

Hidden Commands in f_electron

This describes some of the unfinished, untested, or "may not be quite working" commands. Unless you really know what you are doing, they will probably give you meaningless results.

Use:

```
> f_e hide or
```

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> f_e hide keyword for help
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EXTRA Commands	56
AOMX, CCF, EXPL, EXPM, EXPT, EXSO, FAST, LANC, PRT4, RO RB	
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EXTRA COMMANDS		
Key-word	Values	Notes
AOMX	N	<p>Extended AOM parameters are used. N is the number of ligands and must be the same as given in the AOM command. (You must also have an AOM command.) The parameters are given in N lines:</p> <p>eδs(1), eδc(1), eϕs(1), eϕc(1) : : eδs(N), eδc(N), eϕs(N), eϕc(N)</p> <p>The parameter numbers associated with these are: eδs(1) (141 – 150) eδc(1) (151 – 160) eϕs(1) (161 – 170) eϕc(1) (171 – 180)</p> <p>Note: you are restricted to a maximum of 10 ligands when using this command.</p> <p>The σ, π, δ, ϕ bonding patterns with a ligand are for 0, 1, 2, 3 nodes. The σ, π_s, π_c, δ_s, δ_c, ϕ_s, ϕ_c refers to s, p_y, p_x, d_{xy}, d_{x²-y²}, f_{y(3x²-y²)}, f_{x(x²-3y²)} type of bonding orbital for a ligand on the z axis.</p>
CCF (2)	N1 N2	<p>Correlation Crystal Field, see:</p> <p>Not for the faint hearted!</p> <p>If N1 determines the model used. N1=1 delta-function model N1=2 spin-CCF model N1=3 general CCF model</p> <p>N2= number of CCF parameters specified (max 60).</p> <p>There must be N2 lines following the CCF command: Delta function model (N1=1): k q G(kq)</p>

		general Model (N1=3): i k q G(ikq)
EXPL (3)	N1-N2 or N1,N2,N3.. or N1-N2,N3	An explicit range of S L J> multiplets to be included. You will need to do a calculation with CHK1(1) to see the full S L J> basis in standard order. All S L J M _J > basis functions within the specified S L J> multiplets are included. The S L J> functions are written to debug.dat Note using this command will give incorrect results for GEXS and other properties that depend on a full basis. The BLOC command may not work when using EXPL as some blocked matrices may be of zero dimension.
EXPM		Flags that the ligand field matrix elements of the lowest multiplet are fitted against the matrix elements of the ESO (Extended Stevens Operators). An EXSO command must have been given to provide the ESO matrix. The J value of the lowest multiplet is given by the value defined for the ESO matrix in the EXSO command. To make sense a PRED command should also have been given, so that the lowest multiplet is diagonal in the atomic parameters. This fit does not diagonalise the full matrix (after an the initial pre-diagonalisation), and is used to fit the B _{kq} or AOM parameters to a particular set of B _{k^q} (ESO) values.
EXPT (3)	N1,N2,N3..	Expectation values of the parameters given by numbers N1, N2, etc.
EXSO (2)	N1 N2 N3 N4	The energies of the lowest multiplet will be calculated by using a parameterisation in terms of Extended Stevens operators (ESOs) O _{k^q} in a J basis. N1 the value of 2J+1. N2 the value of kmax (must be even, max. value 20) N3 (0/1) if the K _{kq} constants are used (0) or not (1). If the proportionality constants K _{kq} are used, they are defined in J. Chem. Phys., 137 , 064112 (2012). N4 (0/1) if the main calculation is done (0) or skipped (1).

		<p>Each line will have will have $(2k+1)$ values of the following form:</p> <p>$B_k^q(\text{ESO})$ ($q = -k, \dots +k$)</p> <p>$B_k^q(\text{ESO})$: the coefficient (in cm^{-1}) (Note: These are different to the B_{kq} crystal field parameters.)</p> <p>k, q: are integers. k takes value 2,4,6,8,... while q can take the values $-k \dots +k$</p> <p>The number of lines depends on the value of k_{max} (summing over even k with $q = -k, .. +k$)</p> <table><tr><td>k_{max}:</td><td>2</td><td>4</td><td>6</td><td>8</td><td>10</td><td>12</td></tr><tr><td>lines:</td><td>1</td><td>2</td><td>3</td><td>4</td><td>5</td><td>6</td></tr><tr><td>max values in line:</td><td>5</td><td>9</td><td>11</td><td>17</td><td>21</td><td>25</td></tr></table> <p>If you cannot fit all values on one line, you can use multiple lines, but each new k value must start on a new line.</p> <p>For non-zero values of $B_k^q(\text{ESO})$ with $q < 0$, will give imaginary terms in the resultant matrix. Within the $2J+1$ multiplet the ligand field is given by:</p> $\langle J, M' H_{LF} J, M \rangle = \sum_{k=2,4,6..} \sum_{q=-k}^{+k} B_k^q(\text{ESO}) \langle J, M' O_k^q J, M \rangle$ <p>See Rudowicz & Chung, J.Phys.Cond.Matter, 16, 5825,(2004) and Ryabov, J.Mag.Reson., 140, 141, (1999) for definitions of ESOs.</p> <p>Typically this is used to fit the effective ligand field within the lowest multiplet obtained from a PRED calculation, by fitting the real ligand field to the effective one described by the $B_k^q(\text{ESO})$ within the lowest multiplet.</p>	k_{max} :	2	4	6	8	10	12	lines:	1	2	3	4	5	6	max values in line:	5	9	11	17	21	25
k_{max} :	2	4	6	8	10	12																	
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FAST	L1-L4	<p>Some options to speed up a calculation.</p> <p>L1) Leave out higher M_J values? (only valid for atomic calculations) TODO input highest M_J value</p> <p>L2) Only calculate half of a Kramers doublet. To work, the system must have symmetry such that B_{kq} for odd q is zero (At least $C_2(z)$).</p> <p>L3) Regenerate the other Kramers component?</p>																					

		L4) Not Used
LANC	N1,R1,R2	Lanczos partial diagonalization. N1: The number of Lanczos iterations. R1-R2: The energy range to be searched for energy levels. (Currently only works for real matrices)
PRT4 (1)	L1-L10 (def: all F)	T/F for printing the following matrices in the file: "matrices.dat" L1 Print info about the ESOs in the (2J+1) basis of the ground state multiplet. L2 Print Full ESO & calculated multiplet matrices. L3 Print Full Matrix in decoupled $ SLM_L M_S\rangle$ basis. L4 Print Full Matrix in $ SLM_L M_S=S\rangle$ basis. L5 Print Full Matrix in $ Sf_i(i=1,7)\rangle$ basis, where $f_1, f_2, f_3, f_4, f_5, f_6, f_7$ is the occupancy of the real f-orbitals (=0,1,2) using the definitions and order in the <code>LF1E</code> command. L6 Print L_x, L_y, L_z matrices in $ SLM_L M_S\rangle$ basis. L7 Print L_x, L_y, L_z matrices in $ SLM_L M_S=S\rangle$ basis. L8 – L9 Not used L10 Print a selection of above matrices. If (L10) .True. then a line must follow with i1, i2, j1, j2 All must be within the range for the particular f/d system. The $i1-i2 \times j1-j2$ sub-matrices will be printed. <u>Note:</u> 1-2 only happens if command EXSO used.
RORB	L1 L2	L1: Calculate the orbital population of each state in terms of ml orbitals. L2: Calculate the orbital population of each state in terms of real d/f orbitals. ***not implemented yet

Hidden Command Notes:

- (1) Logical inputs do not need all 10 specified; the remaining not specified will default to .false.
- (2) A multi-line command. The additional lines are expected to immediately follow as a continuation of this command.
- (3) Command can be repeated multiple times.

Definition & order of real orbitals

d [1]	Schaffer	short	full	1-e ⁻ l m _l > states [3]
1	σ	z^2	$\frac{1}{2} (2z^2 - x^2 - y^2)$	$ 2\ 0\rangle$
2	π_s	yz	$\sqrt{3}\ zy$	$i/\sqrt{2} (2\ +1\rangle + 2\ -1\rangle)$
3	π_c	xz	$\sqrt{3}\ zx$	$-1/\sqrt{2} (2\ +1\rangle - 2\ -1\rangle)$
4	δ_s	xy	$\sqrt{3}/2 (2xy)$	$-i/\sqrt{2} (2\ +2\rangle + 2\ -2\rangle)$
5	δ_c	$x^2 - y^2$	$\sqrt{3}/2 (x^2 - y^2)$	$1/\sqrt{2} (2\ +2\rangle - 2\ -2\rangle)$
f [2]				[4]
1	σ	z^3	$\frac{1}{2} (2z^2 - 3x^2 - 3y^2) z$	$ 3\ 0\rangle$
2	π_s	$z^2 y$	$\sqrt{6}/4 (4z^2 - x^2 - y^2) y$	$i/\sqrt{2} (3\ +1\rangle + 3\ -1\rangle)$
3	π_c	$z^2 x$	$\sqrt{6}/4 (4z^2 - x^2 - y^2) x$	$-1/\sqrt{2} (3\ +1\rangle - 3\ -1\rangle)$
4	δ_s	xyz	$\sqrt{15}/2 z (2xy)$	$-i/\sqrt{2} (3\ +2\rangle - 3\ -2\rangle)$
5	δ_c	$z(x^2 - y^2)$	$\sqrt{15}/2 z (x^2 - y^2)$	$1/\sqrt{2} (3\ +2\rangle + 3\ -2\rangle)$
6	φ_s	$y(3x^2 - y^2)$	$\sqrt{10}/4 y(3x^2 - y^2)$	$i/\sqrt{2} (3\ +3\rangle + 3\ -3\rangle)$
7	φ_c	$x(3x^2 - 3y^2)$	$\sqrt{10}/4 x(3x^2 - 3y^2)$	$-1/\sqrt{2} (3\ +3\rangle - 3\ -3\rangle)$

Correlation Crystal field parameters:

Only 60 of the very large number of possible CCF can be specified. The CCF values will have the parameter numbers 141-200. These will be in the order specified in the input file (The i,k,q values are also stored).

CCF parameters	
141	CCF1
142	CCF2
143	CCF3
:	:
:	:
200	CCF60

[1] C.E. Schaffer: *Struct. & Bond.*, 1, 68, (1968).

[2] S.E. Harung, C.E. Schaffer: *Struct. & Bond.*, 12, 201, (1972).

[3] C.J. Ballhausen, *Introduction to Ligand Field Theory*, McGraw-Hill, New York, 1962; pg 64.

[4] W. Urland, *Chem. Phys.*, 14, 393, (1976).

Fitting Program Flow

FitType	Command
1	EXPE
2	EXPE with JUDO
3	EXPB
4	EXPM
5	EXPG
6	EXP1

f_electron.f90 modules:

```

call prepareFit()
call doFit()
call PrintParameters(2)
if (fitType.eq.1 .or. fitType.eq.2) then
  call prepCalc(0)
  call doCalc(1) ! do one last calc with fitted parameters
endif

```

f_e_Fit.f90 Module:

```
prepareFit()
```

if FitType=3, 4 or 6 no matrix diagonalisation.

```
call prepCalc(0)
```

f_e_calculate module:

```
prepCalc()
```

```

call setpEq(ipar) ! can set AOMchanged/BkqChanged to .true.
call makeLinks()
CALL unloadP() ! Everything out of P
if (AOMparameters) then
  if (AOMchanged) then
    if (Lvalue.eq.2) call AOMmatrixD()
    if (Lvalue.eq.3) call AOMmatrixF()
  endif
endif
if (BkqChanged & abs(RotLF(1)).ne.0).gt.1.0d-12) call RotateLF()

```


f_e_Fit.f90 Module:

```
doFit()  
  
    call lmdif1(Nexp,NFit,fitP,fvec,FitTol,info,iwa,wa,lwa,nfev)  
    call loadP()  
    do i=1,Nfit  
        P(FitN(i))=fitP(i)  
    enddo  
    call prepCalc(0)  
!  
lmdif1()  
    call fnc()
```