arguments in any order. The first file name is used as the base file name for any files not explicitly specified. If no command line arguments are specified the program will give a prompt for the file names.

Some of the details of the program are described in H. M. Pickett, "The Fitting and Prediction of Vibration-Rotation Spectra with Spin Interactions," J. Molec. Spectroscopy 148, 371-377 (1991).

CONTENTS

Quantum numbers which are used in the files can be given in several formats:

Linear Sigma States:						[Q]
N	v	J	F_1	F_2	F	[12]
N	J	F_1	F_2	F_3	F	[01]
N	v	J	F_1	Itot	F	[32]
N	v	J	ns	Itot	F	[72]
N	J	F_1	F_2	Itot	F	[21]
N	J	F_1	ns	Itot	F	[61]
N	v	nn	F	-	-	[52]
N	nn	F	-	-	-	[41]

Symmetric Tops:						[Q]
N	K	v	J	F_1	F	[13]
N	K	J	F_1	F_2	F	[02]
N	K	v	J	Itot	F	[33]
N	K	v	ns	Itot	F	[73]
N	K	J	F_1	Itot	F	[22]
N	K	J	ns	Itot	F	[62]
N	K	v	nn	F	-	[53]
N	K	nn	F	-	-	[42]

Asymmetric Tops:						[Q]
N	K_a	K_c	v	J	F	[14]
N	K_a	K_c	J	F_1	F	[03]
N	K_a	K_c	J	I_{tot}	F	[23]
N	K_a	K_c	ns	I_{tot}	F	[63]
N	K_a	K_c	v	nn	F	[54]
N	K_a	K_c	nn	F	-	[43]

In most cases, the spin coupling scheme is $N + S = J$, $J + I_1 = F_1$, …, $F_{n-1} + I_n = F$, but an alternative that can be selected is the scheme …, $I_{n-1} + I_n = I_{tot}$, $F_{n-2} + I_{tot} = F$. The quantum number *nn* is an aggregate spin quantum number which is used when the number of quantum numbers would otherwise be greater than 6. The quantum number *ns* is used as an auxiliary quantum number for n-fold symmetry with n = 3..6. Half integer spins are rounded up to the next integer. The sign of K for symmetric top notation designates parity under rotation about the *b* axis. When the vibronic wave function is

even with respect to reflection in the *ac* plane, then the sign of K will also indicate the parity with respect to inversion. The symmetric top notation can also be used equivalently for linear molecules with orbital or vibrational angular momentum (lambda not zero). If the number of vibrations is one, then v is not included. The sequence J, F1 .. F can be replaced with F1, F2 .. F if no electronic spin is present. The number of spins requested determines the length of the quantum number list. The factoring of the Hamiltonian is determined by the parameter set.

The field QNFMT in *cat* file can be regarded as having 3 sub-fields: QFMT = Q*100 + H*10 + NQN, in which NQN is the number of quanta per state, H is a binary code the existence of half integer quanta for the last three quantum numbers, and Q is the number in square brackets in the table above. The least significant bit of H refers to the F quantum number and is 1 if F is half integer.

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FORMAT of the *lin* file:

line 1-NLINE [12I3,freeform]: QN,FREQ,ERR,WT

> QN = 12 integer field of quantum numbers. Interpreted in a multiple I3 format as the quantum numbers for the line (upper quanta first, followed immediately by lower quanta). Unused fields can be used for annotation. The entire field is printed in file.fit
>
> FREQ = frequency in MHz or wavenumbers
>
> ERR = experimental error. Minus sign means that the frequency and error are in units of wavenumbers. FREQ and ERR will be converted internally to units of MHz.
>
> WT = relative weight of line within a blend (normalized to unity by program)

notes: If an end-of-file is encountered before all the lines are read in, NLINE is set to the number read to that point. If successive lines have the same frequency, the lines will be treated as a blend and derivatives will be averaged using WT/ERR. Any lines with format errors will be ignored.

The freeform input begins in column 37 and extends to the end of the line. See the notes at the end of the next section for more on the freeform input.

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FORMAT of the *par* file and *var* files:

line 1: title

line 2 [freeform]: NPAR, NLINE, NITR, NXPAR, THRESH , ERRTST,FRAC, CAL

> NPAR = maximum number of parameters
>
> NLINE = maximum number of lines
>
> NITR = maximum number of iterations
>
> NXPAR = number of parameters to exclude from end of list when fitting special lines (see notes)
>
> THRESH = initial Marquardt-Levenburg parameter
>
> ERRTST = maximum [(obs-calc)/error]
>
> FRAC = fractional importance of variance
>
> CAL = scaling for infrared line frequencies (only NPAR used by CALCAT)

Option information beginning on line 3:
CHR,SPIND,NVIB,KNMIN,KNMAX,IXX,IAX,WTPL,WTMN,VSYM,EWT,DIAG
> CHR = character to modify parameter names file (must be in first column) sping.nam, default is 'g'. 'a' is used for Watson A set, 's' is used for Watson S set. Other character replaces the 'g' in the name 'sping'. Only used to label the .fit output file. (Ignored on all but first option line.) SPFIT looks for the *nam* files in the current directory and then in the path given by the SPECNAME environment variable. (i.e. put something like SET SPECNAME=C:\SPECTRA\ in AUTOEXEC.BAT for Windows or setenv SPECNAME /spectra/ for unix). The trailing path delimiter is required.
> sign SPIND = If negative, use symmetric rotor quanta. If positive, use asymmetric rotor quanta (Sign ignored on all but first option line.)
>
> mag SPIND = degeneracy of spins, first spin degeneracy in units digit, second in tens digit, etc. (If last digit is zero, spin degeneracies occupy two decimal digits and the zero is ignored.) This field can specify up to 9 spins using up to 19 digits.
>
> sign NVIB = positive, prolate rotor (z = a, y = b, x = c) negative, oblate rotor (z = c, y = b, x = a) (Sign ignored on all but first option line.)
>
> mag NVIB = number of vibronic states on the first option line, identity of the vibronic state on all but the first option line. (max. value = 80 for 16-bit systems, max. value = 359 otherwise)
>
> KNMIN, KNMAX = minimum and maximum K values. If both = 0, then linear molecule is selected.

IXX = binary flag for inclusion of interactions: 1 means no delta N, 2 means no delta J, 4 means no delta F_1 ,etc. [default = 0 includes all interactions] (Ignored on all but first option line.)

mag IAX = axis for statistical weight (1=a; 2=b; 3=c; 4= A, 2-fold top; 5=Bz, 2-fold top; 6= 3-fold top; 7=A, E, 4-fold top; 8=B, 4-fold top; 9=5-fold top; 10=A, E2, 6-fold top; 11=B, E1, 6-fold top) . For mag IAX > 3, axis is b. (See Special Considerations for Symmetric Tops).

sign IAX = If negative, use I_{tot} basis in which the last *n* spins are summed to give Itot, which is then combined with the other spins to give F (Sign ignored on all but first option line.)

WTPL, WTMN = statistical weights for even and odd state

VSYM = If positive, vibronic symmetry coded as decimal digits (odd digit means reverse WTPL with WTMN) example: 10 = (v=0 even, v=1 odd) (Only works for the first 15 states) (Value ignored on all but first option line.) If negative, signal that the next line is also an option line.

EWT = EWT0 + EWT1*100 = weight for states with E symmetry. Ignore if EWT is negative (default) or EWT0 = 99. (WTPL and WTMN apply to singly degenerate symmetries. see Special Considerations for Symmetric Tops). MOD(EWT1, n) is the *l* value. For MOD(EWT1, n) > n /2, a signed *l* = {MOD(EWT1, n) – n} is specified.

> Note: The weights WTPL, WTMN, and EWT0 can be divided by a common multiple if the rotational partition function is divided by the same factor. The A1 and A2 states of a n-fold rotor are for MOD(ABS(K)-EWT1, n) = 0. The B1 and B2 states of a n-fold rotor are for MOD(ABS(K)-EWT1, n) = 0 with EWT1 shifted by n / 2. States with MOD(EWT1,n) ≠ 0 and ≠ n / 2 MUST be specified in adjacent pairs. E symmetry states will be designated with positive K for symmetric top quanta. For asymmetric top quanta with $l > 0$, $K_a + K_c = N+1$. For asymmetric top quanta with $l < 0$, $K_a + K_c = N$. This designation for quanta in l=1 and $l = $ -1 states will also be applied to A symmetry states if there are only delta $l = 0$ operators. If both WTPL and WTMN are not zero, there will be two E states with the same nominal quantum number. (CALMRG will merge the degenerate transitions into a single line.) The values of EWT1 ≥ n can be used to designate odd vibrational states (see Special Considerations for *l*-doubled States).

DIAG =
     -1 for no diagonalization
      0 for energy ordering within Wang sub-blocks

1 for full projection assignment
2 for energy ordering within Wang sub-blocks which follows order of
diagonal elements of Hamiltonian
3 for energy ordering within vibration and spin sub-block set
For many cases only a single option line is needed. If different vibronic states
have different spin multiplicity or different KMIN, KMAX additional lines are
needed. Note that the sign of VSYM signals additional lines. The first option line
sets up the defaults for all the vibrational states, and subsequent option lines
specify deviations from the default. It is possible to mix Boson and Fermion states
in the same calculation, e.g. fitting different isotopomers together, but the
quantum number format (QNFMT) in SPCAT output will be correct only for the
v=0 state.

Parameter lines: IDPAR, PAR, ERPAR / LABEL

where IDPAR is a parameter identifier, PAR is the parameter value,
ERPAR is the parameter uncertainty, LABEL is a parameter label (10
characters are used) that is delimited by **/.** If the sign of IDPAR is
negative, SPFIT constrains the ratio of this parameter to the previous
parameter to a fixed value during the fit.
PARAMETER identifiers (IDPAR) are coded in decimal digit form in the
order
NFF, I2, I1, NS, TYP, KSQ, NSQ, V2, V1.
for NVIB < 10 each element occupies one digit except TYP which
occupies two digits, i.e.
$(((((((FF*10+I2)*10+I1)*10+NS)*100+TYP)*10+KSQ)*10+NSQ1)*10+V2)*10+V1$
for 9 < NVIB < 100: each element occupies one digit except TYP, V1, and
V2 which occupy two digits, i.e.
$(((((((FF*10+I2)*10+I1)*10+NS)*100+TYP)*10+KSQ)*10+NSQ1)*100+V2)*100+V1$
for 99 < NVIB < 359: each element occupies one digit except TYP, V1,
and V2 which occupy three digits, i.e.
$(((((((FF*10+I2)*10+I1)*10+NS)*100+TYP)*10+KSQ)*10+NSQ1)*1000+V2)*1000+V1$

FF = Fourier flag (used for internal rotation) If FF < 11, basic operator
is multiplied by cos (FF * 2π $K_{avg}\rho$ / 3), where ρ is coded by the
absolute value of parameter ID=9100vv. See further discussion
below. If 10 < FF <21, basic operator is multiplied by sin ((FF-
10)* 2π $K_{avg}\rho$ / 3). If 20 < FF <31, basic operator is multiplied by
cos ((FF-20)* 2π $K_{avg}\rho$ / 3), etc. The maximum value of FF may
be limited by the limitations of the freeform input described below.
I2,I1 = spin identifiers [Usually I1 >= I2], I1=0 or I2=0 means N. If I1
= 0 and I2 > 0, perform commutator with i N*N.

NS = power of N• S where S is the first spin If NS > 4, subtract 5 and add $S_z N_z$ operator

TYP = projection type

0 = scalar

$1 = N_a N_a$

$2 = N_b N_b$

$3 = N_c N_c$

$3+n = N_+^{2n} + N_-^{2n}$, n = 1 .. 9 (L = 2n, ΔK = 2n)

11+n = "x" symmetry, n = 1 .. 8 (L = 2n + 1, ΔK = 2n)

20+n = off-diagonal "a" symmetry, n = 0 .. 19 (for prolate basis: L = n + 1, ΔK = 0, 2, 2, 4, 4..)

$20 = N_a$

$21 = N_b N_c + N_c N_b$

40+n = off-diagonal "b" symmetry, n = 0 .. 19 (L = n + 1, ΔK = 1, 1, 3, 3 ..)

$40 = N_b$

$41 = N_a N_c + N_c N_a$

60+n = off-diagonal "c" symmetry, n = 0 .. 19 (for prolate basis: L = n + 1, ΔK = 1, 1, 3, 3 ..)

$60 = N_b$

$61 = N_a N_b + N_b N_a$

80+n = unique contribution for K' = K" = n*10+KSQ

90+2n = Euler series multiplying $N_+^{2n} + N_-^{2n}$

91+2n = constants for Euler and Fourier series

91 = ρ for Fourier series if KSQ = 0, NSQ1 = 0, and V1=V2. Only the absolute value is used for ρ, and the sign is used to designate a special symmetry.

KSQ = power of N_z^2

NSQ1 = power of N*(N+1)

V1, V2 = vibrational identifier. For NVIB < 10: V1 = V2 = 9 matches all V1 = V2. For 9 < NVIB < 100: V1 = V2 = 99 matches all V1 = V2. For 99 < NVIB < 360: V1 = V2 = 999 matches all V1 = V2. Usually, select V1 >= V2. V1 < V2 has special meaning for l-doubled states.

Warning: parameters requested really signify the operator that will multiply the parameter. Parameters not explicitly requested are presumed to be zero. For example, B for a linear molecule or symmetric top is 100, while for an asymmetric top it is 20000.

NOTES:

$N_+ = N_x + i N_y$. If NFF < 11, then parameters with EVEN values of TYP >= 20 and < 80 have an implicit i. If NFF>10, then parameters with ODD values of TYP >= 20 and < 80 have an implicit i. Also, if NFF > 10, then all parameters of TYP < 20 have an implicit i. If EWT1=1 for both of the vibrational states, then

these nominally imaginary parameters are assumed to be real and multiplied by the L_z operator (see below).

The sign of the ρ parameter is used to designate a special symmetry for the Fourier series. If this sign is different for V1 and V2, then 0.5 is subtracted from NFF. For example, if NFF = 2, the basic operator is multiplied by cos $(3\pi K_{avg}\rho / 3)$ instead of cos $(4\pi K_{avg}\rho / 3)$. If the magnitude of ρ is not the same for the two states, replace $K_{avg}\rho$ with $(K_1\rho_1 + K_2\rho_2) / 2$.

Prolate basis is I r, and oblate basis is III l. ΔK behavior for TYP = 20+n and 60+n are reversed for oblate basis.

$\rho_{v,v}$ is specified by 9100vv. TYP=91+2n parameters, including ρ, are constants and are not fitted.

For operators with I2 = 0 and I1 > 0, one value of N is replaced with the appropriate projection of I_{I1}. For operators with I2 > 0 and I1 > 0, two values of N are replaced with appropriate projections of both I. For TYP=1,2,3, the operator is the expected Cartesian projection - I2.I1 / 3. For example, 10000 is the N_zN_z operator, 10010000 is the N_zS_z operator, and 120010000 is the S_zI_z - S.I / 3 operator.

For operators with I2 = I1 > 0, spin corrections appropriate for nuclear quadrupole coupling are applied: SQRT((2I+1)/(2I-1))/4I.

Whenever operators that do not commute are combined, the resulting operator is half the anti-commutator. The order of application is N_zS_z, followed by N_z^2, followed by N^2 and N• S.

When coupling states where a given electronic (or nuclear) spin is different (e.g. spin-orbit coupling), the reduced matrix element for the spin operator, <S|| Op||S'>, is assumed to be unity when S > S' and $(-1)^{S'-S}$ when S < S'.

line (n+1)-end [8F10.6]: ((V(i,j),j=1,i) ,i=1,NPAR)
V = Choleski decomposition of the correlation matrix, optional for file.par (The index *i* is the index for the parameter.)

Notes: In the freeform input, the variables are all preset to reasonable default values. Any character not usually found in an E or F formatted number can separate the input numbers. A space or comma is recommended. Two successive commas indicate that the default value is to be used for that variable. At the end of the line or when a '/' character is encountered, all unspecified variables remain set to their default values. PAR defaults to zero. ERRPAR defaults to a very large number for CALFIT and to zero for CALCAT. If an end-of-file or error is encountered before the parameters are read in, NPAR is set to the number read to that point. If an end-of-file or error is encountered before V is completely read in, V is set to a unit matrix. The variables that are decoded to integer fields (such as IDPAR) cannot be larger than the number of significant digits in a double precision number (typically 15 digits).

Special lines to which NXPAR applies are lines in which the F quantum number is negative. In the quantum number assignment process in the program, the line is flagged and F is set to an appropriate value. When derivatives are accumulated, the last NXPAR derivatives are ignored, and the energies are corrected by subtracting the first order contribution of these parameters. If F < -1, the absolute value of F is used in the energy calculation. If F = -1, the F used is as close to the previous spin quantum number as angular momentum addition rules allow. The value selected will be shown in the fit file line listing in place of the -1.

If IDPAR is less than zero the magnitude is taken. In CALFIT, the parameter value will be constrained to be a constant ratio of the preceding parameter value. In this way linear combinations of parameters can be fit as a unit.

[TOP](#)

FORMAT for the *int* file:

line 1: title

line 2 [freeform]: FLAGS,TAG,QROT,FBGN,FEND,STR0,STR1,FQLIM,TEMP

FLAGS = IRFLG*1000+OUTFLG*100+STRFLG*10+EGYFLG
- · IRFLG = 1 if constants are in wavenumbers
- · IRFLG = 0 if constants are in MHz
- · OUTFLG = 0 for short form *file.out*
- · STRFLG = 1 to enable *file.str* output
- · STRFLG = 2 to enable *file.str* output and print separate entries for each dipole
- · EGYFLG > 0 to enable *file.egy* energy listing
- · EGYFLG= 2,4 to enable *file.egy* derivative listing
- · EGYFLG = 3,4 to enable *file.egy* eigenvector listing
- · EGYFLG > 4 to dump Hamiltonian with no diagonalization

TAG = catalog species tag (integer)

QROT = partition function for TEMP

FBGN = beginning integer F quantum (round up)

FEND = ending integer F quantum (round up)

STR0, STR1 = log strength cutoffs

FQLIM = frequency limit in GHz

TEMP = temperature for intensity calculation in degrees K (default is 300K)

Notes: The freeform input is defined above in the notes for *file.par*. The maximum log of the line strength output to file.cat from SPCAT must be greater than STR0+STR1*(frequency/300GHz)**2. Both STR0 and STR1 default to -100.

line 3-end [freeform]: IDIP,DIPOLE

IDIP = dipole identifier (see below)

DIPOLE = dipole value

IDIP is coded in decimal digit form according to the format (for NVIB < 10):
(((TYP*10 + I1)*10 + V2)*10 + V1)*10 + SYM, or (for 9 < NVIB < 100):
(((TYP*10 + I1)*100 + V2)*100+ V1)*10 + SYM, or (for 99 < NVIB < 360):
(((TYP*10 + I1)*1000 + V2)*1000+ V1)*10 + SYM, with

TYP = dipole type
I1 = spin identifier [I1 = 0 means N or null]
V1,V2 = vibrational states [V1 GE V2]
SYM = symmetry [0 = magnetic, 1 = a, 2 = b 3 = c]

TYP	SYM	Description
0	0	magnetic dipole [N, S, I]
0	1	a dipole, ϕ_a if I1=0, else $\phi_a \times$ I
0	2	b dipole, ϕ_b if I1=0, else $\phi_b \times$ I
0	3	c dipole, ϕ_c if I1=0, else $\phi_c \times$ I
1	0	$i\,(2\phi_z N_z - \phi_x\,N_x - \phi_y\,N_y)/2$ or $i\,(2\phi_z I_z - \phi_x\,I_x - \phi_y\,I_y)/2$
1	1	$i\,\{\phi_b, N_c\}/2 + i\,\{\phi_c, N_b\}/2$ or $i\,\{\phi_b, I_c\}/2 + i\,\{\phi_c, I_b\}/2$
1	2	$i\,\{\phi_a, N_c\}/2 + i\,\{\phi_c, N_a\}/2$ or $i\,\{\phi_a, I_c\}/2 + i\,\{\phi_c, I_a\}/2$
1	3	$i\,\{\phi_a, N_b\}/2 + i\,\{\phi_b, N_a\}/2$ or $i\,\{\phi_a, I_b\}/2 + i\,\{\phi_b, I_a\}/2$
2	0	$i\,(\phi_x\,N_x - \phi_y\,N_y)$ or $i\,(\phi_x\,I_x - \phi_y\,I_y)$
2	1-3	same as TYP = 1
3	any	$\{N^2, TYP = 0\}/2$
4	any	$\{N_z^2, TYP = 0\}/2$
5	1-3	$[N^2, TYP = 0] / 2$
6	0	L = 3, delta K = 2
6	1	L = 3, delta K = 2 if prolate basis

6	2,3	L = 3, delta K = 3 if prolate basis
7	any	TYP=0 * cos(I1*2π K$_{avg}$ ρ / 3)
8	any	TYP=0 * i sin(I1*2π K$_{avg}$ ρ / 3) or cos(20π K$_{avg}$ ρ / 3) if I1 = 0
9	any	{N^4, TYP = 0}/2
10	any	[N^2,[N^2, TYP = 0]]/4
11	any	[N^2 , TYP = 2] / 2
12	any	i {N$_z$, TYP=2}/2

Note: Dipoles with SYM > 0 are assumed to be in units of Debye. Dipoles with SYM = 0 are assumed to be in units of a Bohr magneton. Dipoles which are even order in direction cosine or N are assumed to be imaginary, except between states with EWT1=1. Dipoles between states with EWT1= (0,2), (2,0), and (2,2) are ignored, but the matrix elements are calculated using corresponding dipoles from states with EWT1=1 (see below). For ITYP = 7 or ITYP = 8, I1 is used for the Fourier order and not the spin type. The constant ρ is specified in the parameter set. The sign of the ρ parameter is used to designate a special symmetry for the Fourier series. If this sign is different for V1 and V2, then 0.5 is subtracted from the Fourier order. For example, if IDIP = 72012, the basic *b*-dipole operator is multiplied by cos (3π K$_{avg}\rho$ / 3) instead of cos (4π K$_{avg}\rho$ / 3). If the magnitude of ρ is not the same for the two states, replace K$_{avg}\rho$ with (K$_1\rho_1$ +K$_2\rho_2$) / 2. ITYP = 8 (with I1 > 0) dipoles are multiplied by i, and the symmetry of the states connected is 3 - SYM and the units follow the state symmetry (e.g. 81000 is in Debye). ITYP = 2, 5 are used for first-order Herman-Wallis corrections. ITYP = 3, 4, 6, 11, 12 are used for second-order Herman-Wallis corrections.

TOP

FORMAT of *cat* output file:

[F13.4,2F8.4,I2,F10.4,I3,I7,I4,12I2]:
FREQ,ERR,LGINT,DR,ELO,GUP,TAG,QNFMT,QN

FREQ = Frequency of the line

ERR = Estimated or experimental error (999.9999 indicates error is larger)
LGINT = Base 10 logarithm of the integrated intensity in units of nm^2 MHz

DR = Degrees of freedom in the rotational partition function (0 for atoms, 2 for linear molecules, and 3 for nonlinear molecules)

ELO = Lower state energy in wavenumbers

GUP = Upper state degeneracy

TAG = Species tag or molecular identifier. A negative value flags that the line frequency has been measured in the laboratory. The absolute value of TAG is then the species tag (as given in line 2 of file.int above) and ERR is the reported experimental error.

QNFMT = Identifies the format of the quantum numbers given in the field QN.

QN(12)= Quantum numbers coded according to QNFMT. Upper state quanta start in character 1. Lower state quanta start in character 14. Unused quanta are blank, quanta whose magnitude is larger than 99 or smaller than –9 are shown with alphabetic characters or **. Quanta between -10 and -19 are shown as a0 through a9. Similarly, -20 is b0, etc., up to -269, which is shown as z9. Quanta between 100 and 109 are shown as A0 through A9. Similarly, 110 is B0, etc., up to 359, which is shown as Z9.

Format of *str* output file:

[F15.4,E15.6,I5,1X,24A,I5]: FREQ,DIPOLE,QNFMT,QN,ITEM

FREQ = Frequency of the line

DIPOLE= Reduced matrix element of the transition dipole

QNFMT = Identifies the format of the quantum numbers given in the field QN.

QN(12) = Quantum numbers coded according to QNFMT. Upper state quanta start in character 1. Lower state quanta start in character 14. Unused quanta are blank, quanta whose magnitude is larger than 99 or smaller than –9 are shown with alphabetic characters or **. Quanta between -10 and -19 are shown as a0 through a9. Similarly, -20 is b0, etc., up to -259, which is shown as z9. Quanta between 100 and 109 are shown as A0 through A9. Similarly, 110 is B0, etc., up to 359, which is shown as Z9.

ITEM = identifies number of dipole

Format of *egy* output file:

energy output **[2I5,3F18.6,6I3]:** IBLK,INDX,EGY,PMIX,ERR,QN

IBLK = Internal Hamiltonian block number

INDX = Internal index Hamiltonian block

EGY = Energy in wavenumbers

ERR = Expected error of the energy in wavenumbers

PMIX = mixing coefficient

QN(6)= Quantum numbers for the state

SPECIAL CONSIDERATIONS FOR LINEAR MOLECULES

This program set will calculate a variety of interactions and transitions within a Hund's case(b) basis, including spin orbit interactions which change spin multiplicity. The operator N_a in the asymmetric rotor becomes lambda for the linear molecule. N is the sum of rotational and electronic orbital angular momenta. For linear molecules, it is convenient (but not essential) to think of the angular momentum along the bond as being purely electronic in nature. In the asymmetric rotor language of this program, the first-order spin orbit interaction takes the operator form of a vector dot product of a direction cosine with the spin vector. It can have two distinct symmetries: $S \bullet \phi_a$ connects states of the same lambda, while $S \bullet \phi_b$ and $S \bullet \phi_c$ connect states where lambda differs by one. For $S \bullet \phi_b$ or $S \bullet \phi_c$, the L_b or L_c operator is implicitly included in the parameter. When the spin orbit operator connects different spin multiplicity, the reduced matrix value of $<S||\mathbf{S}||S'>$ is set to unity.

Use of the symmetries in this program takes some care, particularly for linear molecules where it may not be immediately obvious whether to use the b or the c axis to designate perpendicular operators. For consistency with the parity designation for the symmetric top quanta, the vibronic wave function should be chosen so that it is symmetric with respect to the *ab* plane. Then the *b* axis can be used for the inversion-defining axis (i.e. IAX = 2 in the option lines of the .par and .var files can be used to define selection rules under inversion). With this choice, the symmetry of rotation lines in the D_2 group is:

A	even N for Σ and all N for all other even λ (even parity λdoublet)
B(a)	odd N for Σ and all N for all other even λ (odd parity λ doublet)
B(b)	all N for all odd λ (even parity λ doublet)
B(c)	all N for all odd λ (odd parity λ doublet)

For Σ^+ states, the parity is odd for odd N, while for Σ^- states the parity is odd for even N. This means that the Hamiltonian can couple Σ^+ with Σ^- via an operator of B(a) symmetry or B(c) symmetry. An example is an operator like 10200001, which is the $S \bullet \phi_a$ spin orbit interaction operator between state v = 0 and v = 1. For normal coupling not involving Σ^- states (or for coupling between Σ^- states) the operators should have A or B(b) symmetry. Similarly, electric dipole transitions with Δλ even should have B(a) symmetry, and transitions with Δλ = odd

The g, u symmetry for an electronic state is for the parity of the wave function under inversion of the space fixed axes. The nuclear exchange symmetry, on the other hand, affects only the statistical weights and does not have any further impact on the factoring of the Hamiltonian. In general, if IAX = 2, WTPL will be the nuclear spin weight for the A and B(b) states, while WTMN will be the weight for the other two symmetries. For Σ^+_g Σ^-_u and g states with other λ, WTPL is the weight for even permutations, while for Σ^-_g Σ^+_u and u states with other λ, WTPL is the weight for odd permutations. For example, in oxygen, Σ^+_g and Δ_g have WTPL=1 and WTMN=0, while Σ^-_g and Δ_u have WTPL=0 and WTNM=1. The dipole types given above provide for both allowed and forbidden transitions. For transitions that owe their intensity to spin orbit interactions, the effective transition moment will be the product of the interaction and a transition moment to some intermediate state. Examples are a $\Sigma^-_g\Delta$ electric dipole code of 21vv'0 and a magnetic dipole code of 11vv'1. Electric dipole transitions between Σ^+ and Σ^- will use 11vv'0, while magnetic transitions will use 1vv'1. For transitions between Σ^+ and Σ^+ the roles of these operators are reversed. Note that for Σ Σ transitions, 11vv'0 has selection rules of $\Delta N = -2, 0, +2$, while 1vv'1 has selection rules of $\Delta N = -1, +1$.

The correlation between parity and e,f designations follow the recommendations of J. M. Brown *et al.*, J. Mol. Spect. **55,** 500 (1975).

	odd spin multiplicity	even spin multiplicity
e	$p = (-1)^{J-1/2}$	$p = (-1)^{J+1}$
f	$p = (-1)^{J+1/2}$	$p = (-1)^{J}$

An example of .var file for oxygen like molecule:

```
mock oxygen states
4
-3 3 0 0 0 2 0 1 -1 /default for v=0 triplet Sigma-(g)
 1 1 2 2 0 2 1 0 -1 /v=1 is singlet Delta(g)
 1 2 0 0 0 2 1 0  0 /v=2 is singlet Sigma-(g)
         11   1e+7   0 /term value for v=1
         22   2e+7   0 /term value for v=2
110010000  1000.0 0 /spin-spin interaction for v=0
       199 10000.0 0 /B for all v
```

An example of .int file for oxygen like molecule:

```
mock oxygen rotational and electronic transitions
101 99000 200. 0 6 -80. -80. 99999999.
 1000 1. /magnetic moment v=0
 1110 1. /magnetic moment v=1
11011 1. /sigma - delta magnetic moment
 1021 1. /sigma - sigma magnetic moment
```

The quantum number correlations between Hund's case (b) and case (a) can be a bit confusing at first. For example in a doublet Π state N=J-1/2 always correlates with Ω =3/2 and N=J+1/2 always correlates with Ω =1/2 on the basis of projection. For A < 0, e.g. OH, the projection-based correlation follows the energy ordering. For A>0, the lower energy state is N=J+1/2 and Ω =3/2 as long as J+1/2 < sqrt(A/2B). Above this J, N = J+1/2 and Ω =1/2 (based on projection) is higher in energy than and N=J-1/2 and Ω = 3/2. Therefore quantum number assignments based on projections lead to different quanta than those based on energy. For a triplet Σ state, N=J+1 correlates with Σ =0 based on projection, N=J correlates with an odd combination of Σ =1 and Σ =-1, and N=J-1 correlates with an even combination of Σ =1 and Σ =-1.

Since q multiplies the same operator as (B-C) / 2, it is possible to use the sign of q to determine whether there are more electrons in the *ab* plane (q > 0) or whether there are more electrons in the *ac* plane (q < 0).

Explicit approximate relationships for the parameters are:

100100vv'	A
100101vv'	2 A_J
1vv'	B
100400vv'	-p / 2
400vv'	q / 2
200100vv'	a
1200100vv'	c
1200000vv'	b + c / 3
1200400vv'	-d / 2
2200100vv'	1.5 eQq_1
2200400vv'	$-eQq_2/4$
1100100vv'	4 λ S (2S-1)

The extra factors of S in the definition of the spin-spin interaction parameter λ, i.e. a spin-spin interaction 2 λ (S_z^2 - S^2 / 3), is a correction for the special normalization assumed for eQq.

[TOP](#)

SPECIAL CONSIDERATIONS FOR *l*-doubled STATES:

The *l*-doubled states must be specified in adjacent pairs. There are two common situations: (1) an n-fold internal rotor with no operators connecting states of differing σ and all K having the same nuclear spin states, (2) an n-fold symmetric rotor in a degenerate excited state. In the first case, the states with values of (σ mod n) = 0 or n /2 can be treated as $l = 0$ states, and the other degenerate σ can be treated as $l = \pm 1$ states. In either case, values of MOD(EWT1, n) = 0 or = n / 2 will be excluded from further discussion here because the states are not *l*-doubled. The states with l = MOD(EWT1, n) < n / 2 (and $l > 0$) are those with $K\,l > 0$. Paired states with EWT1' = n – EWT1 are those with $K\,l <= 0$. The sign of K represents the parity, as in the non *l*-doubled states. Parameters for operators should be only specified between pairs of vibrational states (0, 0), (0, *l*), (*l*, 0), (*l*, *l*), (*l*, -*l*), and (-*l*, *l*) with $l > 0$. Specifications for parameters for operators between pairs of vibrational states with (0,-*l*), (-*l*, 0), and (-*l*, -*l*) are ignored and the parameters assumed equal to their counterpart. If either EWT1 < n or EWT1 ≥ n for both states and if the parameter would normally be implicitly imaginary (i.e. operators odd-order in angular momentum for the Hamiltonian, or even-order for the dipole moment), then the parameter is assumed to be real and the rotational operator is multiplied by the sign of *l*. If EWT1 < n for one state and EWT1 ≥ n for the other state and if the parameter would normally be implicitly real (i.e. operators even-order in angular momentum for the Hamiltonian, or odd-order for the dipole moment), then the rotational operator is multiplied by the sign of *l*.

DIAG = 0 is not recommended on the first option line in the *par* file, since the first-order energy is not likely to be ordered with *K*.

The *K* quantum numbers for *l*-doubled states are designated specially when asymmetric rotor quanta are used so that the lower *K* doublet is associated with the $l > 0$ state and the upper *K* doublet and $K = 0$ states are associated with $l < 0$. In this way the degenerate states have the same quantum numbers.

With an n-fold symmetric top specified by IAX (or with IAX < 4 and EWT0 < 99 and assumed n = 3), operators obey the selection rule that '*K-l*' can only change by multiples of n. If there are operators diagonal in EWT0 with ΔK that is not a multiple of n, then the operator is rejected (or n is set to 1 if IAX < 4).

For operators that are off-diagonal in *l*, ΔK > 0 and ΔK < 0 operators are independent. To distinguish these cases, ΔK·Δ*l* > 0 if IV2 < IV1 and ΔK·Δ*l* < 0 if IV2 > IV1. For ΔK = 0, IV2 < IV1 for normal operator and IV2 > IV1 indicates multiplication by *i* (and corresponding change in symmetry).

SPECIAL CONSIDERATIONS FOR SYMMETRIC TOPS:

The nuclear spin statistics for symmetric top can be specified in a unique way up to 6-fold groups. Start by considering the D_n point groups that have n-fold rotations around the z axis and n C_2 rotations perpendicular to the z axis. For bosons and for even sets of equivalent fermions, the symmetry of the overall wave function must have A_1 symmetry. For one set of equivalent fermions, the overall symmetry is A2, B2, A1, B1 for n = 3, 4, 5, 6, respectively. The influence of vibronic symmetry is based on user input. B1 and B2 symmetries are specified in separate option lines with ABS(IAX) = 5, 8, 11. The statistical weights for each vibronic state are specified by WTPL, WTMN, and EWT0. WTPL is the weight for rotational symmetry of A1 or B1. WTMN is the weight for rotational symmetry of A2 or B2. EWT0 is the weight for E (E1 or E2 for D_6 symmetry). For even n, the user specifies two option lines with different values of EWT1 in order to cover all symmetries. (One for A1, A2, E2 with EWT1 = 0 and one for B1, B2, E1 with EWT1 = n / 2.) For D_4 symmetry EWT0 will be set zero for IAX = 8. For ABS(IAX) > 3, unspecified weights are assumed to be zero. The symmetry of the vibronic function is defined by l and the symmetry under the perpendicular C_2 operator. The symmetry of the rotational wave functions is A1 or A2 for MOD(K - l, n) = 0, B1 or B2 for MOD(K – l, n) = n/2, and E otherwise. (Two-fold rotations are handled in a straight-forward way using the full symmetry of the D_2 group and will not be considered further in this section.) The two-fold symmetry (e.g. A1 vs. A2) is defined by the Wang symmetry along the b axis and atom 1 is assumed to pass through this perpendicular C_2 axis. The nuclear spin statistics are readily defined in terms of the permutation symmetry of the nuclei. The values given below are for n equivalent nuclei with spin I that lie in a plane perpendicular to the z axis. N is the number of nuclear spin states with a given symmetry. The number following => is the value for I = ½.

For D_2 symmetry:
$N(A) = (2I+1)(I+1) => 3$
$N(Bz) = 0$
$N(By) = 0$
$N(Bx) = (2I+1)(I) => 1$

For D_3 symmetry:
$N(A1) = (2I+1)[(2I+1)^2 + 3(2I+1) + 2]/6 => 4$
$N(A2) = (2I+1)[(2I+1)^2 - 3(2I+1) + 2]/6 => 0$
$N(E) = (2I+1)(I+1)(8I)/3 => 4$

For D_4 symmetry:
$N(A1) = (2I+1)[(2I+1)^3 + 2(2I+1)^2 + 3(2I+1) + 2]/8 => 6$
$N(A2) = (2I+1)[(2I+1)^3 - 2(2I+1)^2 - (2I+1) + 2]/8 => 0$
$N(B1) = (2I+1)[(2I+1)^3 - 2(2I+1)^2 + 3(2I+1) - 2]/8 => 1$
$N(B2) = (2I+1)[(2I+1)^3 + 2(2I+1)^2 - (2I+1) - 2]/8 => 3$
$N(E) = (2I+1)^2(I+1)(2I) => 6$

For D_5 symmetry:
$N(A1) = (2I+1)[(2I+1)^4 + 5(2I+1)^2 + 4]/10 => 8$
$N(A2) = (2I+1)[(2I+1)^4 - 5(2I+1)^2 + 4]/10 => 0$
$N(E1) = (2I+1)[(2I+1)^4 - 1]2/5 => 12$
$N(E2) = N(E1)$

For D_6 symmetry:
$$N(A1) = (2I+1)[(2I+1)^5 + 3(2I+1)^3 + 4(2I+1)^2 + 2(2I+1) + 2]/12 => 13$$
$$N(A2) = (2I+1)[(2I+1)^5 - 3(2I+1)^3 - 2(2I+1)^2 + 2(2I+1) + 2]/12 => 1$$
$$N(B1) = (2I+1)[(2I+1)^5 + 3(2I+1)^3 - 4(2I+1)^2 + 2(2I+1) - 2]/12 => 7$$
$$N(B2) = (2I+1)[(2I+1)^5 - 3(2I+1)^3 + 2(2I+1)^2 + 2(2I+1) - 2]/12 => 3$$
$$N(E1) = (2I+1)[(2I+1)^5 - (2I+1)^2 - (2I+1) + 1]/3 => 18$$
$$N(E2) = (2I+1)[(2I+1)^5 + (2I+1)^2 - (2I+1) - 1]/3 => 22$$

For C_n symmetry, $N(A)' = N(A1) + N(A2)$, $N(B)' = N(B1) + N(B2)$, and $N(E)' = 2 N(E)$. Nuclear spin statistics of symmetries involving the inversion operator, reflection operator, or an improper rotation have the same nuclear spin statistics as the pure rotation sub-group. The symmetry of the rotational state being considered is then multiplied by the nuclear spin symmetry that gives the correct overall symmetry. The rotational weight is the corresponding number of nuclear spin states. As an example consider NH_3 with D_3 rotational symmetry and overall symmetry of A2. For an A1 vibrational state, WTPL = $N(A2) = 0$, WTMN = $N(A1) = 4$, and EWT0 = $N(E)/4 = 1$. For a E vibrational state, use of l-doubling allows the same statistical weights as the corresponding non-degenerate vibrational states. For CH_3F with C_3 rotational symmetry and overall symmetry of A, WTPL = WTMN = $N(A1) + N(A2) = 4$ and EWT0 = $2 N(E) / 4 = 2$.

For reference, the symmetry multiplication table is

A1	A2	B1	B2	E1	E2
A2	A1	B2	B1	E1	E2
B1	B2	A1	A2	E2	E1
B2	B1	A2	A1	E2	E1
E1	E1	E2	E2	A1+A2+E2	B1+B2+E1
E2	E2	E1	E1	B1+B2+E1	A1+A2+E2

For $n = 3$, E $\times$ E = A1 + A2 + E. For $n = 4$, E $\times$ E = A1 + A2 + B1 + B2. Whenever only one resultant of a E $\times$ E product is allowed, N(E) must be divided by 4.

For hyperfine interactions of the n nuclei in an n-fold top, the user can either use standard coupling or (preferably) the I_{tot} basis indicated by the sign of IAX. The standard coupling is more flexible, but the dark states with inappropriate overall symmetry are not readily identifiable. In the I_{tot} basis, only parameters with I_1 or $[I_1 \times I_2]$ need be specified. The actual spin operator used is $I_\alpha = I_1 + \varepsilon I_2 + \varepsilon^2 I_2 + ..$, where $\varepsilon = EXP(2\pi i / n)$. The value of α is given implicitly by $MOD(\Delta l - \Delta K, n)$. A similar Fourier series is provided for $[I_1 \times I_2]^L$ (for L = 0,2) and for quadrupole interactions, namely $[I_1 \times I_1]^{(2)}$. Note that $\alpha = 0$ operators couple spin states with the same symmetry, while other values of α couple ortho and para. For D_n symmetry and the I_{tot} basis, EWT0 = 0 and either WTPL or WTMN is zero based on the overall symmetry required. For C_n symmetry and the I_{tot} basis, EWT0 = 0 and WTPL and WTMN are both zero or one based on the overall symmetry required., The matrix elements of the operators are constructed so that there is no connection between states of different overall symmetry.

SIMPLE EXAMPLES:

Example of parameter types for asymmetric rotors (assuming < 10 vibronic states):

11	energy for v=1
10000	A_{00}
10099	A (all vibrational states with v'=v")
20099	B
30099	C
40099	0.25*(B-C) (if prolate basis selected)
299	-DJ
1199	-DJK
2000	$-DK_{00}$
600001	i N_c interaction between v=0 and v=1
20000099	N•I for second spin
120010099	S_a I_a
220010099	1.5 * quadrupole moment χ_{zz} for second spin
220040099	Quadrupole moment 0.25*(χ_{xx}-χ_{yy}) for second spin

Quadrupole and magnetic spin-spin interactions are defined to be traceless (i.e. χ_{xx}+ χ_{yy} + χ_{zz} = 0 or T_{xx} + T_{yy} + T_{zz} = 0) and all three components cannot be simultaneously fit. The most efficient choice of parameters is shown in the table below. In cases where the user wants an alternative, it is possible to use constrained parameters. For example, to fit χ_{aa} and χ_{cc} (with no multipliers):

```
220010099   100.
-220020099  -100.
220030099    50.
-220020099   -50.
```

specifies χ_{aa} = 100, χ_{cc} = 50, and χ_{bb} = -150.