

# Whats' Inside

SPECTRA is a program that calculates energy levels of f-electron ions. It provides a visual Windows-based interface for performing calculations of [electronic structure](#) and finding parameters of the Hamiltonian for ions with unfilled f-shells. The electronic structure can be calculated for free ion states, [f-ions](#) in solid-state compounds and f-centers in molecular compounds.

**More:**



---

Theoretical spectroscopy of [f-ions](#) is an arcane and complicated field of science. It requires substantial effort to learn and practice. Quantum chemical [ab-initio](#) methods of calculating [electronic structure](#) for f-ions in compounds are still very complex. Besides, they are extremely time-consuming and hardware demanding. On the other side, the method of irreducible tensor operators allows very precise and fast calculations, based on a limited number of well-defined parameters, which can be either fitted to available experimental levels or determined from *ab-initio* calculations. However, the learning curve is very steep, because the researcher needs to understand in detail abstract concepts in group theory and have access to many different reference texts before he can start doing some calculations for his specific application. Such calculations are important because details of the electronic structure of f-ions are directly related to such practically important properties as magnetic ordering and other magnetic phenomena, transitions intensities, sample characterization and so on.

Now, with SPECTRA and your personal computer you can take care of complicated calculations quickly and easily. No more looking through reference books to find needed parameter values, no more figuring out how to build the Hamiltonian matrix, no troubles with [Clebsch-Gordon](#) transformations and the algebra of tensor operators, developed by Racah and Wigner. SPECTRA does it all for you.

# SPECTRA Special Features

Your record keeping and matrix diagonalization needs are taken care of in SPECTRA. The components of the software include parameter fitting control, a reduced matrix elements database with an interactive interface, and different truncation and term selection options. Special modules are under development that will let you calculate crystal field parameters in a given compound, model optical and electron paramagnetic resonance spectra, and study other f-elements related phenomena.

## More:

[Fitting](#)

[Truncation](#)

[Reduced matrix elements database](#)



---

# Fitting

A differential evolution algorithm (a subset of genetic algorithms) is used to fit parameters of the Hamiltonian. The algorithm scans a broad region in parameter space, avoiding falling into a local minimum and provides generally acceptable results even when starting far away from optimum. However, the speed and accuracy of fitting is not as good as in the Levenberg-Marquardt algorithm, which is planned to be included for precise fitting in a future versions of SPECTRA.



---

# Truncation

The full matrix for energy levels calculation in the basis of  $|LSJJm\rangle$  f-states can be extremely large, especially for  $f^6$ - $f^8$  configurations. All calculations done previously for these configurations included different truncation methods in order to reduce the computational burden. In SPECTRA, there are three different options for calculations:

1. Complete basis set of  $|LSJJm\rangle$  states;
2. Reduced set of  $|LSJJm\rangle$  states, based on analysis of wavefunction composition up to a specified truncation energy;
3. Two-step diagonalization,  $|JJm\rangle$  basis is obtained from results of LS matrix diagonalization.

Previously only the third option was available. In that option, the effect of crystal field interaction can be underestimated and the order of energy values can be incorrect.



---

# Reduced matrix elements database

SPECTRA includes the full database of reduced matrix elements for free-ion and crystal field interactions. This database can be accessed in interactive mode. Its content is similar to the well-known book by Nielson and Koster on spectroscopic coefficients.



# Installing SPECTRA

This section lists the system requirements necessary to run SPECTRA, and provides instructions on how to install the software.

## More:

[System requirements](#)

[Registration](#)

[Setting up SPECTRA](#)





---

## System requirements

- A PC with a 150 MHz or faster Pentium or higher processor (dual Pentium II 300 or higher recommended), running Microsoft Windows 95/98 or Windows® NT™ version 4 (recommended).
- A 3.5-inch high-density diskette drive or a CD-ROM drive is necessary if installing SPECTRA from such media. An Internet connection is required for downloading SPECTRA from the Web.
- 32 megabytes of available random access memory (RAM). 256 megabytes of RAM is recommended for f<sup>5</sup>-f<sup>8</sup> configurations.
- A hard disk with approximately 10 Mb of free space on the C:\ drive.
- A VGA monitor (SVGA monitor and a video card supporting 600x800 or higher resolution is recommended).
- A mouse.



# Setting up SPECTRA

To install SPECTRA on your computer you need to obtain two zipped files: spectra.zip and db.zip. The latest versions of both can be found on [SPECTRA Web site](#).

**First**, unzip the db.zip file to the **root** C:\ folder. If using the program WinZip for this step, you should type in the "extract **to**" box the following characters C:\. The box labeled "Use folder names" should be checked. Extract all files from db.zip file in this way. After you finished, there should be a C:\Spectra folder on your hard drive that contains the files elst.dbf, spin.dbf, and recr.dbf and several subfolders. Never try to edit the ".dbf" files manually, because that will lead to irreversible corruption of the contained information.

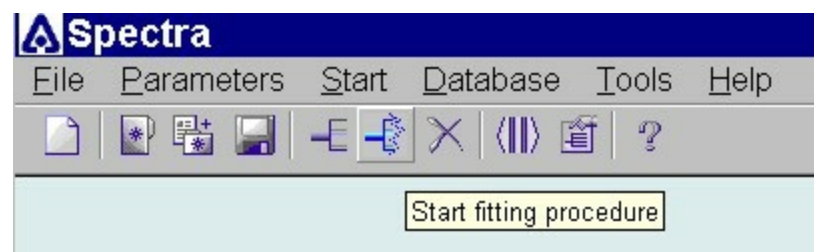
**Second**, unzip the spectra.zip file to the **root** C:\ folder to placed the unzipped spectra.exe file into its correct destination folder, namely C:\Spectra. In the future, if you download a new version of spectra.exe to update SPECTRA, you will need to move to a new folder, rename, or overwrite the old version.

**Third**, run the spectra.exe file. This is typically done by double-clicking on its icon. After explicitly agreeing to the license agreement and the disclaimers that are required by Argonne National Laboratory, you are ready to start working with the program. The text of the agreement will be written on your hard drive. If you delete it, the splash screen window will show up again.

It is perfectly safe to delete the Spectra directory completely from your hard drive in order to uninstall it or to install a new version from the scratch. The installation of SPECTRA does not affect your registry or other system files. However, if you change of the of its directory (folder) or install it on a different hard drive, then the program will not function properly.

# Using The Visual Interface

The main Windows-based interface for SPECTRA consists of a menu and a toolbar with hot spot buttons and tooltips. The toolbar provides an alternative way to access some of the main menu functionality with tooltips serving as context sensitive help for buttons.



## More:

[Help](#)

[Managing project](#)

[Accessing Parameters Values](#)

[Calculating electronic structure](#)

[Fitting](#)

[Database Query](#)

[Options](#)



---

# Help

The Windows Help file is accesible from SPECTRA via menu **Help** item.



Activated toolbar **Help-Conetent** button with tooltip

To activate the help system click **Help** and choose **Content** from the menu. It is also possible to use the hot key sequence: Alt+h, Alt+c.

To get information about the current version of SPECTRA, click **Help** and choose **About** from the menu or use the hot key sequence Alt+h, Alt+a.



---

## Managing project

The project files with extension .des are located in C:\Spectra\Des folder. Each file contains the following information: the name of the ion, the number of electrons on its f-shell, the name of the host material for a given ion, the values of all parameters (free-ion and crystal field) that fully describe the Hamiltonian for a given system.

### More:

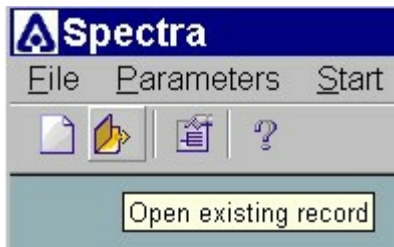
[Open project](#)

[Create a new record](#)



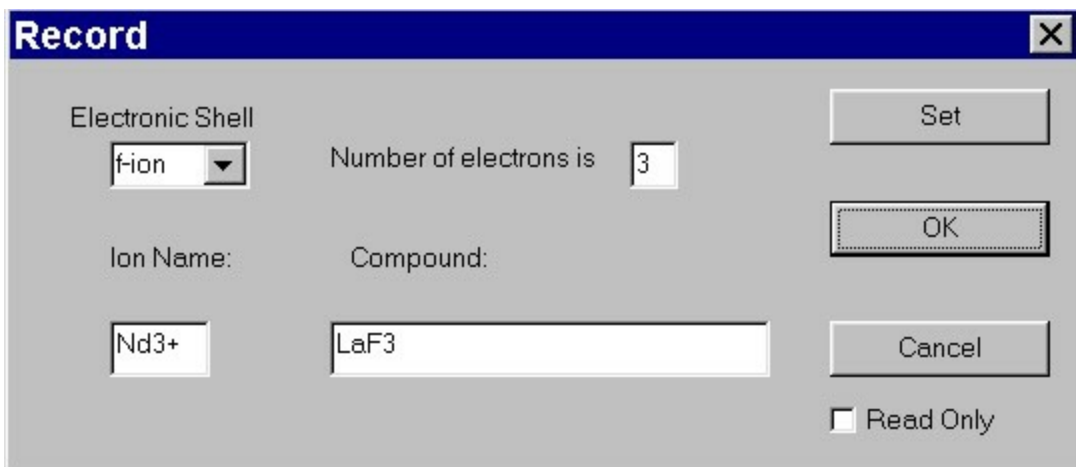
## Open project

To load an already existing project file, click on **File** and then choose **Open** from the menu. The corresponding hot key sequence is Alt+f, Alt+o.



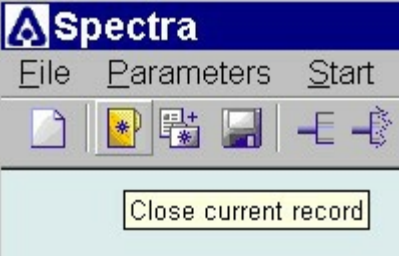
Activated toolbar **File-Open** button with tooltip

You will be asked to choose the file that you wish to open. After that you will see the following dialog box such as that below and that contains a basic description of the record.



You can make any change in the fields of this dialog box, which should be confirmed by pressing the **Set** button. You can not access or change the values of parameters at this step. The **Read Only** checkbox and the d-ion item in the "Electronic Shell" are not currently in use. They are reserved for use in future versions.

After pressing the **OK** button, the database for this particular ion will be opened and all required data will be loaded into memory. You will see the progress bar advance. When loading is finished, the color of the SPECTRA window background will change and a working toolbar will appear. Please note that the **File-Open** button will disappear from the toolbar. That means you can only work with one record at a time. In order to open another record, you need first to close the currently opened project by clicking **File-Close** (Alt+f, Alt+c) in the menu or via toolbar button.



Activated **File-Close** button with tooltip



# Create a new record

A new record can be created in two ways.

First, you can copy one of the existing project .des files by the drag-and-drop method in your Windows Explorer window. Then, you can open the copy and make change in the description fields and the values of paameters. In this way, you can keep the values of parameters from a similar studied host and avoid the problem of finding an appropriate set of parameters for your system.

Second, you can create a new record from scratch by clicking on **File** and then choosing the **New** (Alt+f, Alt+n) option from the menu.



Activated **File-New** button with tooltip

In the new record, all values for parameters initially are set to zero. After you have filled all field in the description box, you can open a new project by the method described in the **Open Project** topic.





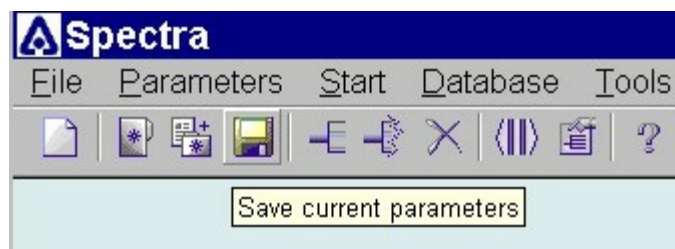
## Accessing Parameters Values

After a project is opened, the user can access the values of all parameters by clicking on **Parameters**, choosing the type of parameters to access, and then clicking the **Open** (Alt+p,Alt+o) option from the menu. There are three types of parameters in the menu:

1. free-ion parameters that describe electron Coulomb interaction and spin-orbit interaction;
2. crystal field parameters (in the [Wybourne normalization](#),) that describe ion-ligand interaction for any symmetry of environment;
3. advanced free-ion parameters that describe more complicated types of free-ion interactions. The inexperienced user is advised not to change these values or try to fit them. It is recommended that these values should either be kept intact or taken from reputable textbook or scientific publications.

The parameter values can be changed. Only integer input is accepted to avoid accidental data corruption. Please take note of the multipliers in the advanced parameters dialog box.

The changed values are kept in memory and can be used to perform calculations or fitting.. To save such values into the opened project, click **Parameters** and choose the **Save Parameters** (Alt+p, Alt+s) option from the menu. All parameters will be written to the hard drive.



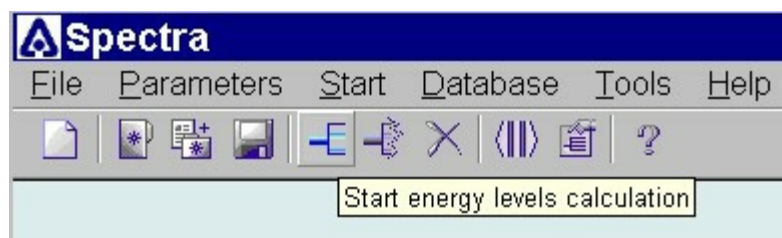
Activated **Parameters-Save Parameters** button with tooltip.

The difference between **Parameters-...-Open** and **Parameters-...-New** options is that in the first case parameters are loaded into memory from the hard drive record and shown in a dialog box. In the second case, parameters are simply copied from the memory. Do not forget to save changed parameters if you consider the new set of parameters more appropriate for your project. As soon as you close the project all values for parameters in memory will be lost. On the other hand, you can freely experiment with parameter sets by making several trial calculations with different parameter values without altering the saved values which can be restored at any moment by choosing the **Parameters-...-Open** option.



## Calculating electronic structure

To calculate energy levels and wavefunctions, click on **Start** and choose **Calculate energy levels** from the menu (Alt+s, Alt+c).

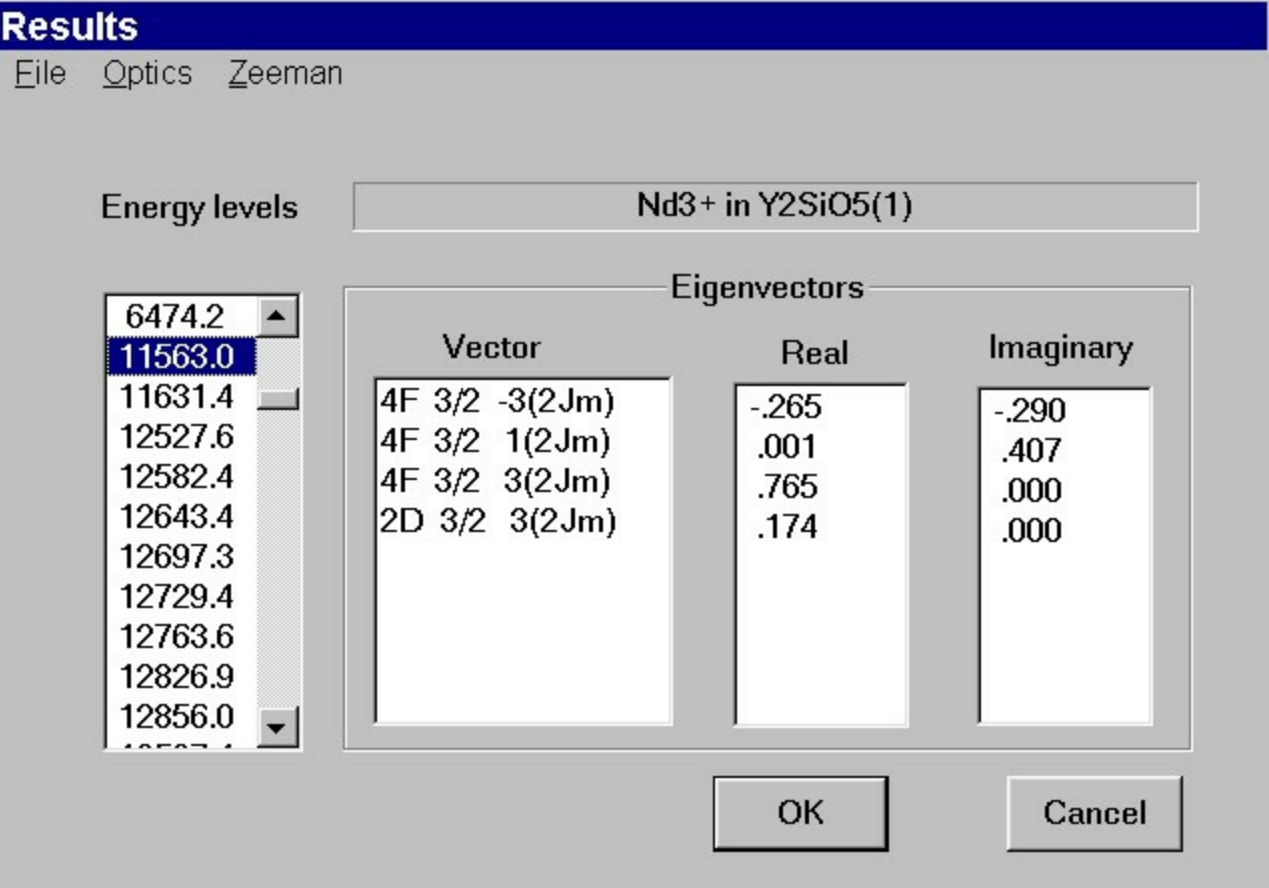


Activated **Start-Calculate energy levels** button with tooltip

By default you will be presented a dialog box, in which you can choose which terms of this specific configuration are to be included in calculations. Select as many terms individually as you wish and then press the **Add** button or press the **Add All** button to select all possible terms.

After the calculations are completed, you will see a dialog box that contains the values of energy levels in wavenumbers and the composition of wavefunctions. To see the wavefunction for a particular level click the energy value in the **Energy levels** column. In the **Vector** column, the description of states will be listed (format:  $2S+1, L, J, 2Jm$ ). In the **Real** column the corresponding coefficient for this state in a wavefunction is listed. Since SPECTRA can handle all crystal-field symmetries, the imaginary part of wavefunction can also be present for systems that lack an inversion center. Coefficients for these states are listed in the **Imaginary** column. Calculated wavefunctions form [orthonormal](#) set.

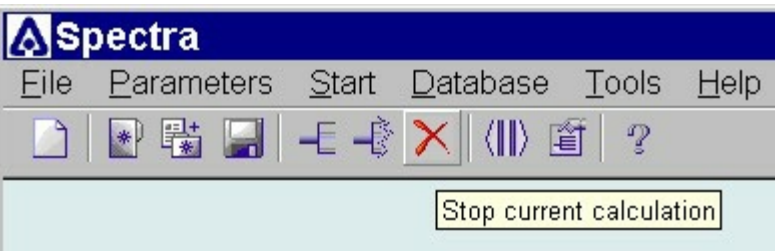
Calculation of other physical properties that are based on the obtained wavefunctions are in a development stage. You may wish to try a g-factor calculation by clicking on **Zeeman** and then choosing the **g-factor values** option from the menu (Alt+z, Alt+g). You will find an ASCII file named vect.txt in your C:\Spectra folder that contains the results of calculations. You are on your own to interpret the format, in which results are presented. It is supposed to be easy to understand, but since it is in development stage, the format can be changed in following version, as well as new features can be added.



You can save the calculated energy structure by clicking **File** and choosing the **Save** option from the menu (Alt+f, Alt+s). The file will be placed in the C:\Spectra folder. This file can be opened from by clicking **Database** and choosing the **Energy levels** option from the menu (Alt+d, Alt+e). The name of the file is determined by the description in a project file, which can be accessed from the **Tools-Options** item in the menu. By default, all precalculated energy structures are placed in C:\Spectra\Lev folder. You can move your own results into this folder at any time. Please, take care not to overwrite earlier results, which you may need for reference.

After you click the OK button, it is possible to start another calculation with a different set of terms or changed values of parameters.

If calculation takes too much time you can interrupt it by clicking **Start** and then choosing the **Stop calculation** option from the menu (Alt+s, Alt+s).



Activated **Start-Stop calculation** button with tooltip

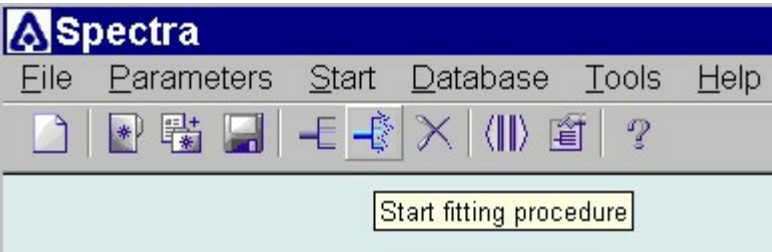
You will be warned that this is an irreversible action, which may cause abnormal termination of calculations with corruption of data in memory for opened project. You are advised to close the project after such action. In general, it is safe at any moment to quit SPECTRA application by clicking **X** button at the far right of title bar or, click the **File** menu, and then click **Exit**.



# Fitting

To fit experimental energy levels, you should create use a text editor to create an ASCII file whose extension is ".exp" in the C:\Spectra\Exp folder. The value for each energy level should be in wave numbers ( $\text{cm}^{-1}$ ) and contain a maximum of one digit after the period. Place each experimental value on a separate line. Any desired comment for a given level can be typed after the value. If some of the expected values are not available from experiment, just type 1 for each such level instead. To obtain meaningful results, the total number of experimental levels being fit should be larger than the number of parameters that you are going to fit.

Start the fitting procedure by clicking **Start** and then choosing the **Fit experimental levels** option from the menu (Alt+s, Alt+f).



Activated **Start-Fit experimental levels** button with tooltip

Next, you can choose which file with experimental levels from C:\Spectra\Exp\ folder to use for fitting. The dialog box, containing the names of files with .exp extension, will appear. After you select the file name and click **OK** button, the following options for fitting will be presented.

Select parameters for fitting procedure

Coulomb Parameters

☒ Constrained fit

Crystal field

☐ Cubic

☒ Hexagonal

☐ Tetragonal

☐ Trigonal

☐ None

Configuration parameters

☐ Alpha ☐ t2 ☐ t6

☒ Beta ☐ t3 ☐ t7

☐ Gamma ☐ t4 ☐ t8

Magnetic parameters

☐ Spin-Orbit interaction

☐ Constrained fit for P2, P4, P8

☐ M0 ☐ M2 ☐ M4

OK Cancel

You can choose the crystal field symmetry that is most appropriate for your system and which free-ion parameters you want to fit. It is recommended that inexperienced users carry out crystal field fitting without changing free-ion parameters. Though the limits of possible variations are restricted to avoid unphysical results, it is better to keep the fitting of free-ion parameters and the fitting of crystal-field parameters separate from each other.

By default Coulomb interaction can be fit only in a constrained mode which means that

$$F_4 = 0.808 \cdot F_2, \quad F_6 = 0.573 \cdot F_2$$

The non-rigid limits (see description of differential evolution algorithm) on the parameter change is defined in percent from the initial starting value. It will be possible for user these limits via dialog box in the future versions of Spectra. Please note that if starting values are zero, then no reasonable coverage of parameters space will happen.

To access the parameter values from fitting click **Parameters** and then choose ...-**New** option from the menu (Alt+p, Alt+n). The fitting results will be presented in a dialog box in which both experimental and calculated values are available for comparison. It is possible to repeat the fitting sequence as many times as you wish. Due to the random nature of differential evolution algorithm, resulting parameter values can vary. It is recommended to save fitting parameters periodically using different project names. You should remember that this problem is highly non-linear and frequently several sets of parameters can be obtained with similar deviation from experimental results. Only by comparing results with other studied isostructural compounds or by doing a semiphenomenological crystal field calculation using, for example, the exchange charge model is it possible to judge the physical reliability of

parameters from fitting. It is possible also to use wavefunction decomposition to analyze the symmetry of specific Stark levels to avoid unrealistic parameter sets.



# Database Query

There are two options currently in the **Database** menu item: **Matrix elements** and **Energy levels**. By selecting **Matrix elements** it is possible to access the database of matrix elements for all interactions that are present in the Hamiltonian used in SPECTRA for [electronic structure](#) calculations.

Reduced matrix elements

Select terms and type of interaction

First Term

4S  
4D  
4F  
4G

Second Term

4S  
4D  
4F  
4G

Interaction Type

spin-orbit  
magnetic(mk)  
magnetic(Pk)  
crystal-field(uk)

New

Update

Query

Cancel

Finish

Reduced matrix element

U2

U4

U6

.94760700

-.02780350

-.72074990

You selected 4D -4G matrix element for crystal-field(uk)

You should select the pair of terms and type of interaction for which the value of the matrix element will be displayed and then press the **Query** button. The values will appear in the corresponding boxes. The values are exactly equal to  $\langle L'S' | \text{operator} | LS \rangle$  matrix elements.

To access records for precalculated energy levels, click **Database** and then select **Energy levels** from the menu (Alt+d, Alt+e).

Activated **Database-Energy levels** button with tooltip





# Options

It is possible to change some of the program options by clicking **Tools** and then choosing **Options** from the menu (Alt+t, Alt+o).

By typing a new **title for current task** you can change the name of the file in which calculated energy levels will be saved.

Unchecking **Manual selection of terms** will lead to automatic selection of all terms for calculations. In this case, the dialog box for manual selection will be skipped.

**Fitting accuracy** determinse the number of independent parameter vectors in the fitting procedure (see the differential evolution method description, this box determines the value of NP). It is not recommended to change this value, since it is optimized both for accuracy and speed of calculations. Increasing this value will allow more precise scan of parameter space, which in some cases might provide a better fitting. However, the time of calculations will increase significantly.

**Results** group box contains two boxes: **Percents** and **Number**. **Percents** box sets a lowest value for coefficients at basis vectors, which will be included in resulting wavefunction for particular Stark level. For example, if calculated wavefunction F for the Stark level consists of n different  $f_k = |L_k S_k J_k M_k\rangle$  states.

$$F = c_1 f_1 + c_2 f_2 + \dots + c_n f_n,$$

then only those  $|L_k S_k J_k M_k\rangle$  states, for which  $|c_k| > (\text{Percents box value})/100$  will be included in final presentation. **Number** box sets a limit on total number of  $|LSJM\rangle$  states, which can be present in calculated wavefunction for Stark level.



# Brief Description of Methods and Algorithms Used in SPECTRA

This part covers the basic methods and algorithms used in SPECTRA. It does not present all these topics in detail, neither can it substitute for understanding group theory and tensor operator techniques as applied to atomic spectroscopy problems.

## More:

[Hamiltonian](#)

[Matrix truncation](#)

[Differential evolution \(DE\) algorithm](#)

[Crystal-field parameters normalization](#)



# Hamiltonian

To calculate [electronic structure](#), the following Hamiltonian is used in SPECTRA.

$$\begin{aligned} H = & \sum_{2,4,6} F^i f_i + \zeta \sum s \cdot l + \alpha L(L+1) \\ & + \mathcal{A}G(G_2) + \mathcal{B}G(G_4) + \sum_{2,3,4,6,7,8} T^i t_i \\ & + \sum_{0,2,4} M^i m_i + \sum_{2,4,6} P^i p_i + H_{CF} \end{aligned}$$

Of the 9 terms in this Hamiltonian, the first 8 represent free-ion interactions, which include electron-electron repulsion and spin orbit coupling, and the 9<sup>th</sup> term represents the crystal-field interactions. The first term represents electron-electron electrostatic interactions where  $f_k$  is the angular part of the interaction operator and the  $F^k$  are the Slater radial integral parameters. The second term accounts for spin-orbit interactions defined as magnetic dipole-dipole interactions between the spin ( $\mathbf{i}$ ) and angular momentum ( $\mathbf{l}$ ) of the f electrons, where  $\zeta$  is the parameter to be adjusted to the experimentally observed energies. The electrostatic and spin-orbit interactions determine the ordering of energy levels arising from a  $f^N$  configuration. The third through eighth terms represent minor modifications that include configuration interactions and two- and three-body interactions (see reference: papers by B.R.Judd and H.H.Marvin). In general, the parameters for the free-ion terms are not sensitive to the host. The variation in these parameters across a series of compounds with similar structure is typically a few percent.



# Matrix truncation

The matrix for final energy structure calculations can be constructed in three ways.

1. All LS-terms are included to build a **complete** set of  $|LSJJm\rangle$  states that include J-J'mixing caused by the crystal field. No limitation on the number and coupling between states are introduced. This is the only formally correct way to calculate energy structure. However, for  $f^6$ - $f^8$  configurations, the time required to complete diagonalization often exceeds reasonable limits (10+ hours). Even though the resulting matrix is sparse, there is no reliable algorithm to speed up calculations for the studied systems. That is why the second variant is used by default. Please note that you can use the first variant as well if you set the truncation energy in the **Tools-Options** dialog box to be higher than the highest free-ion  $|LS\rangle$  state energy.

2. In this variant  $|LS\rangle$  states selected by users for calculation (including complete set of  $|LS\rangle$  states for a given configuration) undergo a filtering process. During this process, the matrix of free-ion  $|LS\rangle$  states is diagonalized and the composition of wavefunctions for levels up to the truncation energy level is analyzed. If the percentage of a given  $|LS\rangle$  state in those wavefunctions is higher than a specified level (accessible via the **Tools-Options** dialog box), then this  $|LS\rangle$  state is included for further use in building  $LSJJm$  states. As in the first variant, a **complete** set of  $|LSJJm\rangle$  states is used in diagonalization. In such way, both free-ion and crystal-field interaction are treated simultaneously; there is no separation into a basic Hamiltonian and perturbation.

The energy of truncation in the second variant can be changed in the **Tools-Options** dialog box. Please, note, that the resulting set of energy levels can include energies higher than the truncation energy because all  $|LS\rangle$  terms present in wavefunctions up to truncation energy will be included into final matrix diagonalization.

3. In this variant (the most widely used), the matrix is diagonalized in two-steps. First, the matrix of free-ion interactions, formed in the basis of  $|LS\rangle$  states, is diagonalized. Then  $|JJm\rangle$  states obtained from the first step as a linear combination of  $|LS\rangle$  states, are constructed and crystal-field interaction is applied. In this variant, the structure of final  $|JJm\rangle$  states is fixed by free-ion interaction at the first step. In the case of strong influence by crystal field interaction, these results can be very different from the first formally correct variant. However, the gain in speed for  $f^6$ - $f^8$  configurations is significant which make this variant the only practically usable alternative for these configurations. You can access this option for diagonalization from the **Start-Fast fit** menu.



# Differential evolution (DE) algorithm

The DE algorithm (see [ref.7](#)) facilitates the determination of a global minimum with physically clear criteria by optimizing an objective function. This approach is more effective, in terms of computation time, in reducing false minima than are gradient methods for this highly non-linear task.

The DE algorithm is a parallel direct search method that utilizes NP D-dimensional parameter vectors:

$$\mathbf{V}_n(x_1, x_2, \dots, x_D), n=1, NP,$$

where D is the number of parameters to be optimized, and NP is usually about 10D. Initial parameter vectors are chosen randomly to uniformly cover the entire parameter space. In each generation, NP competitions are held to determine the composition of the next generation. In particular, the *i*th competition pits the *i*th population vector, known as a target, against the trial vector. The target vector is also one of the trial-vector parents. The trial vector's other parent is a randomly chosen population vector to which a weighted random difference vector has been added. Mating between this noisy random vector and the target vector is controlled by a nonuniform crossover operation that determines which trial vector parameters are inherited from which parent. If the resulting vector yields a lower objective function value than a predetermined generation member, the newly generated vector will replace the vector with which it was compared in the following generation.



# Crystal-field parameters normalization

General formulae for crystal field parameter calculation is determined from decomposition of the *f*-electron energy in the field of ligand with coordinates *R*, *Θ*, *Φ* and electric charge *eq* (*e*- electron charge). The electron coordinates are *r*, *θ*, *φ*.

$$-\frac{e^2q}{|\vec{R}-\vec{r}|} = -e^2q \sum_{p=0}^{\infty} \sum_{k=-p}^p \frac{1}{R} \left(\frac{r}{R}\right)^p C_p^{k*}(\Theta\Phi) * C_p^k(\theta\varphi)$$

where

$$C_p^k = \sqrt{\frac{4\pi}{2p+1}} Y_p^k$$

are spherical operators,  $Y_p^k$  are [spherical harmonics](#).

From proper combination of spherical operators it is possible to construct **real tesseral harmonics** which are used for crystal-field parameter calculations. **Real** polynomials construction can be performed in different ways, depending on choosen normalizations for polynomials ([see](#) ref.1). The final result (energy level values) does not depend on normalization, but the values of crystal-field parameters are normalization dependent. For example, the zero component of the crystal field parameter having rank 4 ( $B_4^0$ ) is proportional to the following real polynomial

$$O_4^0 = 35.*z^4 - 30.*z^2 + 3.$$

*The coefficient of proportionality is different in the most commonly used [Wybourne normalization](#) in comparison with Stevens normalization. Parameters in these normalizations are related to each other via the following equation*

$$a_{pk} B_p^k(WN) = B_p^k(SN), \text{ where } a_{pk} - \text{numerical factors. For example, } a_{40} = 1/8.$$

It is necessary to note that crystal-field parameter calculation currently is very different from the simple point charge model. For more information about the most advanced methods for crystal field parameter calculations see the reference paper by Prof. B. Z. Malkin.

# Recommended textbooks

1. 1. R. D. Cowan, *The Theory of Atomic Structure and Spectra* (University of California Press, Berkeley, 1981).
2. C. W. Nielson and G. F. Koster, *Spectroscopic Coefficients for the  $p^n$ ,  $d^n$ , and  $f^n$  Configurations* (MIT Press, Cambridge, 1963).
3. B. G. Wybourne, *Spectroscopic Properties of Rare Earths* (Interscience, New York, 1965).
4. I. Sobelman, *Atomic Spectra and Radiative Transitions* (Springer, Berlin, 1992), 2nd ed.
5. S. Hufner, *Optical Spectra of Transparent Rare Earth Compounds* (Academic Press, 1978).
6. B. R. Judd, *Operator Techniques in Atomic Spectroscopy* (Princeton University Press, 1998).

# Scientific papers of relevance

1. 1. B.Z. Malkin, in *Spectroscopy of Solids Containing Rare Earth Ions*, Ed. By A. A. Kaplyanskii and R. M. Macfarlane, Ch.2, 13 ( North-Holland, Amsterdam, 1987).
2. W. T. Carnall, J. Chem. Phys., **96**, 8713 (1992).
3. B. R. Judd, Phys. Rev. **141**, 4-14 (1966).
4. H. Crosswhite, H. M. Crosswhite and B. R. Judd, Phys. Rev. **174**, 89-94 (1968).
5. H. H. Marvin, Phys. Rev. **71**, 102 (1947).
6. B. R. Judd, H. M. Crosswhite, and H. Crosswhite, Phys. Rev. **169**, 130 (1967).
7. R. Storn and K. Price, J. Global Optimization, 11, 341(1997).



---

# Glossary of Terms

[\*orthonormal\*](#)

[\*Clebsch-Gordon\*](#)

[\*spherical harmonics\*](#)

[\*tesseral harmonics\*](#)

[\*Wybourne normalization\*](#)

[\*ab-initio\*](#)

[\*electronic structure\*](#)

[\*f-ions\*](#)



# electronic structure

*The values of stationary energy levels and corresponding wavefunction vectors*

## **f-ions**

*Ions having electrons in unfilled f-shell. Most lanthanide and actinide ions are f-ions.*

# ab-initio

*Complete Shroedinger equation for any real system can not be solved exactly. In such sense, there is no true ab-initio method for [electronic structure](#) calculation. The concept of ab-initio methods usually denotes a set of quantum chemical methods, which use both wavefunctions composition and Hamiltonian parameters as varied parameters to achieve convergence in calculation procedure. In crystal-field methods the basis (mathematically complete infinite set of spherical functions) is fixed and limited number of parameters in Hamiltonian is varied to get agreement with experiment.*

# Clebsch-Gordon

*Clebsch-Gordon coefficient is a mathematical symbol used to integrate products of three [spherical harmonics](#). Clebsch-Gordan coefficients commonly arise in applications involving the addition of angular momentum in quantum mechanics.*

# Wybourne normalization

*There are two most commonly used types of normalization for crystal-field parameters: Wybourne (WN) and Stevens (SN). Parameters in these normalizations are related with each other via the following equation*

*$a_{pk}B_p^k(WN)=B_p^k(SN)$ , where  $a_{pk}$  – numerical factors (see reference).*

# orthonormal

*Unit vectors which are orthogonal are said to be orthonormal*

# spherical harmonics

*The spherical harmonics are the angular portion of the solution to Laplace's Equation in spherical coordinates where azimuthal symmetry is not present. Some care must be taken in identifying the notational convention being used. In this entry,  $\Theta$  is taken as the polar (colatitudinal) coordinate with  $\Theta=[0,\pi]$ , and  $\varphi$  as the azimuthal (longitudinal) coordinate with  $\varphi=[0,2\pi]$ .*

# tesseral harmonics

*A spherical harmonic which is expressible as products of factors linear in  $x^2$ ,  $y^2$ , and  $z^2$  multiplied by one of 1,  $x$ ,  $y$ ,  $z$ ,  $yz$ ,  $zx$ ,  $xy$ , and  $xyz$ .*