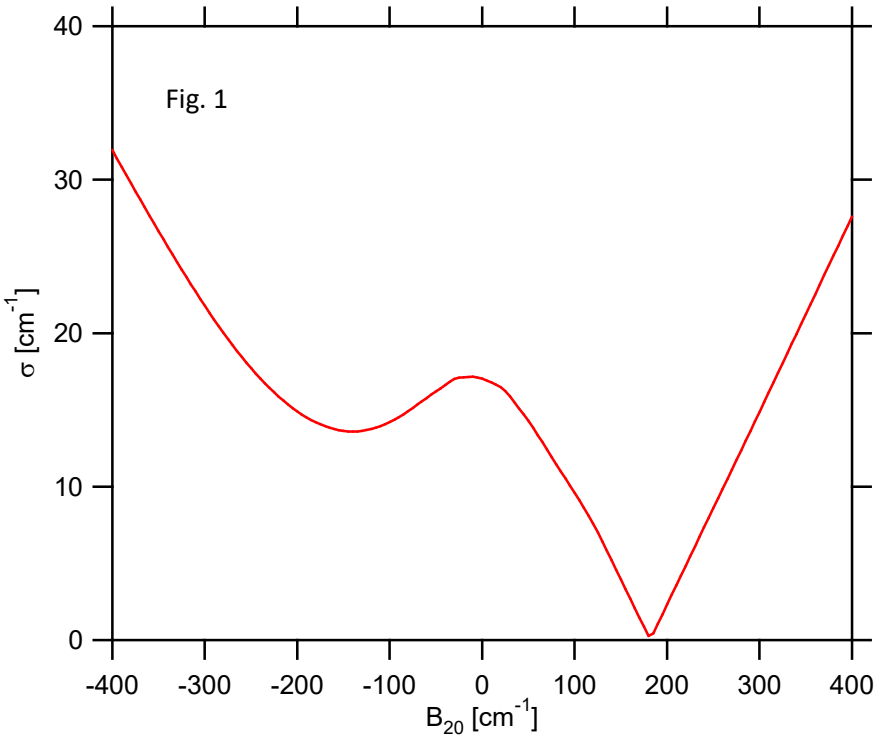
Fitting Calculated to Experimental Energies

The minimization function is a very complex multi-dimensional surface in parameter space. It has very many local minima that a fit will optimize to, that may be quite different from the global minimum. As an example we take the calculation of Er(III)/$LaCl_3$ [1] and reproduce the published energy levels using the published parameters. The 134 calculated energy levels are reported to one decimal place and the minimization function $\sigma = \sqrt{\sum(E_{calc} - E_{exp})^2 / N} = 0.166$ cm^{-1}. The ligand field has C_{3h} symmetry, which can be specified by the non-zero parameters B_{20}, B_{40}, B_{60}, B_{66}. If the parameter B_{20} is varied and all other parameters remain the same, one sees the plot in Figure 1.



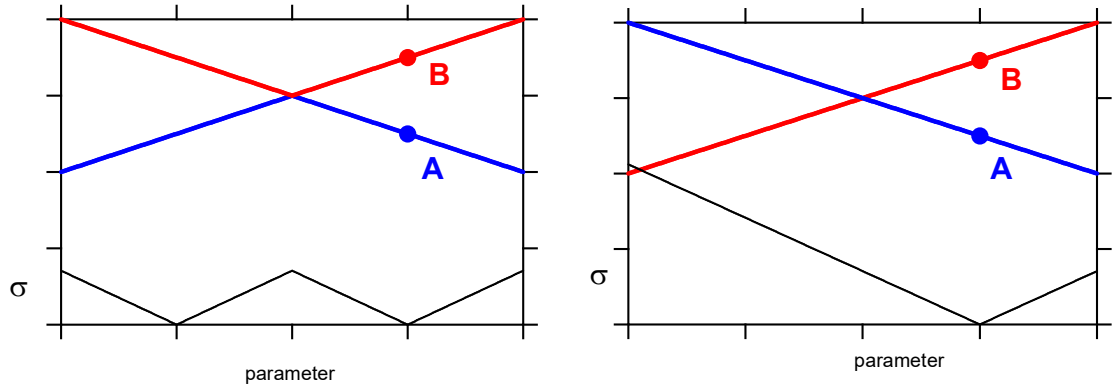
The optimum value is $B_{20} = 181.8$ cm^{-1} where $\sigma = 0.166$ cm^{-1}. If you start close to this value, a fit will quickly minimize to this value at the minimum. However, if you start with an initial value of $B_{20} = -400$ cm^{-1}, the fit will minimize to the local minimum at $B_{20} = -140.59$ cm^{-1}, $\sigma = 13.58$ cm^{-1}.

This problem of local minima in the parameter space is inherent in these types of multi-dimensional fits. It has nothing to do with the errors associated with the experimental data used in the fit. As shown above, when fitting to calculated levels, where one may expect exact agreement, but there is still a local minimum far from the true minimum. This problem is exacerbated when fitting the ligand field parameters which causes the relative energies to vary within each multiplet. In particular, it can cause energy level crossings as a function of the parameters varying.

This is a problem when one simply assigns the experimental levels to the calculated levels based on their energy order. Consider the case of fitting two levels that cross as a function of the parameter that you want to fit. Points A and B are the experimental energies to be fitted. The plot in Figure 2a is for point A to be fitted to the lowest level (blue line) and point B fitted to the 2nd lowest level (red line). Since the two levels cross as a function of the parameter value, the minimization function σ, will have two minima. So in this case it is ambiguous as to what the best parameter value is, there are two values that fit equally well. In practice, you may not even realise that there are two possibilities, and this fit may minimize to a minimum that depends on your choice of starting parameters. However, there may be extra experimental information that allows the assignment as shown in Figure 2b: Point

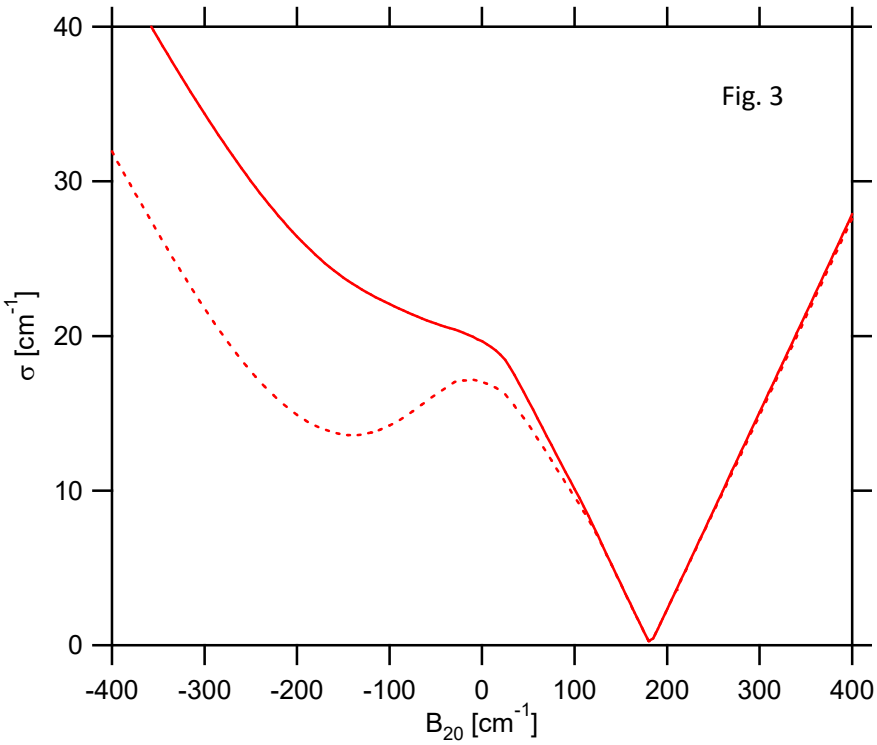
A is assigned to the blue line and point B assigned to the red line. In this case there is a clear single minimum in the σ function. The assignments can be made using the irreducible representations or the symmetry labels of the energy levels.

Fig. 2



The crossing of the levels as a function of the parameter as shown above is almost always due to the two levels being of different irreducible representations. If they were the same irreducible representation, then they would have an avoided crossing rather than a crossing. In the program you can assign each experimental energy level. You can only do this if the parameter you are changing does not change the symmetry of the system.

Assigning Levels using Crystal Quantum Numbers



In the above Figure σ is again calculated as a function of B_{20}, but the assignments are made to the order of the energy levels within each symmetry block (solid line), while the previous calculation of assigning energies to order of all energies. Fitting the levels to symmetry gives a single minimum, so that optimizing B_{20} starting as B_{20} = -400 cm^{-1}, optimizes to the correct values B_{20} = 181.8 cm^{-1}, σ = 0.166 cm^{-1} rather than the local minimum.

Er(III)/$LaCl_3$ has C_{3h} symmetry and the levels of this odd electron system will be Kramers doublets of Γ_7/Γ_8, Γ_9/Γ_{10}, Γ_{11}/Γ_{12} symmetry using the notation of Koster *et al.* [2]. The program using crystal quantum numbers (see Tutorial), and for C_{3h} symmetry these are ±1/2, ±3/2, ±5/2. In this case there is a one to one correspondence between the Γ irreducible representations and the crystal quantum numbers. Each ± pair represents a degenerate Kramers doublet and either can be used to assign the levels.

If you used the command "BLOC 1", the 1 is an option to print some information about the symmetry blocking. This will give you the order of the blocks:

```
-----------------------------------------------------------------------------------------
Symmetry blocking:
-----------------------------------------------------------------------------------------
The minimum q amongst non-zero Bkq is qMin= 6
The ( 364x 364) matrix was blocked (Crystal quantum numbers below):
(  60x  60) (  60x  60) (  62x  62) (  60x  60) (  60x  60) (  62x  62)
   -1/2        +1/2        +3/2        +5/2        -5/2        -3/2
```

We can assign the ±1/2 levels to block 1 or 2, the ±3/2 levels to block 3 or 6 and the ±5/2 levels to block 4 or 5.

Here are the two ways of assigning the energy levels from ref [1] using the EXPE command

```
EXPE 10 1                                EXPE 10 1 1
-11.2    1.0     1                       -11.2    1.0     1  5
29.2     1.0     3                       29.2     1.0     1  3
59.0     1.0     5                       59.0     1.0     2  3
93.6     1.0     7                       93.6     1.0     1  1
107.7    1.0     9                       107.7    1.0     2  5
140.5    1.0     11                      140.5    1.0     3  3
179.0    1.0     13                      179.0    1.0     2  1
222.6    1.0     15                      222.6    1.0     3  1
6548.1   1.0     17                      6548.1   1.0     3  5
6567.8   1.0     19                      6567.8   1.0     4  3
```

Using assignments by energy ordering (left-hand side), the level 140.5 cm^{-1} is assigned to the 11th calculated level. Using assignments using the crystal quantum numbers (right hand side) this level is assigned as the 3rd level of block 3 (that is the ±3/2 levels). Note we have only used one of the Kramers doublet energies, there is no advantage to doing both.

Both methods of assigning levels give rise to the same results:

```
  Level    Rel.Eng. (deg)|   - Exp     del    | CrQN|
-----------------------------------------------------
 363- 364    97573.8 ( 2)|                    | +5/2|
      :
  19-  20     6567.8 ( 2)| -    6567.8   -0.0 | -3/2|
  17-  18     6548.1 ( 2)| -    6548.1    0.0 | -5/2|
  15-  16      222.6 ( 2)| -     222.6   -0.0 | -1/2|
  13-  14      178.9 ( 2)| -     179.0   -0.1 | +1/2|
  11-  12      140.5 ( 2)| -     140.5   -0.0 | +3/2|
   9-  10      107.6 ( 2)| -     107.7   -0.1 | +5/2|
   7-   8       93.5 ( 2)| -      93.6   -0.1 | +1/2|
   5-   6       58.9 ( 2)| -      59.0   -0.1 | +3/2|
   3-   4       29.1 ( 2)| -      29.2   -0.1 | +3/2|
   1-   2      -11.3 ( 2)| -     -11.2   -0.1 | -5/2|
-----------------------------------------------------
sqrt(sum(Ec-Eex)^2/Nex)= |      0.16587E+00   |
```

But the one that uses the assignment to crystal quantum numbers is easier to converge to the global minimum in parameter space as shown in Figure 3 above.

Assigning Levels using Spin Quantum Numbers

This is only appropriate for transition metal ions, for lanthanides the states are mixed too strongly by spin-orbit coupling. If you are fitting the ligand field parameters by using experimental spin allowed transitions, you run into a problem if you assign the levels to the calculated levels by their energy order. It is the same problem as encountered above, the energy levels cross as a function of the ligand field.

[1] Yeung *et al*., J. Alloys & Compounds, 575, 54, (2013).

[2] Koster, Dimmock, Wheeler & Schatz, Properties of the 32 Point Groups, MIT Press, (1963).