f_electron

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Appendices

f_electron

1.0 Introduction

The program is designed to be run from the command line, reading an input file and generating an output file:

```
> f_electron
> f_electron myin.dat myout.dat
> f_electron help
> f_electron help keyword
> f_electron version
```

```
> f_electron
```

If no input or output file is provided on the command line, it is assumed that there is an input file "input.dat" and the output file "output.dat" is written.

```
> f_electron myin.dat myout.dat
```

The input file 'myin.dat' will be read and 'myout.dat' will be written. Note that if the file has an extension it should be included. If 'myin.dat' cannot be found in the same directory as the program, an error will occur.

```
> f_electron help
```

The possible commands and parameters that can be given in the input file are listed.

```
> f_electron help keyword
```

More detailed help on the particular command or parameter given by 'keyword'.

```
> f_electron version
```

The program version and compile date are given.

In the same folder as the program f_electron.exe, there should be five data files additional to the input file: d_electron.dat, f_electron.dat, ccf.dat, group.dat and license.dat.

Input File

The structure of the input file should be as follows:

keyword   value1 value2 ..

The **first 4 characters** contain the 'keyword', followed by one or more values. Make sure that none of the 'values' appears in the first 4 characters of a line.

For this reason it is best to avoid the use of tabs. The number of values depends on the keyword. The keywords can be Commands or Parameters. The values must be separated by spaces.

In this manual, the type of input expected for the values are given as:
      N1 N2 ... integer numbers
      R1 R2 ... real numbers
      L1 L2 ... logical T or F
      T1 T2 … text

● The keywords should usually only be given once. If multiple lines are given with the same keyword, then the values from the last one is used. The preceding lines with the same keyword are ignored. (The exceptions are: CONS, INTR, LINK, TITL, VARI which can be given multiple times.)

● The order of the keywords is not important, except for the keyword END. The END keyword starts the calculation. Any lines in the input file after the END keyword are ignored.

● There are only 2 compulsory commands and these are CONF and END.

● Comments can be put at the end of any line by using a '!'. Any text following a "!" is ignored. A blank line or a line where the first character is "!" is ignored.

● The keywords are given in the Tables below for Command or Parameters. The keywords can be upper or lower case or a mixture of the two.

● The keyword is assumed to be the **first 4 characters** in a line.

● Note that each line is limited to 124 characters. This may cause problems, for example, if you try to give a list of 100 values for a particular parameter.

2.0 Commands

Notes for the following Tables

[N] Bracketed values indicate that they are optional.

(1) Compulsory command.

(2) A series of Logical inputs do not need to be all specified; the remaining that are not specified will default to False.

(3) Command can be given multiple times.

(4) A multi-line command. The additional lines are expected to immediately follow as a continuation of this command.

(5) This is also a parameter that can be varied in a fit.

2.1 Calculation Commands

CALCULATION COMMANDS		
Key-word	Values	Notes
BLOC	[N1]	Symmetry blocking will be carried out, based on the crystal quantum number (see [1] pp156-7). If optional N1=1 then the crystal quantum numbers are printed. This is a "cheap" alternative to using SYML which requires the calculation of eigenvectors.
CONF (1)	N1 N2	This is a compulsory command. N1 = L quantum number, 2/3 for d/f-electron calculation. N2 = Number of electrons: 1-9/1-13 for d/f electrons.
CONS (3)	T1 R1	A constant. Can be a number or an algebraic expression. T1: Name of constant (<10 char). R1: Value of constant, or expression. examples: CONS sr2 1.414213 CONS pi atan(1)*4 CONS trig acos(1/sqrt(3))*180/pi The precision of the constant is DBLE (~16 fig). This command can be given multiple times to define multiple constants. Up to 30 constants can be defined. See: "Parameters, Variables and Constants" (A6 below).

ECHO	L1 (def: F)	T/F for the input file to be echoed to the output file as each line is read. (Can be useful for debugging problems.)
EDIP	N1-N4, N5, N6, R7	Calculation of the intensities of electric dipole allowed transitions between a set of initial and final levels. There is an automatic summation over any initial or final state degeneracies. N1,N2 is the range of the initial levels (inclusively), N3,N4 is the range of the final levels (inclusively). If N5=1, the calculation is made in cartesian coordinates If N5=2, the calculation is also made for left (A_L) and right (A_R) circularly polarised light, MCD ($\Delta A = A_L - A_R$) and MLD ($\Delta A = A_x - A_y$). (Note: it is assumed that the direction of the incident light is k‖z and the magnetic field is H‖z and H‖x for MCD and MLD respectively.) If N5=3, the electric dipole amplitudes, instead of intensities are given, including relative phases. (Note: in this case there is no summing over degeneracies.) If N6=1-4 for the units to be calculated as f, Debye^2, $\times 10^{-24}$ cm^2, Area (ε (mol^{-1} L cm^{-1}) $\times$ cm^{-1}). (TO DO: Only N6= 2 & 3 are implemented) R7: A factor that the transitions are multiplied by to account for solvent effects. This should probably be set to 1.0 if dipole amplitudes are requested (N5=3).
GEXS	N1 N2 N3	If N1≠0 then the principle axes of the g-tensor are calculated: N2-N3 is the range of pairs of energy levels which are treated as isolated Kramers doublets for the calculation of g-values. There must be an even number of states given (N3-N2+1 must be even) (This is usually only meaningful for odd electron systems only, unless picking doubly degenerate states of non-Kramers systems.) Assumes a pseudo-spin ½ system. For ground state g-values put: GEXS 0 1 2 If N2 is negative, then this flags that the Kramers doublet pairs are listed explicitly: GEXS 0 -1 2 4 5 7 8

		Treats states 1,2 and 4,5 and 7,8 as Kramers doublets. Useful for picking degenerate levels in even electron systems. (note: program limited to the first 200 values)
GRID	N1 N2	N1, N2 the number of the variable to be used in forming a grid. (N1, N2 Must be >0 and <= Nvariables).
INTR (3)	T1 R1	Sets certain internal parameters given by T1 to have the value R1, overriding the default values. T1 (default value) **FImax**: (0.05) The minimum value of the coefficient to be included in the Free Ion output; see OPTN(3,4) **MJmax**: (0.05) The minimum value of the coefficient to be included in the MJ output; see OPTN(6,7). **CFbit**: (0.001) The limit (in cm^{-1}) for a CF matrix element to be considered zero. (Sometimes exact symmetry is hard to specify with a finite number of decimal places). It also determines whether the ligand field is complex; and whether block diagonalization is possible. **Edegen**: (0.01) The threshold (in cm^{-1}) below which two energy levels are to be considered degenerate. **Ndecpts**: (1) The number of decimal points used to print the energies. Valid values are 0-3. **PFactor**: (1.0) The factor by which the output to matrix.dat is multipled (Only needed if one of PRTn is true) **TestCrit**: (1.0) The criteria that will be used to flag when a test is not met (see command TEST).
JUDO	N1-N4, N5,R1-R4	The parameterization of the electric dipole induced intensities using the Judd-Ofelt model. N1,N2: the range of the initial levels (inclusive) N3,N4: the range of the final levels (inclusive). Note: that this range refers to level number of the multiplets (not the individual levels) after summing over the degeneracies. N5: Calculate intensities in units of 1-4: f, Debye^2, cm^2 or Area. R1-R4: Dielectric, Ω_2, Ω_4, Ω_6 The dielectric factor is often used as: $(n^2+2)^2/9n$ (n refractive index) for solutions [2], and the Ω_λ parameters are in the 3 J-O parameters in units of 10^{-20} cm^2 [2].

LINK (3)	N1 N2 R3 R4	The parameter number N1 is related to the parameter number N2 according to: $P(N1) = R3 \times P(N2) + R4$ Multiple LINK commands can be given. The "LINKing" will be carried out in the order given. Numbers N1, N2 refer to the standard order of parameters given in Appendix 5. **Note**: Multiple LINK parameters can be given, but P(N1) can only appear once (P(N2) can appear multiple times). P(N1) cannot be in a LINK and FIT at the same time (while P(N2) can).
MDIP	N1-N4, N5, N6, R7	Calculation of the intensities of magnetic dipole transitions between a set of initial and final levels. There is an automatic summation over any initial or final state degeneracies. N1,N2 is the range of the initial levels (inclusively), N3,N4 is the range of the final levels (inclusively). If N5=1, the calculation is made in cartesian coordinates If N5=2, the calculation is also made for left (A_L) and right (A_R) circularly polarised light, MCD ($\Delta A = A_L - A_R$) and MLD ($\Delta A = A_x - A_y$). (Note: it is assumed that the direction of the incident light is k‖z and the magnetic field is H‖z and H‖x for MCD and MLD respectively.) If N5=3, the magnetic dipole amplitudes, instead of intensities are given, including relative phases. (Note: in this case there is no summing over degeneracies.) If N6=1-3 for the units to be calculated as Bohr magneton^2, $\times 10^{-7}$ Debye^2, $\times 10^{-24}$ cm^2. (If N5=3, Bohr magneton, $\times 10^{-3}$ Debye, $\times 10^{-12}$ cm) R7: A factor that the transitions are multiplied by to account for solvent effects. Set to 1.0 if dipole amplitudes are requested (N5=3).
MFLD (5)	R1 R2 R3	Applied Magnetic Field: Hx, Hy, Hz (in Tesla)

OFFS (2)	N1 N2	Energy offsets
		N1: type of offset to be used
		N2: Number of levels to be offset (N2 lines follow this command) Maximum number = 50.
		
		N1=1 The energy offsets of the diagonalised $\|[SL]J>$ multiplets obtained from diagonalising the atomic terms. The N2 following lines will have the form:
		    I1, Eng
		I1 is the diagonalised $\|[SL]J>$ <u>multiplet</u> (in energy order) to be shifted by Eng.
		
		N1=2 Particular eigenvalues from the full calculation will be offset. This is most sensibly used if groups of levels that have been identified as belonging to the same multiplet are shifted by the same amount. The N2 following lines will have the form:
		    I1, I2, Eng
		I1,I2 is the inclusive range (in energy order) of the <u>individual levels</u> that will be shifted by Eng.
		
		This command must be given after the CONF command.

OPTN (2)	L1-L10 (def: all F)	Sets some options for the calculation. Each option is T/F 1) Energies relative to the lowest energy? 2) Calculate spin projections? 3) Calculate free ion %? (short 40char format) 4) Calculate free ion %? (long 80char format) 5) Do NOT include spin-spin interactions? (see [10]) 6) Calculate the MJ%? (short 40char format) 7) Calculate the MJ%? (long 80char format) 8) Skip writing matrix & diagonalisation? 9) Write matrix & skip diagonalisation? 10) Not used. Note: L2-L4, L6,L7 requires more time (as eigenvectors must be calculated). L8 is useful to avoid a long calculation when you are testing input. Note L3&L4 and L6&L7 are mutually exclusive.

PRED	N1	The ligand field will be evaluated in the basis of the N1 lowest states found in an atomic only calculation. ie The Eigenvectors found from the atomic calculation are used to create an N1 × N1 block of the ligand field matrix elements. It would make sense to choose N1 to include complete multiplets. If N1 is equal to the full basis, then this is equivalent to the full diagonalisation in the "prediagonalised" basis. Eigenvectors (if calculated), are back transformed into the original basis. Therefore properties should be correctly calculated (albeit with the effectively truncated basis)
REDF (5)	R1 R2 R3	The orbital reduction factors k_x, k_y, k_z. (Must be 0≤k≤1) Reduces the orbital angular momentum in g-value and magnetic dipole intensity calculations. (Note the spin-orbit coupling parameter ZETA is not reduced by these factors.)
ROTL (5)	R1 R2 R3	The ligand field (effectively the molecule) will be rotated by the Euler angles R1, R2, R3 (= α, β, γ). Rotate about z axis by α, about new y by β, about new z by γ. Angles are expected in degrees. Equivalently, this is a rotation about the space-fixed X, Y, Z axes: Rotate about Z by γ, about Y by β, about Z by α. The rotation is made after the Ligand Field is evaluated either (i) initially, (ii) if a B_q^k has been changed, or (iii) if an AOM parameter has been changed. OUTP(5) is useful for showing the ligand field before and after the rotation.
SPIN	N2 N2	Calculates the "spin-allowed" character for transition from the [N1,N2] range of initial states (inclusive) to all higher excited states. The N1, N2 refers to the state numbers without degeneracy, although the results are given summed over all degeneracies. The values for the initial states will be set to 1.0 For zero spin orbital coupling spin allowed transitions will be 1.0 and spin-forbidden transitions will be 0.0.

SYML	T1 [N2 N3]	T1 is the label of the point group. Recognised point groups are given in Appendix 1 below. The ligand field will be checked to ensure that it has the symmetry of this point group. N2 = 0/1 use Mullikan single group /Gamma double group notation. (Appropriate when if spin-orbit coupling is zero/ non-zero respectively.) N3 = 0/1 if projections onto each character is made. The **defaults values** for N2, N3 are 1 0. This command can be quite time-consuming.
TITL (3)	T1	Title of calculation (120 characters max.) This line can be repeated and can be used for comments or documentation. It is written to the output file.
VARI (3)	T1 R1 R2 R3 …	Defines the variable which can take the one or more values. T1: name of variable (10 char). Can be given in lower or upper case, but converted to lowercase internally. (ie: variables cannot be distinguished by case). R1 R2 ... : The values of the variable. Can be a single value. The maximum number of values is 100. This command can be given multiple times for the same variable (to add more values); or different variables. Up to 30 different variables can be defined, each with up to 100 values.
VARI (3)	T1 from R1 to R2 step R3	An alternative way of specifying the variable is by: VARI T1 from R1 to R2 step R3 This will set the variable T1 to have the INT((R2-R1)/R3) + 1 values between R1 and R2. See: "Parameters, Variables and Constants" (Appendix 6) below.
VARI (3)	T1 from R1 step R2 for N1	Another alternative way of specifying the variable: This will set the variable T1 to have N1 values, the ith value being R1 + i*R2 for i=0, (N1-1).

XREF	N1 N2	A coordinate system, is defined by two ligands given by numbers N1 and N2; together with the metal atom assumed to be at the origin O. The z-axis will be in the O→N1 direction. The y-axis will be perpendicular to the plane defined by the O, N1, N2 atoms. The x-axis will complete a right handed cartesian coordinate system. An error will result if O, N1, N2 are collinear.

2.2 Output Commands

None these commands need to be given, a default output will be given based on the calculation commands given.

OUTPUT COMMANDS		
Key-word	Values	Notes
FEXT	T1	T1 text (<22 chars) that is appended to the name of debug, matrices, plot files. This is to ensure these files are not overwritten in a batch job.
OUTP (2)	L1-L10 (def: all F)	Controls the extra output printed. Each option is T/F 1) Print ligand distance/angle matrix. 2) Print equivalent Crystal Field parameters. 3) Print one electron (d)f-orbital matrix & energies. 4) Print equivalent intensity parameters. 5) If ROTL, print CF parameters before and after rotation. 6) Print all energies, even if degenerate 7) Print info on the matrices sizes. 8) Print all parameters for each calculation in multiple calculations. 9) Print the one e$^-$ AOM energies & eigenvectors. 10) not used. 1) - 3), 9) is for AOM parameterization.
PLT1 (2)	L1-L10 (def: all F)	Controls the output to a plotfile "plot.dat". Each option T/F 1) Energies only 2) Energies + Spin faction 3) Energies + Spin-allowed intensities 4) Energies + MJ fraction 5) Magnetic Dipole Intensities 6) Electric Dipole Intensities (JO) 7) Parameters 8) Ligand Field B_q^k values, up to B_q^4(B_q^6) for d(f) systems 9) g-values 10) orbital energies (TODO)
PLT2 (2)	L1-L10 (def: all F)	Controls the output to a plotfile "plot.dat". Each option T/F 1) Prints the minimized function (σ) in a fit. 9)-10) not used.

PRNG	N1 N2 N3 (def: print all)	Control how many levels are printed. N1=1: The levels with energies (cm^{-1}) in range [N2: N3] N1=2: The levels numbered in range [N2: N3] will be printed. N2 must be < N3.
VECT	N1 N2 [N3]	Print a range ([N1 N2] inclusive) of eigenvectors. The first N3 coefficients will be printed in the standard basis order. (All coefficients printed if N3 left off.)
WARN (2)	L1-L10	Prints warning messages if 1) B_q^k parameters are not consistent with point group. 2) A_{ltp} parameters are not consistent with point group. 3) – 10) not currently used. For 1) & 2) a point group must be specified (see command SYML)
WORD	L1	If L1 true, prints extra (wordy) output.

2.3 Fitting Commands

The fitting commands `FIT` and `FITO` are given below. A "`FIT`" is the optimization of parameters values against some "experimental" criteria. The experimental data to be fitted against are specified by the `EXPn` commands below. The `EXPn` command can specify energies, intensities, g-values, B_q^k values or one-electron ligand field matrix elements. These quantities can be calculated and the calculated values compared to the "experimental" values. There are many different types of fits possible.

As well as fitting the parameters to measured experimental data, the "experimental" data can themselves be calculated data. For example, you may want to reproduce a previous energy level calculation from the literature. Or you may want to use the existing values for the ligand field in terms of the B_q^k and express these in terms of the Angular Overlap Model by using the ligand positions and allowing the AOM parameters to optimise so that the calculated B_q^k are fitted to the "experimental" B_q^k. It is possible to calculate the one electron ligand field matrix in *ab initio* programs like ORCA. It is possible to fit the AOM parameters to best reproduce this matrix.

Some general words of advice.

- Some parameters may be more sensitive to the experimental data than others. It is quite easy to generate fits that don't make sense.
- There are often many local minima that your fit may converge to that is not the global minimum.
- There are many equivalent ways to express a ligand field depending on your choice of axes.
- As well as fitting parameters, you can fit "Variables". This means you can define parameters in terms of variables which can then be fitted. This very powerful technique for linking and thereby reducing the number of parameters; see the tutorials for some examples.
- It is up to the user to make sure they are doing things that make sense.

FITTING COMMANDS		
Key-word	Values	
EXP1		The FIT will calculate the one-electron LF matrix from the LF parameterised by the AOM or B_q^k parameters and minimized against a provided "experimental" one-electron LF matrix. (Obviously you cannot use the LF1E command to specify the ligand field for this fit.)
		The complete lower triangle of the one-electron LF matrix must be given. This will be 7(5) lines with a total of 28(15) MEs for f(d) systems resp. The weight should be given after each matrix element.
		f11 w11 f21 w21 f22 w22 : f71 w71 f72 w72 f73 w73 f74 w74 f75 w75 f76 w76 f77 w77
		It is important when using this that the MEs that you calculate are in the same coordinate system as the the MEs given in this EXP1 command. While it is easy to identify the Z axis, it is often more difficult to identify the the X & Y axes. If there is a C_2 axis perpendicular to Z, then this will usually be the Y axis.

EXPB (4)	N1	N1 lines immediately following this command.
		A fit will be made against the crystal field B_q^k coefficients.
		
		Each line will be in the format:
		  Bkq(1), Wgt(1), Bkqlabel (1)
		   :
		  Bkq(N1), Wgt(N1), Bkqlabel (N1)
		
		Bkq: the B_q^k or B'^k_q value to be fitted (in cm^{-1}).
		Wgt: the relative weight of this value in the fit.
		Bkqlabel: the 3 or 4 character label Bkq or B′kq that identifies the particular B_q^k or B'^k_q. For example: B_1^2 is written as B21 and B'^6_3 would be written as B′63. There can be a maximum of 14 (27) parameters for d (f) electrons. Coefficients that are not given are not included in the fit. To fit a coefficient to have a value of zero, it must be explicitly given as 0 here.

		This fit does not diagonalise the matrix. Typically this command is used to: 1) fit AOM parameters/angles to a particular set of B_q^k values. 2) The Euler angles in ROTL α, β, γ are variables so the rotated CF fits the B_q^k values given, ie for example to find axes where the imaginary part of the CF is zero.

EXPE (4)	N1 N2 [N3] (N3 def 0)	N1 lines immediately following this command.
		Each line will contain either Energy (N2=1) or both Energy & Intensity (N2=2) data:
		
		   E W Nass1 Nass2 ... (N2=1)
		E: the energy (in cm^{-1})
		W: the relative weight of this value.
		NassN: the calculated levels that this energy is assigned to (can have up to 20 calculated values to each experimental value).
		
		   E WE I WI Nass1 Nass2 ... (N2=2)
		
		Here WE and WI are separate weights for the energy (E) and intensity (I) respectively. The intensity (I) values are expected to be in the units given in the JUDO or EDIP commands.
		
		The N1 lines of experimental values have to be in energy order for both the E experimental and the NassN calculated values.
		
		If N3=1 the for both N2=1 or N2=2 the level will be assigned to the calculated Nass1 level of the NAss2 crystal number block (The BLOC command must be used)

EXPG (4)	N1	N1 lines immediately following this command. Each line will contain: g_1 w_1 g_2 w_2 g_3 w_3 Nass1 g_1, g_2, g_3: the g-values in ascending order. w_1, w_2, w_3: the relative weighting of these values. Nass1: the lower calculated level of the Kramers doublet that these g-values are assigned to. Calculations on even electron systems should be made with care.

FIT (4)	N1 N2 R3	A least squares fit will be made. N1: Number of parameters to be varied. N2: The maximum number of iterations (function calls). R3: The fitting tolerance. The fit will continue until the fitting function is minimized below the R3 tolerance or exceeds N2 iterations. N1 lines <u>must</u> immediately follow this command, each line of the form: 　　Npar　　Pmin　　Pmax Npar gives the number of the parameter to be fitted in terms of the "standard order" as given in Appendix 5. The fitted value is constrained to be between Pmin and Pmax. Note: An EXPx command must also be given so that there is something to minimize in fitting the parameters. The Leveberg-Marquardt algorithm from MINPACK is used. J.J. Moré, B.S. Garbow, K.E. Hillstrom, "User Guide for MINPACK", ANL-80-74, Argonne National Laboratory, (1984).
FITO	L1- L8	The fit options: L1: If true, Print the reshaping matrices, and 14x14 matrices of the non-varying and parameter matrices. (Ignore if PRED$\neq$0.) L2: If true, Print full covariance matrix of the parameters. L3: If true, Print minimized function & parameters at each iteration. L4: If True, print parameters to a file "fit.out" L5: If True, print fit matrix to be diagonalised at each iteration. (Ignore if PRED$\neq$0.) L6: If true, then the parameters limits are hard, otherwise $100\times$ (P-Plimit)^2 is added to the penalty function. L7: The fit sums over degeneracies. L8: Include the mean deviation: $\delta = \sum |E_{exp} - E_{calc}|/N_{exp}$

2.4 Debugging Commands

These commands are not useful for the general user.

FNCR can be used to reproduce known errors in the literature.

<table>
<tr><td colspan="3" align="center">DEBUGGING COMMANDS</td></tr>
<tr><td>Key-word</td><td>Values</td><td align="center">Notes</td></tr>
<tr>
<td>BASE</td>
<td>T1</td>
<td>T1: "J" Use the $|\tau\ S\ L\ J\rangle$ basis.
T1: "MJ" Use the $|\tau\ S\ L\ J\ M_J\rangle$ basis.
(don't use the quotation marks)</td>
</tr>
<tr>
<td>CHK1
(2)</td>
<td>L1 – L10
(def: all F)</td>
<td>T/F for extra checks to be made. The extra information is put into the file: "debug.dat":
1) Basis
2) Un matrices
3) V11 matrices
4) EE matrices
5) abg matrices
6) Mn/Pn/Sn matrices
7) Tn matrices
8) AOM matrices
9) Eigenvalues
10) Point Groups</td>
</tr>
<tr>
<td>CHK2
(2)</td>
<td>L1 – L10
(def: all F)</td>
<td>T/F for extra checks to be made. The extra information is put into the file: "debug.dat":
1) Only write matrices, skip the diagonalisation.
2) Check that the wavefunctions make correct Kramers doublets. (Odd e- systems only).
3) Check $SOC = L_x S_x + L_y S_y + L_z S_z$ explicitly.
4) Check intensity parameter conversions.
5) Check CCF matrices.</td>
</tr>
<tr>
<td>ECHO</td>
<td>L1
(def: F)</td>
<td>T/F for the input file to be echoed to the output file as each line is read.</td>
</tr>
</table>

FNCR (2)	L1-L8 (def: all F)	T/F for using the errors that exist in some copies of the "fncross" files from the Reid programs for the following matrices:

f^n	1	2	3	4	5	6	7
1) Un	-	.	.	.	.	.	x
2) V11	-	.	.	.	x	.	.
3) Fn	-	.	.	.	x	x	x
4) abg	-	.	.	.	.	.	.
5) Mn/Pn	-	x	x^+	x^0	x^+	x^0	x^+
6) Tn	-	-	x	.	.	x	x

7) Incorrect t_2 matrix for complementary configs. These options are useful to reproduce published calculations that have these errors. (affects f^n, n=8-11)

8) The errors in the "fnmp" files of Crosswhite have been used instead. The "fncross" files contain the "fnmp" errors plus a few extra. The main errors are in the reduced matrix elements for Mn/Pn [17] and Tn [15]. Other errors are minor.
The "x" indicates which RMEs have errors. The superscripts indicates the fncross files have additional errors to those in fnmp files. The subscript "0" indicate the fnmp files have zero errors for the Mn/Pn RMEs.

PRT1 (2)	L1-L10 (def: all F)	T/F for printing the matrices in the |SL> basis to the file "matrices.dat" (maximum of 20×20 elements)
1) Uk
2) V11 matrix
3) Fn matrices
4) Mn matrices
5) Pn matrices
6) Sn matrices.
7) Tn matrices.
8) gik matrices (CCF)
9) Not used
10) Print a selection of above matrices

If (10) .True. then a line must follow with i1, i2, j1, j2
All must be within the range for the particular f/d system. The i1-i2 × j1-j2 sub-matrices will be printed. This over-rides the 20×20 limit and a full matrix can be printed. |
| (4) | | |

PRT2 (2) (4)	L1-L10 (def: all F)	T/F for printing the matrices in the |SLJ> basis to the file "matrices.dat". The |SLJ> basis can be invoked with the commands BASE or JUDO. A maximum of 20×20 elements will be printed (except 2). 1) Full Matrix (multiplied by PFactor, see INTR). 2) Full matrix as array of (*/.) (max.100×100 elements) 3) <||Uk||> matrices. Also gives <||Uk||> in the diagonalised |[SL]J> states. 4) L / S matrices 5) <||kL+gS||> matrices (plus in diag. |[SL]J> states.) 6) – 9) Not used 10) Print a selection of above matrices. If (10) .True. then a line must follow with i1, i2, j1, j2 All must be within the range for the particular f/d system. The i1-i2 × j1-j2 sub-matrices will be printed. This over-rides the 20×20 limit and a full matrix can be printed. Note: 1-2 only if JUDO or BASE J is used. 3 only print MEs for transition between states specified in JUDO. 4-5 only for BASE J with MDIP or GEXS used.
PRT3 (2) (4)	L1-L10 (def: all F)	T/F for printing the matrices in the complete |SLJMJ> basis to the file "matrices.dat". A maximum of 20×20 elements will be printed (except as given below). Only the lower triangle is printed. 1) Full Matrix multiplied by PFactor (see INTR) 2) Full matrix as array of (*/.) (max.100×100 elements) 3) <|Ukq|> matrices (non zero MEs, max 100) 4) <|Ukq|> matrices (full, max 14×14) 5) <| ED |> matrices in complete basis. 6) L/S magnetic moment matrices. 7) <|kL+gS|> matrices in complete basis. 8) LF matrices in original basis and PRED) basis. 9) Not used. 10) Print a selection of above matrices. See above. If (10) .True. then a line must follow with i1, i2, j1, j2

		All must be within the range for the particular f/d system. The i1-i2 × j1-j2 sub-matrices will be printed. This over-rides the 20×20 limit and a full matrix can be printed.
		
		Note: 3-5 happens only if `EDIP` is given
		        6-7 happens only when `MDIP` or `GEXS` is given
		        8 happens only when `PRED` is given

`TEST`		Appends the results $\sigma = \sqrt{W(E_{exp}-E_{calc})^2/N}$ from a fit to the file "test.out", where the fit can be to energy, intensity or g-value calculations. The file "test.out" must already exist or the program will stop. If σ is > TestCrit then this is flagged in the output. TestCrit is an internal constant with the default value = 1.0 but this can be set with the command `INTR`. This command is intended for use with a series of calculations run from a batch job, in which the results are kept as a record. Also recorded is the version, compile date, run date and input filename. It tests whether new program versions still give the same results as previous versions.
`TIME`		Prints more detailed timing information to the output file.

3.1 Atomic Parameters

ATOMIC PARAMETERS		
Keyword	Values	Notes
EAVE	R1	EAVE is added to the diagonal. This has no effect if OPTN(1)=T. If OPTN(1)=F, this results in the calculated energies having +EAVE added.
F2 *	R1	Slater parameters F^2, F^4, F^6 *
F4	R1	(aka electron repulsion parameters)
F6	R1	(aka electrostatic parameters)
ZETA	R1	Spin-orbit coupling parameter
ALPH	R1	The α, β, γ two body CI parameters.
BETA	R1	2nd order Coulomb interactions with higher
GAMM	R1	configurations of same parity.
M0	R1	M^0, M^2, M^4 magnetic parameters for H_{soo} (spin-other-orbit). These are also used in the H_{ss} (spin-spin) if OPTN(6)=T [10]
M2	R1	
M4	R1	
P2	R1	P^2, P^4, P^6 parameters
P4	R1	H_{el-so} (electrostatically correlated spin-orbit
P6	R1	interactions)
T2	R1	T^2, T^3, T^4, T^6, T^7, T^8 parameters
T3	R1	Three body parameters of Coulomb interactions
T4	R1	Only for f^N and f^{14-N} for N>2.
T6	R1	
T7	R1	
T8	R1	

Note: These 20 atomic parameters all have the energy units of cm^{-1}.
Starting values for these parameters can be taken, eg, from table 5, pg 168, ref [1].

EAVE, ZETA can be given for any d^n, f^n.
Fn parameters are only for d^n, d^{10-n}, f^n, f^{14-n}, n >1. F2,F4,F6 are subscripts, the relationships to Fn where n is a superscript, En and B/C are given in Appendix A2.2.
ALPH, BETA, GAMM, Mn, Pn parameters are only for f^n, f^{14-n}, n >1.
Tn parameters are only for f^n, f^{14-n}, n >2.

* Either F2, F4 or B, C can be used for d-systems, but not a mixture of the two.

3.2 Ligand Field Parameters

<table>
<tr><th colspan="3">LIGAND FIELD PARAMETERS</th></tr>
<tr><th>Key-word</th><th>Values</th><th>Notes</th></tr>
<tr>
<td>AOM
(1)</td>
<td>N1
(def: 0)</td>
<td>

If this command is given, the ligand field is specified by the Angular Overlap Model (AOM).

| N1 | is the number of ligands.
If N1 = 0, then there are no ligands. (In which case AOM does nothing, the same as not giving AOM)
If N1>0, then each ligand is specified by:
  Name, e_σ, $e_{\pi x}$, $e_{\pi y}$, θ, ϕ, χ
If N1<0, then each ligand is specified by:
  Name, e_σ, $e_{\pi x}$, $e_{\pi y}$, x, y, z

e_σ, $e_{\pi x}$, $e_{\pi y}$ are the AOM parameters.
In most cases $e_{\pi x} = e_{\pi y}$; $e_{\pi x} \neq e_{\pi y}$ gives the π bonding anisotropy. The ligand positions can be specified by θ, ϕ, χ AOM angles; or by the x, y, z Cartesian coordinates.

There must be |N1| lines following the AOM command each with either:
 "Name, e_σ, $e_{\pi x}$, $e_{\pi y}$ θ, ϕ, χ" or "Name, e_σ, $e_{\pi x}$, $e_{\pi y}$ x, y, z".
The angle χ need not be included, the default value is zero.

Notes:

The specification of the ligand field implicitly specifies the axes of the basis functions. To take full advantage of any potential symmetry blocking (BLOC command), a sensible z-axis must be chosen.

For the symmetry labels to work correctly, the axes must conform to that of the symmetry operations in the character tables of Koster, *et al.* [3].

The axes/coordinate system can also be influenced by the commands XREF and ROTL.

</td>
</tr>
</table>

CF (1)		The ligand field is specified by the crystal field parameters B_q^k. These B_q^k parameters follow the definitions of [1].

The 27 (14) B_q^k parameters (no B_0^0) are given in 15 (8) lines immediately following the CF command for f (d) electrons:

$$
\begin{array}{ll}
B_0^2 & \\
B_1^2 & B'^2_1 \\
B_2^2 & B'^2_2 \\
B_0^4 & \\
B_1^4 & B'^4_1 \\
B_2^4 & B'^4_2 \\
B_3^4 & B'^4_3 \\
B_4^4 & B'^4_4 \\
B_0^6 & \\
B_1^6 & B'^6_1 \\
B_2^6 & B'^6_2 \\
B_3^6 & B'^6_3 \\
B_4^6 & B'^6_4 \\
B_5^6 & B'^6_5 \\
B_6^6 & B'^6_6 \\
\end{array}
$$

B_q^k real, B'^k_q imaginary coefficients [1]
(B_q^k, B'^k_q are both real numbers)

Some symmetry relations:
$C_2(z) \rightarrow$ no B_q^k with q odd
$C_2(y) \rightarrow$ no B'^k_q
$C_n(z) \rightarrow$ no $B_q^k \neq 0$ only for q multiple of n

25

| LF1E (1) | | If this command is given, the ligand field is specified by the one electron matrix elements in the following 5 (d-electrons) or 7 lines (f-electrons) in the following order: |

```
d11
d21  d22
d31  d32  d33
d41  d42  d43  d44
d51  d52  d53  d54  d55

f11
f21  f22
f31  f32  f33
f41  f42  f43  f44
f51  f52  f53  f54  f55
f61  f62  f63  f64  f65  f66
f71  f72  f73  f74  f75  f76  f77
```

The assumed order is
d-orbitals: Schaffer, *Struct.&Bond.*,**5**,68,(1968).

z^2	yz	xz	xy	x^2-y^2
σ	πs	πc	δs	δc

f-orbitals: Urland, *Chem.Phys.*,**14**,393,(1976).
Harnung & Schaffer, *Struct.&Bond.*,**12**,201,(1972).

z^3	yz^2	xz^2	xyz	$z(x^2$-$y^2)$	$y(3x^2$-$y^2)$	$x(x^2$-$3y^2)$
σ	πs	πc	δs	δc	φs	φc

The parameters are the lower triangle of the one-electron ligand field matrix. In the real f- (d-) orbital basis, all values are real. The trace of diagonal elements is just an overall shift of all levels.

Therefore there are 27 (14) unique parameters for f (d) electrons, the same as in the B_q^k CF parameterisation.

3.3 Intensity Parameters

INTENSITY PARAMETERS		
Key-word	Values	Notes
ALTP (1)	N1 N2	The electric dipole intensity parameters. This is only valid for f-electron calculations. The parameters (both A^λ_{tp} and B^λ_{ki}) are assumed to be in units of $\times 10^{-12}$ cm. N1=1 A^λ_{tp} parameters N1=2 B^λ_{ki} parameters (i=x,y,z) N1=3 or 4 AOM parameters (TODO) N2=1 All parameters are pure real N2=2 All parameters are pure imaginary N2=3 All parameters are complex A^λ_{tp} parameters (N1=1) 　　A^2_{10}, A^2_{11} 　　$A^2_{20}, A^2_{21}, A^2_{22}$ 　　$A^2_{30}, A^2_{31}, A^2_{32}, A^2_{33}$ 　　$A^4_{30}, A^4_{31}, A^4_{32}, A^4_{33}$ 　　$A^4_{40}, A^4_{41}, A^4_{42}, A^4_{43}, A^4_{44}$ 　　$A^4_{50}, A^4_{51}, A^4_{52}, A^4_{53}, A^4_{54}, A^4_{55}$ 　　$A^6_{50}, A^6_{51}, A^6_{52}, A^6_{53}, A^6_{54}, A^6_{55}$ 　　$A^6_{60}, A^6_{61}, A^6_{62}, A^6_{63}, A^6_{64}, A^6_{65}, A^6_{66}$ 　　$A^6_{70}, A^6_{71}, A^6_{72}, A^6_{73}, A^6_{74}, A^6_{75}, A^6_{76}, A^6_{77}$ The 45 in total parameters will be restricted by the symmetry of the molecule. See table 1 from [8] given below. A single value/variable is need for each A^λ_{tp} parameter if N2=1, 2 or the complex pair (R1, R2) if N2=3. The A^λ_{tp} parameterisation is according to Reid & Richardson [7]. There should be 9 lines immediately following the ALTP command. Note the A^λ_{tp} parameters are in general complex, but that A^λ_{t0} is pure real (t odd) or pure imag (t even) so this gives a total of 90 - 9 = 81 possible parameter values.

Some symmetry relations:

A^2_{10}, A^2_{11}

$A^2_{20}, A^2_{21}, A^2_{22}$

$A^2_{30}, A^2_{31}, A^2_{32}, A^2_{33}$

$A^4_{30}, A^4_{31}, A^4_{32}, A^4_{33}$

$A^4_{40}, A^4_{41}, A^4_{42}, A^4_{43}, A^4_{44}$

$A^4_{50}, A^4_{51}, A^4_{52}, A^4_{53}, A^4_{54}, A^4_{55}$

$A^6_{50}, A^6_{51}, A^6_{52}, A^6_{53}, A^6_{54}, A^6_{55}$

$A^6_{60}, A^6_{61}, A^6_{62}, A^6_{63}, A^6_{64}, A^6_{65}, A^6_{66}$

$A^6_{70}, A^6_{71}, A^6_{72}, A^6_{73}, A^6_{74}, A^6_{75}, A^6_{76}, A^6_{77}$

cylindrical ligand bonds:
no A^λ_{tp} for $t = \lambda$

for $C_2(z)$: no A^λ_{tp} for p odd

TABLE I. Occurrences of the identity irrep in t'' of the $A^{\lambda *}_{t \to p}$ for various symmetry groups.

Group	$t'' = 1''$	$2''$	$3''$	$4''$	$5''$	$6''$	$7''$	Number of intensity parameters[a]		
								$t = \lambda \pm 1$	$t = \lambda$	Total
C_1	3	5	7	9	11	13	15	54	27	81
C_2	1	3	3	5	5	7	7	24	15	39
C_3	1	1	3	3	3	5	5	18	9	27
C_4	1	1	1	3	3	3	3	12	7	19
C_6	1	1	1	1	1	3	3	8	5	13
C_s	2	2	4	4	6	6	8	30	12	42
C_{2v}	1	1	2	2	3	3	4	15	6	21
C_{3v}	1	...	2	1	2	2	3	12	3	15
C_{4v}	1	...	1	1	2	1	2	9	2	11
C_{6v}	1	...	1	...	1	1	2	7	1	8
$C_{\infty v}$	1	...	1	...	1	...	1	6	...	6
C_{3h}	...	...	2	2	2	2	2	10	4	14
D_2	...	2	1	3	2	4	3	9	9	18
D_3	...	1	1	2	1	3	2	6	6	12
D_4	...	1	...	2	1	2	1	3	5	8
D_6	...	1	...	1	...	2	1	1	4	5
D_{2d}	...	1	1	1	1	2	2	6	4	10
D_{3h}	...	...	1	1	1	1	1	5	2	7
S_4	...	2	2	2	2	4	4	12	8	20
T	...	...	1	1	...	2	1	3	3	6
T_d	...	...	1	...	...	1	1	3	1	4
O	...	...	...	1	...	1	...	...	2	2

INTENSITY PARAMETERS		
Key-word	Values	Notes
`ALTP` `(1)`	N1 N2	B^λ_{ki} parameters (N1=2) B^2_{0x}, B^2_{0y}, B^2_{0z} B^2_{1x}, B^2_{1y}, B^2_{1z} B^2_{2x}, B^2_{2y}, B^2_{2z} B^4_{0x}, B^4_{0y}, B^4_{0z} ⋮　⋮ B^4_{4x}, B^4_{4y}, B^4_{4z} B^6_{0x}, B^6_{0y}, B^6_{0z} ⋮　⋮ B^6_{6x}, B^6_{6y}, B^6_{6z} The 45 B^λ_{ki} parameters can be related to the A^λ_{tp} by the expressions in [9]. There should be 15 lines immediately following the `ALTP` command. Note that the B^λ_{ki} parameters are in general complex, but the B^λ_{0i} are pure real so this gives a total of $90 - 9 = 81$ possible parameter values.

(1) Multi-line command. Additional lines follow immediately after this command.

Appendices

A1 Point Groups

The following point groups are recognised. Using a particular point group below assumes a certain orientation of the molecular axes. The character tables and definition of the axes are those used in KDWS [3].

Valid point group symbols:

1	C1	2	Ci	3	C2	4	Cs	5	C2h
6	D2	7	C2v	8	D2h	9	C4	10	S4
11	C4h	12	D4	13	C4v	14	D2d	15	D4h
16	C3	17	C3i	18	D3	19	C3v	20	D3d
21	C6	22	C3h	23	C6h	24	D6	25	C6v
26	D3h	27	D6h	28	T	29	Th	30	Td
31	O	32	Oh						

Note that the symbols (and not the numbers) are used in the SYML command. The numbers refer to the numbering in KDWS [3]. The point group symbols can be given as upper, lower or a mixture or upper and lower cases.

Some additional point groups have also been defined using a non-standard orientation of the axes:

33	TdT	34	OT	35	OhT	36	C2Y	37	CsY

TdT: The tetrahedral point group using the trigonal axes. The molecular Z axis is along a C_3 axis (along a M-L bond), the molecular Y axis is perpendicular to a σ_d plane.

OT, OhT: The octahedral point group using the trigonal axes. The molecular Z axis is along a C_3 axis (bisecting 3 M-L bonds) and the molecular Y axis is along a C_2 axis (bisecting 2 M-L bonds).

C2Y: The C_2 point group, but with the symmetry element $C_2(y)$ instead of $C_2(z)$.

CsY: The C_s point group, but with the symmetry element σ perpendicular to y.

A2 Conversions

A2.1 Relationships between O_h AOM and CF Ligand Fields

The (x, y, z) cubic and (X, Y, Z) trigonal axes are defined as in: Sugano, Tanabe, Kamimura, "Multiplets of Transition Metal Ions", AP, (1970), pg 130-1.
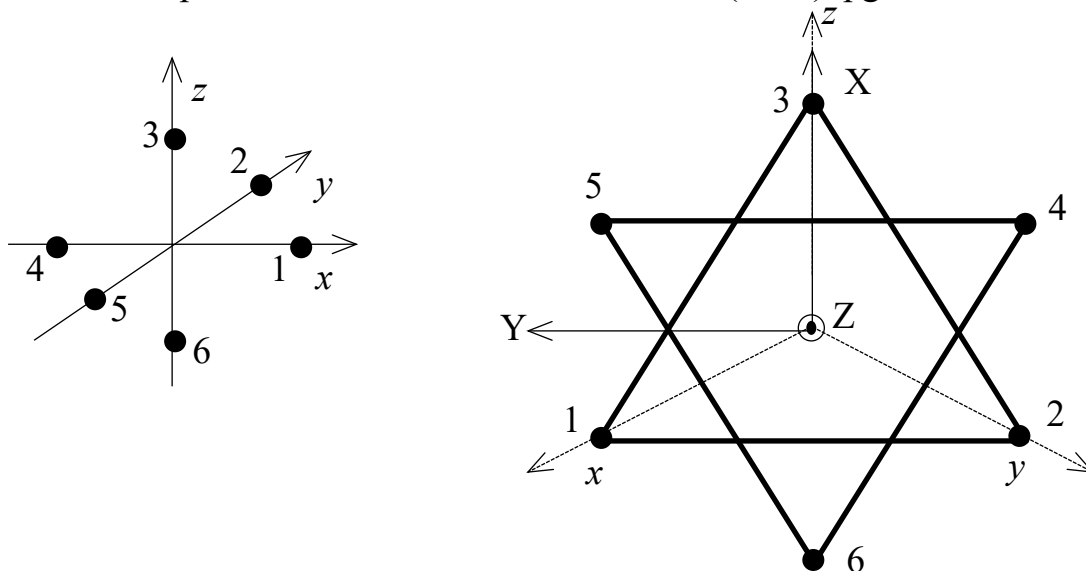
The relationship between AOM and the B_q^k parameters in O_h for d-orbitals.

	O_h (cubic axes)		O_h (trigonal axes)	
	θ	ϕ	θ	ϕ
1	$\pi/2$	0	θ_T	$2\pi/3$
2	$\pi/2$	$\pi/2$	θ_T	$4\pi/3$
3	0	0	θ_T	0
4	$\pi/2$	π	$\pi - \theta_T$	$5\pi/3$
5	$\pi/2$	$3\pi/2$	$\pi - \theta_T$	$\pi/3$
6	π	0	$\pi - \theta_T$	π
B_0^2	0		0	
B_1^2	0	0	0	0
B_2^2	0	0	0	0
B_0^4	$21/10(3\sigma-4\pi)$		$-7/5(3\sigma-4\pi)$	
B_1^4	0	0	0	0
B_2^4	0	0	0	0
B_3^4	0	0	$-\sqrt{\frac{10}{7}}B_0^4$	0
B_4^4	$\sqrt{\frac{5}{14}}B_0^4$	0	0	0

$\theta_T = \cos^{-1}(1/\sqrt{3}) = 54.7356..°$

Note that there is only one independent parameters: B_0^4 for both cubic and trigonal axes.

The relationship between AOM and the B_q^k parameters in octahedral geometry for f-orbitals.

	O_h (cubic axes)		O_h (trigonal axes)	
	θ	ϕ	θ	ϕ
1	$\pi/2$	0	θ_T	$2\pi/3$
2	$\pi/2$	$\pi/2$	θ_T	$4\pi/3$
3	0	0	θ_T	0
4	$\pi/2$	π	$\pi - \theta_T$	$5\pi/3$
5	$\pi/2$	$3\pi/2$	$\pi - \theta_T$	$\pi/3$
6	π	0	$\pi - \theta_T$	π
B_0^2	0		0	
B_1^2	0	0	0	0
B_2^2	0	0	0	0
B_0^4	$3/2(3\sigma+\pi)$		$-(3\sigma+\pi)$	
B_1^4	0	0	0	0
B_2^4	0	0	0	0
B_3^4	0	0	$-\sqrt{\frac{10}{7}}B_{40}$	0
B_4^4	$\sqrt{\frac{5}{14}}B_0^4$	0	0	0
B_0^6	$39/56\,(2\sigma\text{-}3\pi)$		$\frac{26}{21}(2\sigma\text{-}3\pi)$	
B_1^6	0	0	0	0
B_2^6	0	0	0	0
B_3^6	0	0	$\frac{1}{8}\sqrt{\frac{70}{3}}B_0^6$	0
B_4^6	$-\sqrt{\frac{7}{2}}B_{60}$	0	0	0
B_5^6	0	0	0	0
B_6^6	0	0	$\frac{1}{8}\sqrt{\frac{77}{3}}B_0^6$	0

Note that there are only two independent parameters: B_0^4 and B_0^6 for cubic axes and for trigonal axes. For trigonal axes: $\theta_T = \cos^{-1}(1/\sqrt{3}) = 54.7356..°$

The requirement of two parameters is consistent with the fact that there are two energy gaps in the LF splitting of the f-orbitals. (Compared to the single energy gap and single parameter for d-electron systems in O_h symmetry.)

t_{1u} ≡ $2\sigma + 3/2\pi$

t_{2g} ≡ $3\sigma - 4\pi$

t_{2u} ≡ $5/2\pi$

a_{2u} — 0

e_g = 0

O_h d-orbitals

O_h f-orbitals

The relationship between B_0^4, B_0^6 and σ, π in O_h symmetry for cubic axes is:

$$\begin{pmatrix} B_0^4 \\ B_0^6 \end{pmatrix} = \begin{pmatrix} 9/2 & 3/2 \\ 78/56 & -117/56 \end{pmatrix} \begin{pmatrix} \sigma \\ \pi \end{pmatrix} \qquad \begin{pmatrix} \sigma \\ \pi \end{pmatrix} = \begin{pmatrix} 2/11 & 56/429 \\ 4/33 & -56/143 \end{pmatrix} \begin{pmatrix} B_0^4 \\ B_0^6 \end{pmatrix}$$

For O_h symmetry with trigonal axes it is:
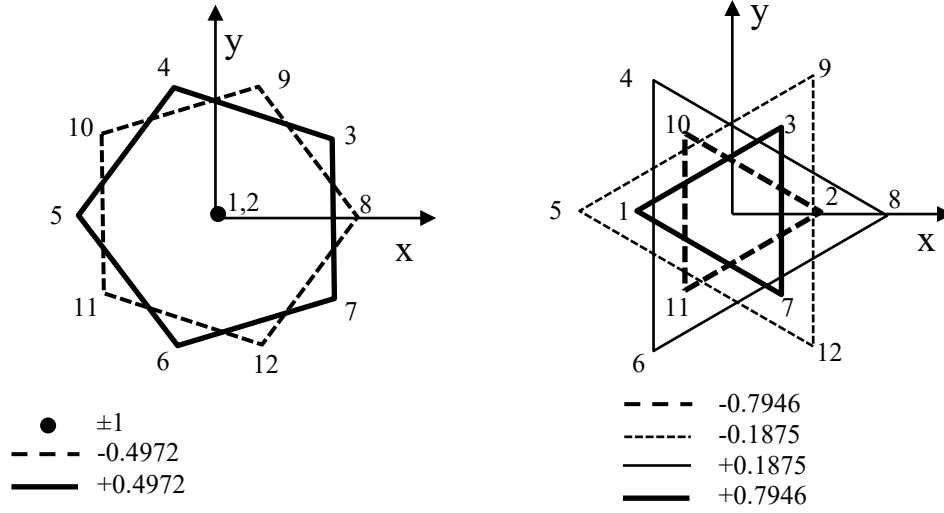
$$\begin{pmatrix} B_0^4 \\ B_0^6 \end{pmatrix} = \begin{pmatrix} -3 & -1 \\ 52/21 & -26/7 \end{pmatrix} \begin{pmatrix} \sigma \\ \pi \end{pmatrix} \qquad \begin{pmatrix} \sigma \\ \pi \end{pmatrix} = \begin{pmatrix} -3/11 & 21/286 \\ -2/11 & -63/286 \end{pmatrix} \begin{pmatrix} B_0^4 \\ B_0^6 \end{pmatrix}$$

A2.2 Relationships between I_h AOM and CF Ligand Fields

The atom positions and coordinate system for an icosahedron that taken from [1] (Figure 12, Table 15) for Z $\|C_5$ or Z$\|$ C_3.

The pentagon and triangles indicate atoms with the equal z values indicated, for a regular icosahedron with unit 1 bond lengths.

AOM angles:

	I_h (z $\|$ 5-fold axis)		I_h (z $\|$ 3-fold axis)	
	θ	ϕ	θ	ϕ
1	0	0	α_2	π
2	π	0	$\pi - \alpha_2$	0
3	α_1	$\pi/5$	α_2	$\pi/3$
4	α_1	$3\pi/5$	$\pi - \alpha_1 - \alpha_2$	$2\pi/3$
5	α_1	π	$\alpha_1 + \alpha_2$	π
6	α_1	$7\pi/5$	$\pi - \alpha_1 - \alpha_2$	$4\pi/3$
7	α_1	$9\pi/5$	α_2	$5\pi/3$
8	$\pi - \alpha_1$	0	$\pi - \alpha_1 - \alpha_2$	0
9	$\pi - \alpha_1$	$2\pi/5$	$\alpha_1 + \alpha_2$	$\pi/3$
10	$\pi - \alpha_1$	$4\pi/5$	$\pi - \alpha_2$	$2\pi/3$
11	$\pi - \alpha_1$	$6\pi/5$	$\pi - \alpha_2$	$4\pi/3$
12	$\pi - \alpha_1$	$8\pi/5$	$\alpha_1 + \alpha_2$	$5\pi/3$

$$\alpha_1 = cos^{-1}\left(\frac{\cos 72°}{1 - \cos 72°}\right) = 63.43..° \qquad \alpha_2 = sin^{-1}\sqrt{\frac{2(1 - 2\cos 72°)}{3(1 - \cos 72°)}} = 37.37..°$$

B_0^2	0		0	
B_1^2	0	0	0	0
B_2^2	0	0	0	0
B_0^4	0		0	
B_1^4	0		0	0
B_2^4	0	0	0	0
B_3^4	0	0	0	0
B_4^4	0	0	0	0
B_0^6	429/175 (4σ-6π)		-143/105 (4σ-6π)	
B_1^6	0	0	0	0
B_2^6	0	0	0	0
B_3^6	0	0	$\sqrt{\frac{7}{3}}\,B_0^6$	0
B_4^6	0	0	0	0
B_5^6	$-\sqrt{\frac{7}{11}}\,B_0^6$	0	0	0
B_6^6	0	0	$-2\sqrt{\frac{7}{33}}\,B_0^6$	0

Note that there is only one independent parameters: B_0^6 for z‖ C_5 and z‖ C_3 axes. The requirement of one parameter is consistent with the fact that there in only one energy gap in the LF splitting of the f-orbitals. (Compared to the single energy gap and single parameter for d-electron systems in O_h symmetry.)

$$t_{2u} \quad \equiv\equiv\equiv \quad 4\sigma - 6\pi$$

$$g_u \quad \equiv\equiv\equiv\equiv \quad 0$$

I_h f-orbitals

Comment: Both coordinate systems give the same energy splitting of f-orbitals. Both are defined with the Y axis coincident with a C_2 axis. Note that if the molecule is rotated 180° about the Z axis, the Y-axis will still be along the C_2 axis but the values of B_6^6 (C_5 system) and B_3^6 (C_3 system) will change sign.

A2.3   Different definitions of Electrostatic/ e-e repulsion parameters:

The program uses either the Slater-Condon parameters F^2, F^4 or the Racah parameters B, C for d-electrons; and the Slater-Condon parameters F^2, F^4, F^6 for f-electrons. Note the offset parameters F^0 or A are not used.

d-electrons: The relationship between F^k, F_k and B, C parameters is given by

$$\begin{pmatrix} F_0 \\ F_2 \\ F_4 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 7/5 \\ 0 & 1 & 1/7 \\ 0 & 0 & 1/35 \end{pmatrix} \begin{pmatrix} A \\ B \\ C \end{pmatrix} \qquad \begin{pmatrix} A \\ B \\ C \end{pmatrix} = \begin{pmatrix} 1 & 0 & -49 \\ 0 & 1 & -5 \\ 0 & 0 & 35 \end{pmatrix} \begin{pmatrix} F_0 \\ F_2 \\ F_4 \end{pmatrix}$$

and using $F^0 = F_0$; $F^2 = 49\,F_2$; $F^4 = 441\,F_4$ [14]

$$\begin{pmatrix} F^0 \\ F^2 \\ F^4 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 7/5 \\ 0 & 49 & 49/7 \\ 0 & 0 & 441/35 \end{pmatrix} \begin{pmatrix} A \\ B \\ C \end{pmatrix} \qquad \begin{pmatrix} A \\ B \\ C \end{pmatrix} = \begin{pmatrix} 1 & 0 & -49/441 \\ 0 & 1/49 & -5/441 \\ 0 & 0 & 35/441 \end{pmatrix} \begin{pmatrix} F^0 \\ F^2 \\ F^4 \end{pmatrix}$$

f-electrons: the tables of Neilson & Koster [4] give the coefficients to the F^k parameters for d-electron and E^k for f- electron systems. The relationship is given (pg vi) as:

$$\begin{pmatrix} E^0 \\ E^1 \\ E^2 \\ E^3 \end{pmatrix} = \begin{pmatrix} 1 & -2/45 & -1/33 & -50/1287 \\ 0 & 14/405 & 7/297 & 350/11583 \\ 0 & 1/2025 & -1/3267 & 175/1656367 \\ 0 & 1/135 & 2/1089 & -175/42471 \end{pmatrix} \begin{pmatrix} F^0 \\ F^2 \\ F^4 \\ F^6 \end{pmatrix}$$

Inverting this gives:

$$\begin{pmatrix} F^0 \\ F^2 \\ F^4 \\ F^6 \end{pmatrix} = \begin{pmatrix} 1 & 9/7 & 0 & 0 \\ 0 & 75/14 & 10725/14 & 825/14 \\ 0 & 99/7 & -12870/7 & 396/7 \\ 0 & 5577/350 & 5577/10 & -5577/50 \end{pmatrix} \begin{pmatrix} E^0 \\ E^1 \\ E^2 \\ E^3 \end{pmatrix}$$

These expressions can also be obtained from Wybourne ([5], pp 28-9), who relates the E^k to F_k (note subscript); and using the following expressions (Goerllner-Wallend, [1], pg 165):

$$F^0 = F_0; \quad F^2 = 225\,F_2; \quad F^4 = 1089\,F_4; \quad F^6 = 184041/25\,F_6$$

Note: that F^k is most commonly used for f-electron systems.

An approximation that is sometimes used is that the ratio of the e-e repulsion parameters F^4/F^2 and F^6/F^2 are equal to the values determined for hydrogenic orbitals. While it is not advised to depend on this ratio, sometimes it is useful to use to reproduce a calculation in the literature. From [5, pp 40-41] and converting from F_n to F^n, one finds:

$$F^4/F^2 = 451 \,/\, 675 \quad F^6/F^2 = 1001 \,/\, 2025$$

A2.4   Different definitions of the Ligand Field Parameters

A2.4.1 The Wybourne Convention

This program uses the definition of the ligand field as given by of Goerller-Walrand and Binnemans [1].

$$H_{LF} = \sum_k^{2,4,6} \left(B_0^k C_0^k + \sum_{q=1}^k B_q^k (C_{-q}^k + (-1)^q C_q^k) + B'^k_q \, i \, (C_{-q}^k - (-1)^q C_q^k) \right)$$

Note that we use the notation B_q^k, and C_q^k as used in [1]. Both B_q^k and B'^k_q are real numbers. They are the real and imaginary parts of the ligand field as expressed in terms of the C_q^k tensor operators. The C_q^k operators have the same transformation properties as the spherical harmonics Y_{kq}:

$$C_q^k = \sqrt{\frac{4\pi}{2k+1}} \, Y_k^q$$

This definition of the ligand field is also known as the Wybourne definition [5].

Note that the number of parameters (not counting B_{00} which shifts all d or f states by the same amount) is 14 and 27 for d or f bases. This is $(\ell+1)(2\ell+1)$ or the number of lower triangle matrix elements in a (5×5) or (7×7) matrices in a d- or f-orbital basis.

A2.4.2 Using Unit Tensor Operators

The ligand field can also be defined in terms of unit tensor operators U_q^k. For example the octahedral ligand field in Richardson *et al.* [12] uses:

$$H_{LF} = B_0^{(4)} U_0^{(4)} + B_4^{(4)} \left(U_4^{(4)} + U_{-4}^{(4)} \right) + B_0^{(6)} U_0^{(6)} + B_4^{(6)} \left(U_4^{(6)} + U_{-4}^{(6)} \right)$$

The relationship with the B_q^k parameters for f electrons is

$$B_0^{(k)} = B_q^k (-7) \begin{pmatrix} 3 & k & 3 \\ 0 & 0 & 0 \end{pmatrix}$$

$$B_q^{(2)} = \frac{-14}{\sqrt{105}} B_q^2, \quad B_q^{(4)} = \sqrt{\frac{14}{11}} B_q^4, \quad B_q^{(6)} = \frac{-70}{\sqrt{3003}} B_q^6$$

Both $B_0^{(4)} = 2392$ cm^{-1} and $B_0^{(6)} = -330$ cm^{-1} and $B_0^4 = 2120.28$ cm^{-1} and $B_0^6 = 258.34$ cm^{-1} ligand fields (with $\zeta = 623$ cm^{-1} and using the usual relations: $B_4^{(4)} =$

$\sqrt{\frac{5}{14}}\ B_0^{(4)}$ and $B_4^{(6)} = -\sqrt{\frac{7}{2}}\ B_0^{(6)}$ for an octahedral LF) gives the Ce(III) f^1 calculated energy levels:

	E / cm^{-1}		
1	0	E"	Γ_6
2	570	U'	Γ_8
3	2160	E"	Γ_7
4	2662	U'	Γ_8
5	3048	E'	Γ_6

A2.4.3 Using Spherical Harmonics

A general ligand field for f-electrons can be defined as in Urland [13]:

$H_{LF} = R_2c_{20}\ Y_2^0 + R_2c_{21}\ (Y_2^1 - Y_2^{-1}) + R_2c_{22}\ (Y_2^2 + Y_2^{-2})$
$+ R_4c_{40}\ Y_4^0 + R_4c_{41}(Y_4^1 - Y_4^{-1}) + R_4c_{42}(Y_4^2 + Y_4^{-2}) + R_4c_{43}(Y_4^3 - Y_4^{-3}) + R_4c_{44}(Y_4^4 + Y_4^{-4}) +$
$R_6c_{60}\ Y_6^0 + R_6c_{61}(Y_6^1 - Y_6^{-1}) + R_6c_{62}(Y_6^2 + Y_6^{-2}) + R_6c_{63}(Y_6^3 - Y_6^{-3}) + R_6c_{64}(Y_6^4 + Y_6^{-4})\ +$
$R_6c_{65}(Y_6^5 - Y_6^{-5}) + R_6c_{66}(Y_6^6 + Y_6^{-6})$

Here the R_kc_{kq} parameters are complex for q$\neq$0, again making 27 parameters. The relationship with B_q^k used here

$$B_q^k = (-1)^q \sqrt{\frac{2k+1}{4\pi}}\ Re(R_kc_{kq}), \quad B'^k_q = -(-1)^q \sqrt{\frac{2k+1}{4\pi}}\ Im(R_kc_{kq})$$

A2.4.4 Using Operator Equivalents

Some older references (in particular Dieke and Crosswhite references in the 1960s) specify the ligand field in terms of operator equivalents, or Steven's operators, with parameters: $A_q^k < r^k >$. The relationship between these parameters and the B_q^k used here have been given by [1, Table 6], [21, Table A1] and are reproduced below.

B_0^2	$2\,A_0^2 <r^2>$	B_0^4	$8\,A_0^4 <r^4>$	B_0^6	$16\,A_0^6 <r^6>$
B_1^2	$\dfrac{-1}{\sqrt{6}}A_1^2 <r^2>$	B_1^4	$\dfrac{-2}{\sqrt{5}}A_1^4 <r^4>$	B_1^6	$\dfrac{-8}{\sqrt{42}}A_1^6 <r^6>$
B_2^2	$\dfrac{2}{\sqrt{6}}A_2^2 <r^2>$	B_2^4	$\dfrac{4}{\sqrt{10}}A_2^4 <r^4>$	B_2^6	$\dfrac{16}{\sqrt{105}}A_2^6 <r^6>$
		B_3^4	$\dfrac{-2}{\sqrt{35}}A_3^4 <r^4>$	B_3^6	$\dfrac{-8}{\sqrt{105}}A_3^6 <r^6>$
		B_4^4	$\dfrac{8}{\sqrt{70}}A_4^4 <r^4>$	B_4^6	$\dfrac{16}{3\sqrt{14}}A_4^6 <r^6>$
				B_5^6	$\dfrac{-8}{3\sqrt{77}}A_5^6 <r^6>$
				B_6^6	$\dfrac{16}{\sqrt{231}}A_6^6 <r^6>$

A2.4.5 Specifying the Ligand Field Strength

The ligand field strength is defined as [1], eq (70). [6]:

$$\frac{N_v}{\sqrt{4\pi}} = \left[\sum_{k=2,4,6} \frac{1}{2k+1} \left(\left(B_0^k\right)^2 + 2\sum_{0<q\le k}\left(\left(B_q^k\right)^2 + \left(B'^k_q\right)^2\right)\right) \right]^{1/2}$$

This is invariant to the rotation of the ligand field as it should be, whereas the common expression for a real ligand field below is not.

$$\frac{N_v}{\sqrt{4\pi}} = \left[\sum_{k,q} \frac{1}{2k+1}\left(B_q^k\right)^2 \right]^{1/2}$$

A3   Higher-order parameters

A3.1 α, β, γ Two particle Configuration Interaction parameters

The two body configuration interaction parameters α, β, γ, parametrize the second-order Coulomb interactions with higher configurations of the same parity.

The parameters enter into the Hamiltonian as:

$$\alpha\, L(L+1) + \beta\, G(G_2) + \gamma\, G(R_7)$$

α is sometimes called a "Trees' correction" and has also been used in d-electron calculations. $G(G_2)$ and $G(R_7)$ are the Casimir's operator for groups G_2 and R_7 respectively.

A3.2 M^n, n=0, 2, 4 Marvin parameters

These parameters take into account the "spin-other-orbit" interactions (H_{soo}) and also the spin-spin interactions (H_{ss}). The method of calculation the matrix elements is given by Judd [16]. The reduce matrix elements for H_{ss} have been given explicitly by Yeung [20]. Sometimes in the literature, the spin-spin interactions have not been included [10]. By default, H_{ss} is always included in this program unless it is explicitly requested to leave it out by setting L5 in the `OPTN` command (for example to compare to a literature calculation that has also left it out.)

Some errors in M^n matrix elements have been noted [17]

A3.3 P^n, n=2, 4, 6 Electrostatically correlated spin-orbit interactions

The P^n parameters allow for the effect of additional configurations upon the spin–orbit interaction. The method of calculation the matrix elements is also given in the paper by Judd [16]. Some errors in P^n matrix elements have been noted [17].

A3.4 T^n, n=2, 3, 4, 6, 7, 8 Three particle parameters

These three electron effective operators represent the coupling of the ground state f^n configuration to excited state configurations outside the f^n configuration via the interelectronic Coulomb interaction. The matrix elements for f^3 have been published [18] as well as a method of generating those for other f^n configurations [19]. Note that there are errors in the literature on the use of the T^2 parameter for complementary f^n configurations with some corrections given in [15].

A4 Fitting

A4.1 Standard Parameter & Variable Order

The parameters are referred to by number in the FIT and LINK commands. The Variables may also be referred to by their number in a FIT command.

Therefore an unambiguous order must be used for the parameters/variables.

B_q^k Ligand Field parameterisation					
1	EAVE	21	B_{20}		
2	F2 [a]	22	B_{21}	42	B_{21}'
3	F4	23	B_{22}	43	B_{22}'
4	F6	24	B_{40}		
5	ZETA	25	B_{41}	45	B_{41}'
6	ALPH	26	B_{42}	46	B_{42}'
7	BETA	27	B_{43}	47	B_{43}'
8	GAMM	28	B_{44}	48	B_{44}'
9	M0	29	B_{60}		
10	M2	30	B_{61}	50	B_{61}'
11	M4	31	B_{62}	51	B_{62}'
12	P2	32	B_{63}	52	B_{63}'
13	P4	33	B_{64}	53	B_{64}'
14	P6	34	B_{65}	54	B_{65}'
15	T2	35	B_{66}	55	B_{66}'
16	T3				
17	T4				
18	T6				
19	T7				
20	T8				

[a] For d electron systems, you can use either F2 and F4 for the Racah parameters B and C to specify the electron-electron repulsion (but not a mixture of the two).

AOM Ligand Field parameterisation (up to 20 different ligands)													
1	EAVE	21	$\sigma(1)$	41	$\pi_x(1)$	61	$\pi_y(1)$	81	$\theta(1)$	101	$\phi(1)$	121	$\chi(1)$
2	F2	22	$\sigma(2)$	42	$\pi_x(2)$	62	$\pi_y(2)$	82	$\theta(2)$	102	$\phi(2)$	122	$\chi(2)$
3	F4	23	$\sigma(3)$	43	$\pi_x(3)$	63	$\pi_y(3)$	83	$\theta(3)$	103	$\phi(3)$	123	$\chi(3)$
4	F6	24	$\sigma(4)$	44	$\pi_x(4)$	64	$\pi_y(4)$	84	$\theta(4)$	104	$\phi(4)$	124	$\chi(4)$
5	ZETA	25	$\sigma(5)$	45	$\pi_x(5)$	65	$\pi_y(5)$	85	$\theta(5)$	105	$\phi(5)$	125	$\chi(5)$
6	ALPH	26	:		:		:		:				:
7	BETA	27	:		:		:		:				:
8	GAMM	28											
9	M0	29											
10	M2	30											
11	M4	31											
12	P2	32											
13	P4	33											
14	P6	34											
15	T2	35											
16	T3	36											
17	T4	37											
18	T6	38											
19	T7	39	$\sigma(19)$	59	$\pi_x(19)$	79	$\pi_y(19)$	99	$\theta(19)$	119	$\phi(19)$	139	$\chi(19)$
20	T8	40	$\sigma(20)$	60	$\pi_x(20)$	80	$\pi_y(20)$	100	$\theta(20)$	120	$\phi(20)$	140	$\chi(20)$

Note that while the ligands can be specified by x,y,z coordinates, these x,y,z values cannot be varied in a fit, so are not given standard parameter numbers.

LF1E Ligand Field parameterisation (d-electrons)									
21	d11								
22	d21	23	d22						
24	d31	25	d32	26	d33				
27	d41	28	d42	29	d43	30	d44		
31	d51	32	d52	33	d53	34	d54	35	d55

LF1E Ligand Field parameterisation (f-electrons)													
21	f11												
22	f21	23	f22										
24	f31	25	f32	26	f33								
27	f41	28	f42	29	f43	30	f44						
31	f51	32	f52	33	f53	34	f54	35	f55				
36	f61	37	f62	38	f63	39	f64	40	f65	41	f66		
42	f71	43	f72	44	f73	45	f74	46	f75	47	f76	48	f77

The 81 possible independent A^λ_{tp} or B^λ_{ki} parameters are specified as 45 complex numbers. These parameters occupy numbers 201-290 in the following order, although some of them are required to be zero.

Intensity Parameters								
A^λ_{tp}	B^λ_{ki}	Real	Imag		A^λ_{tp}	B^λ_{ki}	Real	Imag
A^2_{10}	B^2_{0x}	201	202		A^6_{50}	B^6_{0x}	249	250
A^2_{11}	B^2_{0y}	203	204 $^+$		A^6_{51}	B^6_{0y}	251	252 $^+$
A^2_{20}	B^2_{0z}	205 *	206 $^+$		A^6_{52}	B^6_{0z}	253	254 $^+$
A^2_{21}	B^2_{1x}	207	208		A^6_{53}	B^6_{1x}	255	256
A^2_{22}	B^2_{1y}	209	210		A^6_{54}	B^6_{1y}	257	258
A^2_{30}	B^2_{1z}	211	212 *		A^6_{55}	B^6_{1z}	259	260
A^2_{31}	B^2_{2x}	213	214		A^6_{60}	B^6_{2x}	261 *	262
A^2_{32}	B^2_{2y}	215	216		A^6_{61}	B^6_{2y}	263	264
A^2_{33}	B^2_{2z}	217	218		A^6_{62}	B^6_{2z}	265	266
A^4_{30}	B^4_{0x}	219	220		A^6_{63}	B^6_{3x}	267	268
A^4_{31}	B^4_{0y}	221	222 $^+$		A^6_{64}	B^6_{3y}	269	270
A^4_{32}	B^4_{0z}	223	224 $^+$		A^6_{65}	B^6_{3z}	271	272
A^4_{33}	B^4_{1x}	225	226		A^6_{66}	B^6_{4x}	273	274
A^4_{40}	B^4_{1y}	227 *	228		A^6_{70}	B^6_{4y}	275	276 *
A^4_{41}	B^4_{1z}	229	230		A^6_{71}	B^6_{4z}	277	278
A^4_{42}	B^4_{2x}	231	232		A^6_{72}	B^6_{5x}	279	280
A^4_{43}	B^4_{2y}	233	234		A^6_{73}	B^6_{5y}	281	282
A^4_{44}	B^4_{2z}	235	236		A^6_{74}	B^6_{5z}	283	284
A^4_{50}	B^4_{3x}	237	238 *		A^6_{75}	B^6_{6x}	285	286
A^4_{51}	B^4_{3y}	239	240		A^6_{76}	B^6_{6y}	287	288
A^4_{52}	B^4_{3z}	241	242		A^6_{77}	B^6_{6z}	289	290
A^4_{53}	B^4_{4x}	243	244					
A^4_{54}	B^4_{4y}	245	246		both	zero		
A^4_{55}	B^4_{4z}	247	248		A^λ_{tp} *	zero		
					B^λ_{ki} $^+$	zero		

For A^λ_{tp} parameters: 202, 205, 212, 220, 227, 238, 250, 261, 276 are zero.

For B^λ_{ki} parameters: 202, 204, 206, 220, 222, 224, 250, 252, 254 are zero.

Other Parameters	
301	Ω_2 Judd-Ofelt parameters
302	Ω_4
303	Ω_6
304	Hx Magnetic field (Tesla)
305	Hy
306	Hz
307	α Euler angles, rotation of the ligand field
308	β (See command ROTL)
309	γ
310	kx Orbital reduction parameters
311	ky (See command REDF)
312	kz

Offset Parameters	
351	Offset parameters defined in command OFFS.
:	
400	

Variables	
401	variable1
402	variable2
403	variable3
404	variable4
:	:
:	:
450	variable50

A4.2 Fitting Criteria

The Standard deviation (also called the root-mean-squared rms deviation) is defined by $\sigma = \sqrt{\Sigma_i^N \quad (E_{expi} - E_{calci})^2 / N}$ where the sum is over the N experimental energy levels to be fitted [22]. Similar expresions can be defined for Intensitied, weightings, degeneracies, etc.

A5 Algebraic expressions

Any of the parameters or constants can be specified by an algebraic expression. A Variable **<u>cannot</u>** be specified by an algebraic expression, but an algebraic expression can contain a variable.

Algebraic expressions can be built from:

Operators: +, -, *, /, ^, unary(-)

Functions: note all functions have a single argument (in brackets).

Trigonometric Functions: sin, cos, tan, sinh, cosh, tanh, asin, acos, atan,

Trigonometric Functions: sind, cosd, tand assumes the argument in degrees.

Other Functions: log, log10, nint, anint, aint, exp, sqrt, abs

Numbers:

Constants: defined with the command "CONS"

```
        example:  CONS  pi   4.*atan(1.0)
```

Variables: defined with the command "VARI"

```
        example:  VARI  ang   3
```

Note: A space is the limiter between the name of a constant or variable and it's value/expression.

Note: Do not include an "=" symbol in the algebraic expression.

```
    CONS pi=4*atan(1)
```
Is interpreted as a constant called "pi=4*atan(1)" with an undefined value. It will give a fatal error.

```
    CONS pi= 4*atan(1)
```
Is interpreted as a constant called "pi=" with a value 3.14159... The program will run, but "pi=" is probably not the constant name that you meant.

```
    CONS pi =4*atan(1)
```
Will give a fatal error, "=" is not recognised in expressions.

Note: Spaces are also used as delimiters between multiple values/expressions. So do not include spaces within an algebraic expression.

```
L1 1000 200 200 90 10+alpha
```

Gives θ=90, ϕ=10+alpha; but

```
L1 1000 200 200 90 10 +alpha
```

Gives θ=90, ϕ=10, χ=+alpha

A6 Parameters, Variables and Constants

1) The name of Constants and Variables are not case sensitive. Internally there are both converted to lowercase, but you can use any mixture of cases you want.

Constants:

2) Constants can be specified by a formula expression, but must be able to be evaluated immediately at input, so cannot contain Variables. They do not change their values during the program. They can contain other constants, but must be defined before use.

```
CONS X1   1
CONS X2   sqrt(2)
CONS Y   X1+X2          this is OK
```

but

```
CONS Y   X1+X2
CONS X1   1
CONS X2   sqrt(2)     constant Y will not be defined
```

Since the Constants will be constant during a calculation, they cannot be referred to by a parameter number.

3) If you try using a constant that is not defined.

```
CONS thetat   acos(1/sqrt(3))*180/pi
```

without `pi` being define, means that `thetat` never gets defined.

If `thetat` is then used, for example in defining a ligand position, an error results:

```
L1   eSig   EPi   thetat    0
```

```
***FATAL: Parameter: 61 theta(1)  contains unknown variables: thetat
```

Variables:

4) Variables are meant to be varied. Either by specifying a number of values, or by allowing it to vary in a fit. They must be numerical values. A Variable **<u>cannot</u>** be specified by an algebraic expression, it must be a single number or a list of numbers.

   If a Variable is not varied during a program, it acts just like a Constant.

   The ith Variable can be referred to as the $P(400+i)^{th}$ parameter, where i is determined by the order that that the variables are given in the input.

5) Parameters can be specified by an algebraic expression which can contain Constants and Variables. It may also be just a number.

6) At the time that the calculation occurs (after the "END" command is given) all the Variables and Constants used in any formula must have been defined, otherwise an error occurs.

   examples:

   ```
   ZETA    2*sqrt(3)-4*sind(30)
   F2       log(4)*3.12*sigma
   ```

   In the 2nd expression, sigma must have been defined as a Variable or a Constant somewhere in the input, or an error will result.

7) If a fit is made where a variable is to be fitted, only the first value in a list of multiple values is taken as the initial value of this variable.

8) A variable cannot be expressed in terms of other variables.

A7 Plot files

Energies:

a) If no symmetry labels and no symmetry blocking, all energies are printed for each calculation.

b) If no symmetry labels and symmetry blocking, energies are printed separately for the separate crystal quantum numbers.

c) If symmetry labels, energies are printed separately for each irreducible representation of the point group (regardless of the symmetry blocking).

Note: There will be problems for accidental degeneracies (wrong irreps) when passing through a higher symmetry during a series of calculations.

A8 Rotation of the Ligand field

The command **ROTL** is used to rotate the ligand field, which is the same as rotating the molecule. The rotation is made after the ligand field is evaluated, either with the initial values after input, or when the ligand field has changed. This can occur if one or more of the B_q^k values or the AOM parameters have been changed because they are dependent on a variable, or changing during a fit. (Using this command in a Fit does not really make sense, and is not recommended.)

Set OUTP(5) to show the ligand field in terms of the B_q^k parameters before and after the rotation.

A9 Example CPU times

f-electron calculations in LaCl₃   (11/3/15)

C_{3h} symmetry; Real Matrix
i7 2.4 GHz 64bit DELL
Program version 1.20; GCC 4.6.2 win32 thread

f^n	Ln(III)	full basis	No Symmetry				Symmetry blocking			
			E	V1	V2	V3	E	V1	V2	V3
1	Ce	14	0.03	0.00	0.00	0.00	0.00	0.02	0.03	0.00
2	Pr	91	0.02	0.03	0.08	0.14	0.02	0.03	0.05	0.12
3	Nd	364	0.39	0.90	1.44	2.84	0.11	0.14	0.41	2.15
4	Pm	1001	6.47	18.80	22.76	46.91	0.55	1.06	3.01	29.48
5	Sm	2002	55.43	150.77	167.00	272.13	2.03	5.21	13.40	126.84
6	Eu	3003	202.32	548.64	569.61	832.78	4.99	15.09	32.92	311.27
7	Gd	3432	308.85	816.91	836.84	1180.40	7.02	22.11	46.18	414.39
8	Tb	3003	202.40	541.70	567.63	825.28	5.10	15.29	33.26	314.54
9	Dy	2002	55.79	150.26	166.98	276.45	2.06	5.24	13.57	126.69
10	Ho	1001	6.27	18.80	22.73	47.77	0.53	1.01	3.00	29.87
11	Er	364	0.36	0.90	1.44	2.89	0.09	0.12	0.41	2.12
12	Tm	91	0.03	0.05	0.08	0.14	0.02	0.02	0.03	0.12
13	Yb	14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

E: Energies only, no eigenvectors calculated.

V1: Eigenvectors calculated; Free Ion% and Spin%.

V2: Eigenvectors calculated; Free Ion%, MJ%, symmetry labels.

V3: Eigenvectors calculated; Free Ion%, MJ%, MDIP 1 1 2 3 100

A10 Useful Constants

Bohr magneton: $\beta = 0.466\,860$ cm^{-1} T^{-1} = 9.274009×10^{-3} Debye

Bolzmann's constant: $k_B = 0.695\,030\,25$ cm^{-1} K^{-1}

Conversion between intensity units.

Dipole moment:
1 Debye = $10^{-19}/c$ C.cm (Coulomb.cm) where c = speed of light in m/s.

Calculated transition moment $<m_\rho>$ is in units of [10^{-12} cm] for A^{λ}_{tp} or B^{λ}_{ki} given in [10^{-12} cm].
To convert to Debye, multiply by electron charge (in C) and divide by ($10^{-19}/c$).

$<m_\rho>$ [Debye] = $1.6022 \times 10^{-19} \times (2.9979 \times 10^{8}/ 10^{-19}) \times 10^{-12} \times <m_\rho>$ [cm]
              = $4.80319 \times 10^{-4} \times <m_\rho>$ [cm]

To convert $|<m_\rho>|^2$ [cm^2] to $|<m_\rho>|^2$ [Debye^2]:
$|<m_\rho>|^2$ [Debye^2] = $2.30763 \times 10^{-7} \times |<m_\rho>|^2$ [cm^2]

Unicode characters: ∓ 2213 (Alt-X); ± 00B1

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