

# Supplemental Materials:

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## 1. The 3rd order calculation program

The program-scripts enable to simulate differential conductance spectra as observed on spin systems in a scanning tunneling experiment as well as other physical properties. They are based on the perturbative model described in the main text and allow to play with the parameters and study their effects. Additionally, the program can be used to fit experimental data obtained on single spin systems as well as on spin dimers against the model.

While I have thoroughly checked the scripts for bugs, there is absolutely no guarantee that the output generated from the program is physically correct, in particular that the perturbative model is applicable or that the calculation is error-free. Nevertheless, I am convinced that the program might help to easily grasp some physics in spin systems in a playful way. If the user finds some bugs or errors, I would be very pleased for a short notice to have the opportunity to fix and further develop the program. If the program or outputs generated by the program is used for publications please cite the main manuscript.

### 1.1. Getting started

To use the script it is necessary to download *Scilab*, an open source software for numerical computation from the Scilab Enterprise web page <http://www.scilab.org>. The software is available for different operating systems (GNU/Linux; Mac OS X; Windows XP, Vista, 7, 8) and should also work on moderately powerful hardware.

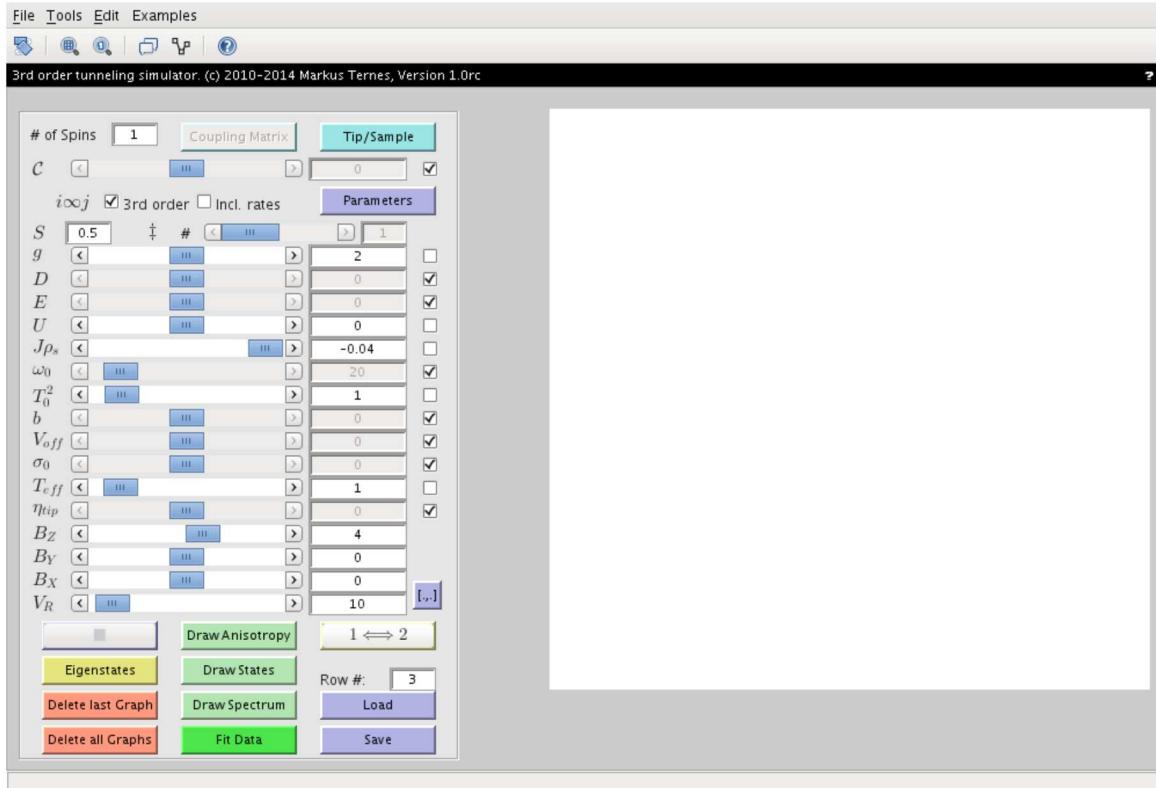
Next, the following scripts have to be placed in one folder, whereby I recommend to create a new folder only for these scripts:

- Spin-Hamiltonians-1.0.sce
- Spin-additional-functions-1.0.sce
- Spin-fit-functions-1.0.sce
- Spin-Gui-1.0.sce

After executing the main script (`Spin-Gui-1.0.sce`) inside the *Scilab* environment a graphical user interface (GUI) as shown in Figure 1 will be created. This GUI provides an easy way to change all parameters of the program. The GUI is divided into two areas. On the left side sliders, input-fields, check-boxes, and push-buttons enable to control the parameters and start different calculations, while on the right side the computed results are displayed. Hovering with the mouse over the control elements will display a brief explanation of the function of each element.

The meaning of the sliders and input-fields are summarized in table 1. While the sliders have only a limited range, the input-fields allow to set arbitrary values as long as they are useful.

To compute now a differential conductance spectrum, one has to press the **Draw Spectrum** button. Different spectra can be plotted over each other and deleted



**Figure 1.** The GUI after starting the script. Slight variations might occur depending on the version of *Scilab* and the operation system of the computer.

with the two delete buttons **Delete all Graphs** and **Delete last Graph**. The first application of “**Delete last Graph**” will remove the labels, while consecutive applications erase successively the spectroscopic calculations. The spectra are scaled by  $T_0^2$  as long as the switch “**Normalize Data**”, which can be found under **Parameters** is not applied.

The program allows also to calculate the energies of the eigenstates with respect to the applied magnetic field ranging from zero field up to the field set by the  $B_X$ ,  $B_Y$ ,  $B_Z$  sliders. To start this calculation, the button **Draw States** has to be pressed. Also here, the plot depends on a switch in the parameter menu. When the switch “**Adjust states to zero**” is set, the lowest eigenstate is automatically set to zero. The different behaviors of the plot states and plot spectrum functions are displayed in figure 2.

The reader of this description is highly encouraged to play with the parameters of the spin system to get a feeling for the power of the program. Some other spin systems which have been used in the main manuscript can be found in the pull-down menu “**Examples**”. Parameters which are initially disabled can be switched on with the check-boxes next to them, with the exception of the anisotropy parameters  $D$  and  $E$  when  $S = 1/2$ . He or she should also try the check-box “**3rd order**” which enables or disables the calculation of the 3rd order contributions of the spectrum.

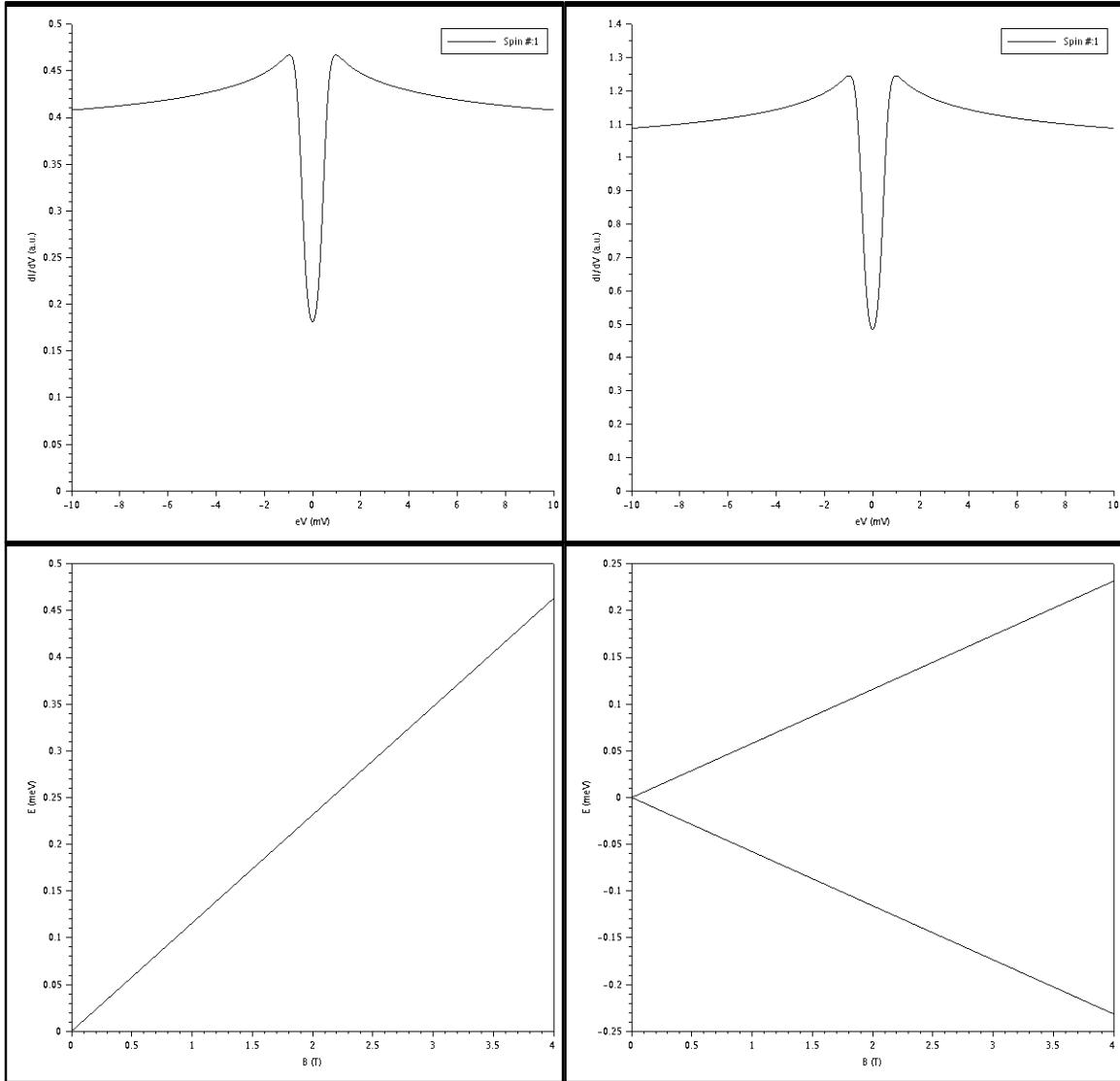
Furthermore, the check-box “**Incl. rate**” can be switched on to calculate the

Parameter	Function
# of Spins:	The number of coupled spins in complex spin systems (see section 1.3).
$\mathcal{C}$ :	The scaling factor for the coupling strength between coupled spins. This slider and input-field is only active when the number of coupled spins is larger than one (see section 1.3).
$S$ :	The total spin for the actual spin system (in $\hbar$ ).
#:	If there are more than one spin coupled, this slider enables to select the parameter set for the corresponding spin (see section 1.3).
$g$ :	The gyromagnetic factor for the actual spin system.
$D, E$ :	The axial and in-plane component of the magnetic anisotropy for the actual spin system (in meV).
$U$ :	The Coulomb scattering parameter for the actual spin system.
$J\rho_s$ :	The Kondo scattering parameter for the actual spin system with the substrate electrons.
$\omega_0$ :	The band-width of the scattering substrate electrons for the actual spin system (in meV).
$T_0^2$ :	The tunnel barrier coupling constant. It will be used as scaling factor when fitting spectroscopic data (see section 1.5), and is important when spectra are calculated using rate equations.
$T_{eff}$ :	The effective temperature of the simulation (in K).
$b, V_{off}, \sigma_0$ :	Parameters for fitting experimental data. $V_{off}$ is a voltage offset (in mV), $\sigma_0$ a conductance offset, and $b$ an additional sloped offset $\sigma_b = b \times V$ .
$\eta_{tip}$ :	The spin polarization of the tip (see section 1.2).
$B_X, B_Y, B_Z$ :	The three components of the externally applied magnetic field (in T).
$V_R$ :	The voltage range $-V_R \leq V \leq +V_R$ used for calculating the spectrum (in meV). When fitting data, this parameter is the voltage range in which data is fitted (see section 1.5).
Column #	The column of the spectroscopic data in tabulated data files when imported (see section 1.5).

**Table 1.** Summary of the functions of the sliders and input-fields.

spectrum using rate equations. Here, it is important to remember that the tunnel barrier coupling constant  $T_0^2$  which is in most tunneling experiments rather small and only of order  $\approx 10^{-4} - 10^{-3}$  is crucial for the calculating. When such a calculation is performed the abscissa values of the plot are given in units of the quantum of conductance, i.e.  $2e^2/h = 77.5 \mu\text{S}$ . When the option “**Normalize data**” is set under parameters, the calculation is multiplied with  $T_0^{-2}$  so that spectra with different tunnel barrier couplings are plotted on the same scale.

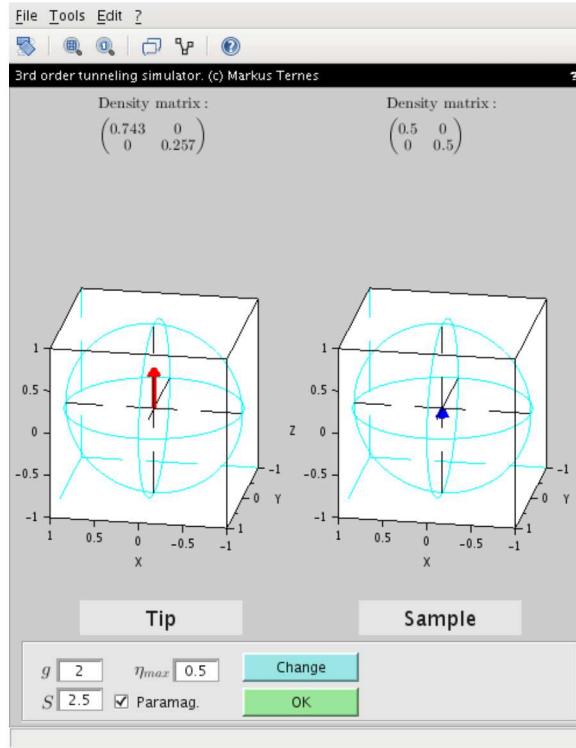
Note, however, that depending on the complexity of the spin system solving the rate equations can be quite time consuming. To stop any running calculation the



**Figure 2.** Drawing spectra and states for an example  $S = 1/2$  spin. Top row: The displayed output of the differential conductance (left panel not normalized, right panel normalized). Bottom row: The displayed output of the state energies versus magnetic field (left panel aligned to zero energy, right panel not aligned).

button can be used. While normally grayed-out, the button turns red when a longer calculation has started. When then pressed, the color changes to yellow until the calculation is finally aborted.

To save calculated data or the program status the **Save** button has to be pressed. Note, that the program will save always only the last calculation or program status. When data is saved, an ascii-file is created which contains a header at the beginning in which all parameters of the calculation are stored in a human readable form (see table 2), followed by the space-separated data. Thus, this function enables to export data which then can be easily imported into other programs for further evaluation or



**Figure 3.** Submenu for changing the spin polarization in tip and sample. The central pictures illustrate the Bloch spheres of the ensemble states in tip and sample, respectively.

plotting.

With the **Load** button a previously saved program status can be imported into the script. Additionally, this function enables to import experimental data as we will discuss in section 1.5.

### 1.2. Setting the spin polarization in tip or sample

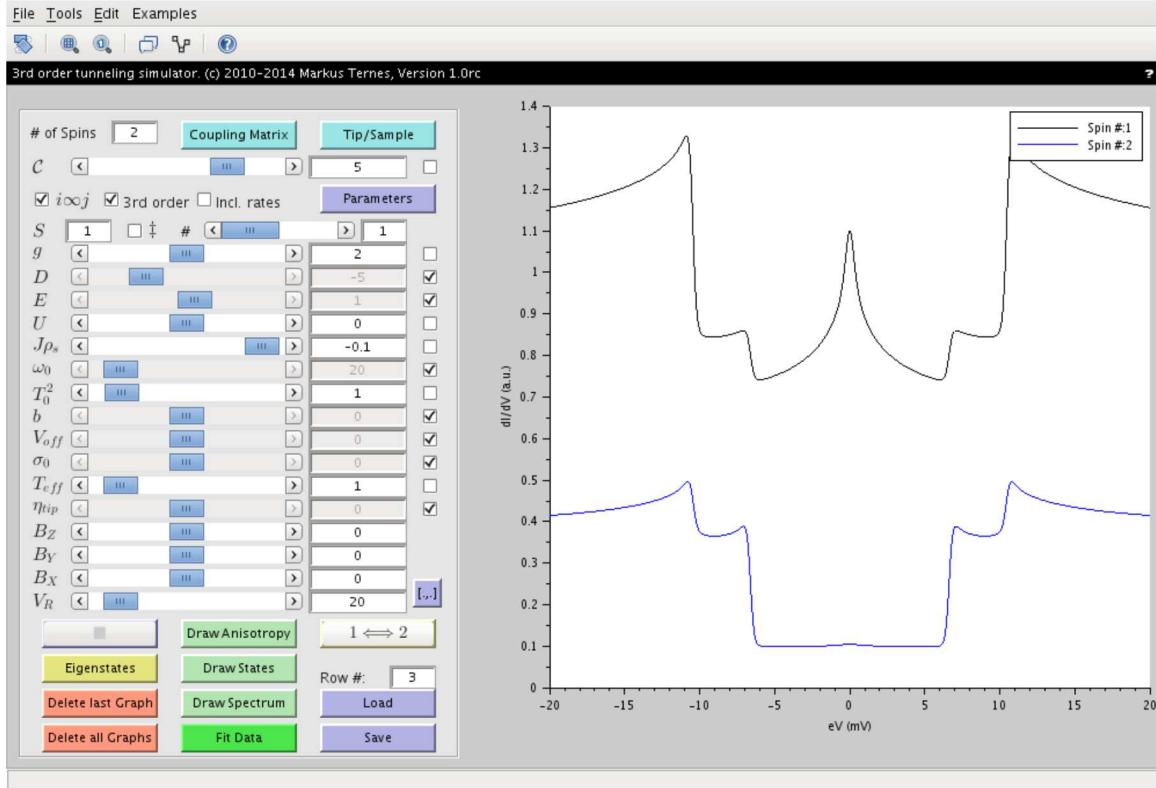
To change the spin polarization in tip or sample you have to press the **Tip/Sample** button. A new menu pops up in which, from top to bottom, the density matrices of the tip and sample electrons and the corresponding Bloch spheres are displayed (see Figure 3).

The spin polarization which is the asymmetry between the majority and minority spin  $\eta = \frac{\rho_{\text{maj}} - \rho_{\text{min}}}{\rho_{\text{maj}} + \rho_{\text{min}}}$  can be directly typed in for the corresponding principle directions  $(x, y, z)$  when pressing the **Change** button. Alternatively, the spin-polarization of the tip can also be calculated assuming a paramagnetic spin at the tip apex by setting the switch “**Paramag.**”. The apex spin is characterized by its total spin  $S$ , its gyromagnetic factor  $g$ , and its saturation spin polarization  $\eta_{\text{max}}$ . Then, the spin-polarization is calculated via the Brillouin function:

$$\eta_{\text{tip}} = \eta_{\text{max}} \left( \frac{2S+1}{2S} \coth \left( \frac{2S+1}{2S} x \right) - \frac{1}{2S} \coth \left( \frac{1}{2S} x \right) \right), \quad (1)$$

Header parameter	Function
T:	The effective temperature $T$ , but here in units of meV
lt:	The intrinsic lifetime $\Gamma$ (in meV) as set in “ <b>Parameters</b> ”.
xrange:	The voltage range $V_R$ .
ptip, psample:	The spin polarization of tip and sample as polarization vector $[p_x, p_y, p_z]$ .
S, g, D, E, U, b:	The same as the corresponding parameters found in table 1
J:	The Kondo scattering parameter $J\rho_s$ .
w:	The band-width of the scattering substrate electrons $\omega_0$ .
position:	The tip position when calculating multi-spin systems with rate equations.
jposition:	Internal function.
A:	The tunnel barrier coupling constant $T_0^2$ .
x0:	The voltage offset $V_{off}$ .
y0:	The conductance offset $\sigma_0$ .
B:	The magnetic field as vector $[B_x, B_y, B_z]$ .
heisenberg_coupling:	The scaling parameter $\mathcal{C}$ for <i>all</i> interactions between coupled spins.
sample_entanglement:	No function.
sef:	No function.
paramagnetic:	The status (“%t” for true, “%f” for false) of the checkbox “ <b>Paramag.</b> ” in the “ <b>Tip/Sample</b> ” submenu.
paramag_S, paramag_g:	The spin and gyromagnetic factor of the paramagnetic tip as set in the “ <b>Tip/Sample</b> ” submenu.
eta:	The $\eta_{max}$ value of the paramagnetic tip as set in the “ <b>Tip/Sample</b> ” submenu.
no_eval:	The “# of evaluations” value as set in “ <b>Parameters</b> ”.
max_no_eigenstates:	The “Max # of eigenstates” value as set in “ <b>Parameters</b> ”.
third_order_calc:	The status of the checkbox “ <b>3rd order</b> ”
rate_calc:	The status of the checkbox “ <b>incl. Rate</b> ”
entanglement:	The status of the checkbox “ $i\propto j$ ”
allatomsequ:	The status of the checkbox “ $\ddagger$ ”
Heisenberg_Matrixvalues	The coupling parameters $\mathcal{J}_{ij}$ as table with $i =$ row number, $j =$ column number+1.
DM_Matrixvalues	The coupling parameters $\vec{\mathcal{D}}_{ij}$ as table with $i =$ row number, $j =$ column number+1.

**Table 2.** Summary of the header parameters of a saved data-file.

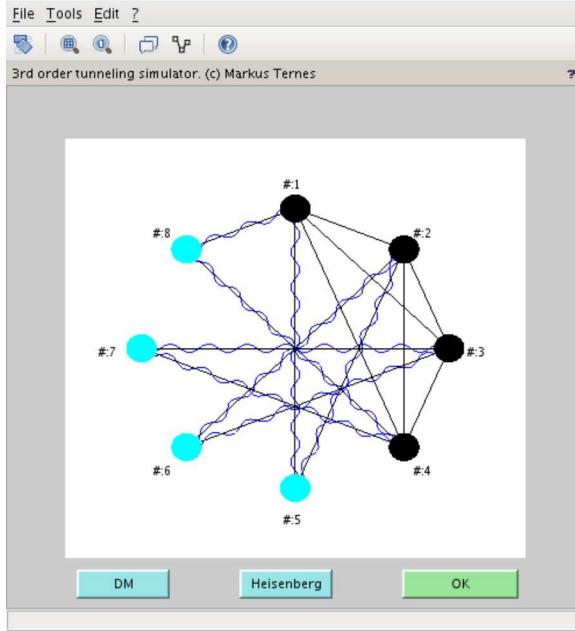


**Figure 4.** GUI after calculating the spectra of a coupled dimer. The different spectra on the two sites can be distinguished by their color.

with  $x = \frac{g\mu_B S |\vec{B}|}{2k_B T}$ . Under this condition, the spin-polarization will be recalculated each time the magnetic field strength or the temperature is changed. The slider  $\eta_{tip}$  is then grayed out and can not be varied but displays the actual spin-polarization. When the switch “Paramag.” is not set, the slider and input-field allow to change the magnitude of the spin-polarization whereby the direction remains. When  $\eta_{tip}$  is set to zero and then afterward changed, the spin polarization is assumed to be aligned (for  $\eta_{tip} > 0$ ) or anti-aligned (for  $\eta_{tip} < 0$ ) with the  $\vec{B}$ -field.

### 1.3. Calculating coupled spins

More complex spin structures containing several spins, which are coupled via Heisenberg or non-collinear Dzyaloshinsky-Moriya interactions, can also be calculated. To show how this is done, we want to consider a bipartite spin system consisting of an antiferromagnetically coupled  $S = 1/2$  and a  $S = 1$  spin, as discussed in the main manuscript. First, the input-field “# of Spins” has to be set to two. Next, the parameters of each spin has to be set individually, whereby the slider “#” enables to switch between the different spins (see figure 4). Note, however, if the checkbox “‡” is set, changes in the parameters of any spin are automatically applied to all spins, enabling the convenient setting of spin systems consisting of equal spins.

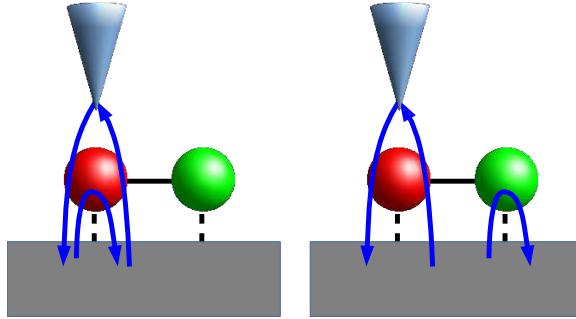


**Figure 5.** Submenu for changing the coupling constants in complex spin structures. In this example a complex system containing eight spins, four with  $S=1/2$  (black circles) and four with  $S=2$  (turquoise circles) are coupled via Heisenberg (straight lines) and Dzyaloshinsky-Moriya interactions (wavy lines).

Next, the coupling between the two spins has to be adjusted. For this the submenu **Coupling Matrix** has to be opened which schematically displays the individual spins as colored circles, whereby the spin  $S$  of each constituent can be distinguished by different colors (see figure 5). The submenu has the buttons **DM** and **Heisenberg** which enable to set the Heisenberg and Dzyaloshinsky-Moriya interaction strength between pairs of spins, respectively. Here, it is important to know that the Dzyaloshinsky-Moriya interaction has always to be a three dimensional vector for which the  $x, y, z$  values have to be comma-separated. The Heisenberg interaction is considered isotropic as long as only one value is given. For anisotropic Heisenberg interaction also here comma-separated values to describe the vector can be given. Finally, all coupling constants set in this submenu are multiplied with the value of the slider “ $\mathcal{C}$ ” enabling an easy change of the total interaction strength from the main menu. This results in an interaction Hamiltonian between the spins of the form:

$$\hat{H}_{\text{int}} = \mathcal{C} \times \left( \sum_{i,j} \vec{\mathcal{J}}_{ij} \hat{\mathbf{S}}^i \cdot \hat{\mathbf{S}}^j + \sum_{i,j} \vec{\mathcal{D}}_{ij} \hat{\mathbf{S}}^i \times \hat{\mathbf{S}}^j \right). \quad (2)$$

To realize our example, we can set  $\mathcal{J}_{12} = 1$  and  $\vec{\mathcal{D}}_{12} = (0, 0, 0)$  and control the Heisenberg interaction strength directly with  $\mathcal{C}$ . If the coupled system is set up correctly the spectra or the state energies are computed when the corresponding buttons are pressed. The simulation of the differential conductance will now result in two spectra, which we would measure when the tip is placed over the corresponding atom. Note, that



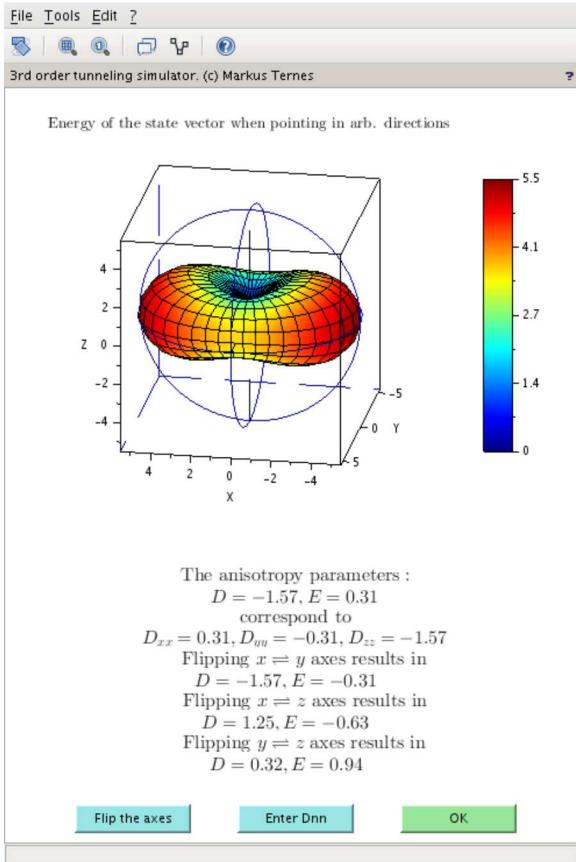
**Figure 6.** When the spectra of 2 or more coupled spins are calculated the checkbox “*i∞j*” determines if processes like on the right are allowed or if the calculation is restricted to processes which only act on the probed spin as illustrated on the left.

the script assumes that the tunneling current flows entirely to either atom; interference effects between both channels are not included. Due to the longer calculation time when rate equations are used, only the spectrum over the spin set with the “#” slider will be computed when the switch “**Incl. rate**” is set.

In these calculations the checkbox “*i∞j*” is important because it determines the behavior of the substrate interactions when 3rd order contributions are included. Not set, spin-spin interactions of electrons which originates and end in the substrate are only accounted for when they act on the spin over which the tip is placed, while these interactions on any spin are included when the checkbox “*i∞j*” is set. The difference is illustrated in figure 6. When the conductance is calculated for the tip placed over the left spin, 3rd order contributions like shown on the right panel are only included when the checkbox “*i∞j*” is set. Mathematically, the difference lies in the calculation of the scattering matrix elements. Either the spin operator acting on the spin system contains only components of this spin, i.e. it is written as  $\hat{\mathbf{S}}^i$  with *i* as the probed spin, or it is the weighted total spin of the full system:

$$M_{if}^{s \rightarrow s} = \begin{cases} M_{if}^{s \rightarrow s} = (J\rho_s)^{(i)} \langle \varphi_f, \psi_f | \frac{1}{2}\hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{S}}^i | \varphi_i, \psi_i \rangle & \text{if } i \in j \text{ is not set.} \\ M_{if}^{s \rightarrow s} = \sum_i (J\rho_s)^{(i)} \langle \varphi_f, \psi_f | \frac{1}{2}\hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{S}}^i | \varphi_i, \psi_i \rangle & \text{if } i \in j \text{ is set.} \end{cases} \quad (3)$$

In particular when calculating large spin systems, the number of eigenstates which have to be evaluated increases rapidly, drastically slowing down the calculation. To have reasonable calculation times the submenu **Parameters** offers some setting to increase the program speed: The parameter “**Max # of eigenstates**” has the strongest influence and determines the maximal number of low-lying eigenstates which will be calculated. If this value is set too small than eigenstates which lie in the energy range of interest are neglected and in the calculated spectra features might be missing. The parameter “**Min state occupancy**” determines the minimal weight a thermally excited state has to have to be considered as starting ground state. Furthermore, the square of this value determines the upper limit below which matrix elements are neglected for calculating the conductance. Furthermore, the parameter “**# of evaluations**” determines the number of intermediate *B*-field steps which are calculated when plotting



**Figure 7.** Submenu for displaying the magnetic anisotropy, shown for a Fe atom on Cu<sub>2</sub>N as an example. Additionally, this submenu allows to flip the anisotropy axes as well as to calculate the anisotropy parameter via the spin-orbit coupling constant and the unquenched orbital momenta.

the state energy versus magnetic field.

#### 1.4. Visualizing and flipping the anisotropy directions

The button **Draw Anisotropy** opens a new window which visualizes the magnetic anisotropy of the active spin as set with # (see Figure 7). In this visualization the lowest lying eigenstate of the *isolated* spin is rotated by applying spherical rotation operators and the relative energy is calculated and graphically displayed. This allows to determine that the spin system shown in Figure 7 has its easy axis along the  $z$ -coordinate while the magnetic hard axis is along the  $x$ -coordinate. By convention, the anisotropy parameter  $D$  and  $E$  are usually expected to obey the relations  $|D| \leq 3E$  and  $E \geq 0$ . This convention makes the  $z$ -axis always to the main anisotropy axes.

Under some circumstances it might be necessary to divert from this convention and flip the axes. For example, when coupling different spins, their main anisotropy axis might not be the same. To make this transformation easy for the user the button **Flip the axes** can be utilized. A preview of the effect on the anisotropy parameters is

given as seen in Figure 7. Note, while the anisotropy Hamiltonian is always calculated in the following way:

$$\hat{H}_{\text{ani}} = \sum_i \left( D_i (\hat{S}_z^i)^2 + E_i \left[ (\hat{S}_x^i)^2 - (\hat{S}_y^i)^2 \right] \right), \quad (4)$$

sometimes the anisotropy is described in  $D_{xx}$ ,  $D_{yy}$ ,  $D_{zz}$  values where the Hamiltonian is calculated as:

$$\hat{H}_{\text{ani}} = \sum_i \left( D_{xx} (\hat{S}_x^i)^2 + D_{yy} (\hat{S}_y^i)^2 + D_{zz} (\hat{S}_z^i)^2 \right). \quad (5)$$

These values can be entered into the program and converted by the submenu **Enter Dnn**. Note, that for the correct conversion **lambda** = 1 has to be used.

Additionally, this input mask can be used to enter the magnetic anisotropy via the spin-orbit coupling  $\lambda^i \hat{\mathbf{S}}^i \cdot \hat{\mathbf{L}}^i$  with the parameter  $\lambda_i$  as the spin-orbit constant and  $\Lambda_{xx}^i$ ,  $\Lambda_{yy}^i$ , and  $\Lambda_{zz}^i$  as the amount of unquenched orbital momentum for the  $i$ -th spin along the corresponding direction. The ordinary anisotropy parameter are then correctly calculated to:

$$D_i = -\lambda_i^{-2} (2\Lambda_{zz}^i - \Lambda_{xx}^i - \Lambda_{yy}^i), \quad E_i = -\frac{\lambda_i^{-2}}{2} (\Lambda_{xx}^i - \Lambda_{yy}^i), \quad (6)$$

when meV and meV<sup>-1</sup> are used as units for the input fields.

Note, however, that the spin-orbit couplings are *not* used to also adapt the gyromagnetic factor according to the relation:

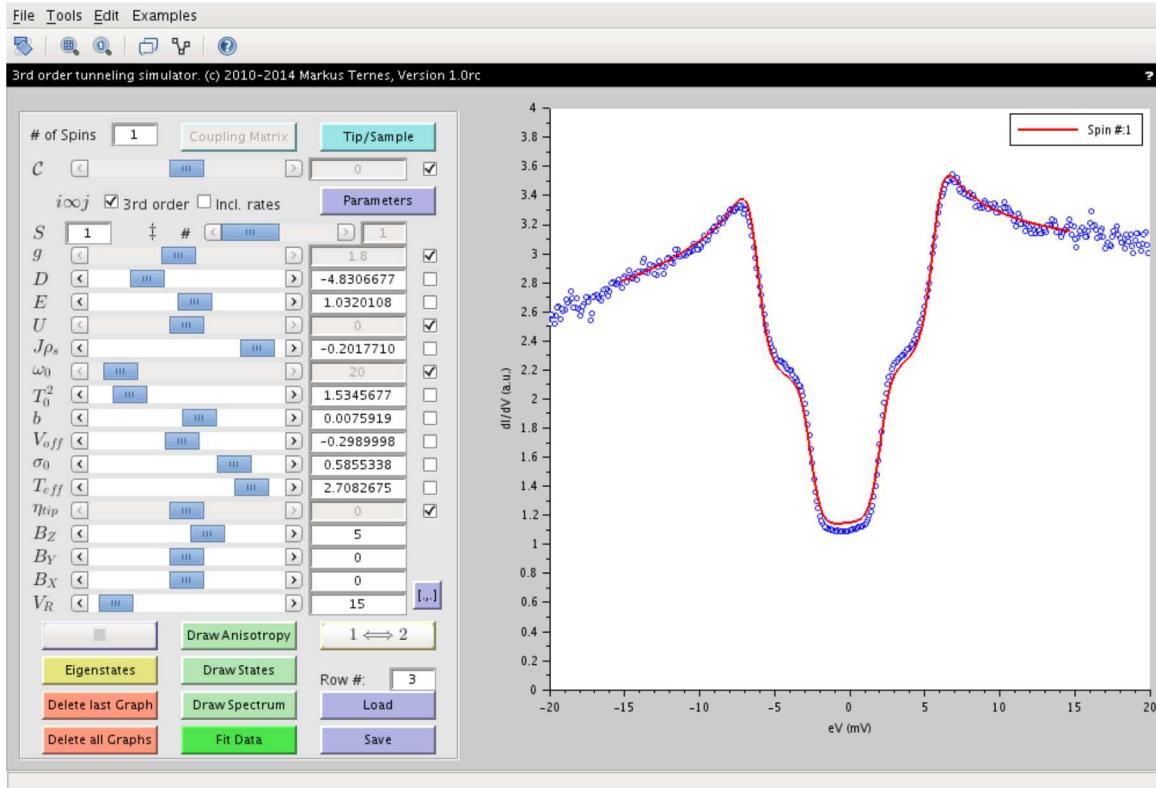
$$g_{jj}^{(i)} = g_0 (1 - \lambda_i \Lambda_{jj}^i). \quad (7)$$

This would require to define the gyromagnetic factor as a tensor instead of the simple scalar used in the program.

### 1.5. Fitting spectroscopic data

One of the presumably most important features of the program is the possibility to fit experimentally obtained differential conductance data against the model and extract physically relevant parameters. For this, the experimental data can be loaded into the program by pressing the **Load** and then the **ASCII Data** button. The data has to be provided as space-separated list, in which the first column contains the bias voltage (in mV) and the second column the differential conductance. Preceding header lines will be automatically ignored.

Because some commercially available software, as for example the Nanonis software, exports spectroscopic data in a tabulated form, the program can also load such files. If a file is detected which contains more than 2 column, the field “**Column #**” determines which column will be used as spectroscopic data. Negative values can be set to automatically invert the data. Note that the bias voltage has always to be located in the first column and will be automatically multiplied by 1000 to convert from the usually used volts to the mV used in this program.



**Figure 8.** The GUI after a successful fit to an experimental spectrum.

The data will be plotted as blue circles (see figure 8) and automatically redrawn when the **Delete All** button is pressed. The fitting quality depends strongly on reasonably good starting parameters which you should search for by try-and-error. Afterward, lock all parameters which the least-square fit shall not optimize with the corresponding checkboxes. Note that the fitting speed depends significantly on the number of free parameters and the size of the data. To restrict the fit to the area of interest, the range can be limited by reducing the voltage range with the slider and input-field  $V_R$ . Reasonable limits of the parameters must be set in the submenu available by pressing the **[.;.]** button.

The fit can then be started with the **Fit Data** button. The program asks for the maximum number of calls to the cost-function and the maximum number of iteration steps. The fit stops when either one of these limits is reached or the search is interrupted externally by applying the stop button **[■]**.

The optimized parameters are displayed in the corresponding input fields and the spectrum is drawn as red line (see Figure 8). It is possible to toggle between the start and optimized parameter values with the button **[1  $\leftrightarrow$  2]**. The simulated data together with the parameters can then be saved and used externally.

Also bipartite spin systems can be fitted in an analogous way, but it is important to select the spin system on which the spectrum was observed with the slider “#”.

Only the parameters of this spin will be optimized, except when the “” checkbox is enabled. Then the program assumes that both spins have identical parameters and will vary them simultaneously. In a bipartite system the coupling constant  $C$  can also be fitted, but depends on the settings of the coupling matrices (see equation 2) which will not be varied.

Complex systems which contains more than two spins or simulations which uses rate equations to calculate the conductance can not be fitted inside this program.

### 1.6. Fitting step-energy data

Measuring the gyromagnetic factor  $g$  is evidently not possible at zero magnetic field, but fitting  $g$  at applied field is difficult because there is a strong cross-correlation between  $g$  and the magnetic anisotropy parameters  $D$  and  $E$  due to large off-diagonal covariance matrix elements in the fitting routine.

To nevertheless determine the magnetic anisotropy parameter and the gyromagnetic factor, a second fitting procedure is implemented in the program. This one will optimize only  $D$ ,  $E$ , and  $g$  on data which contain the energies of the transitions from the ground state to higher excited states in dependence of the applied magnetic field. An example how such a file should look like is given in table 3.

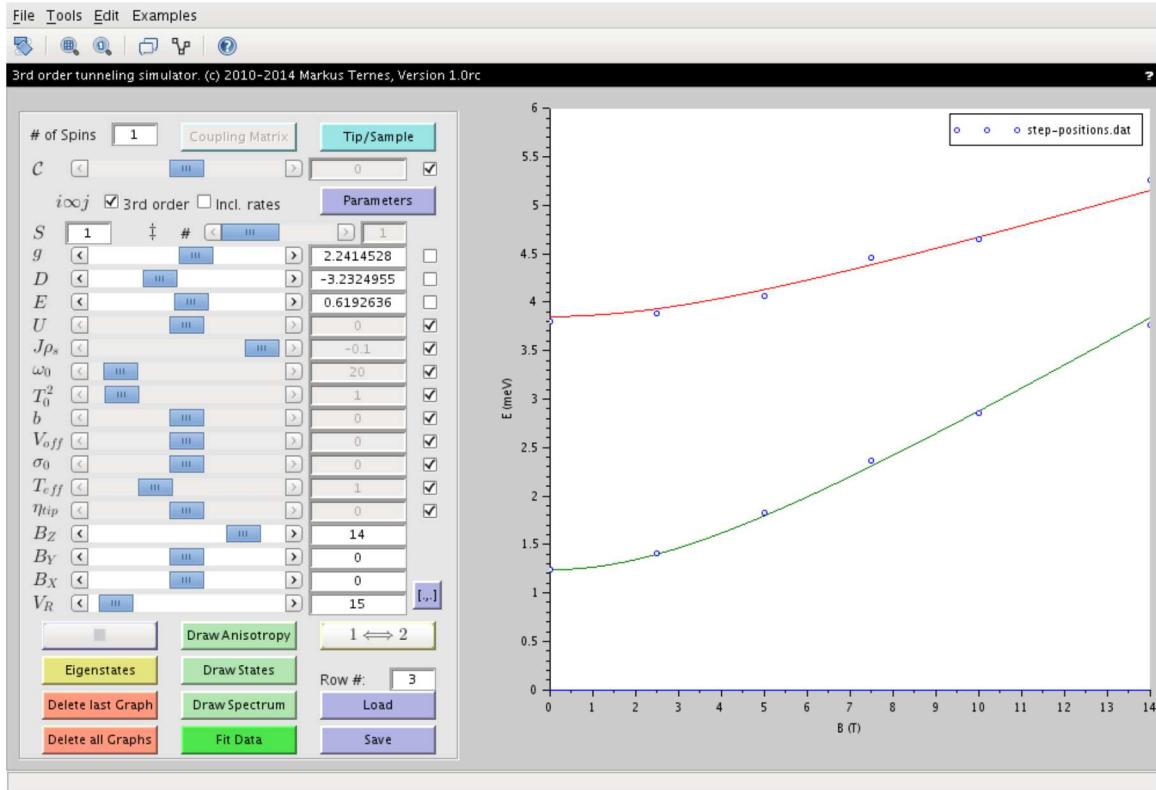
B-field (T)	step1 (mV)	step2 (mV)
0	1.24	3.80
2.5	1.41	3.89
5	1.83	4.06
7.5	2.37	4.46
10	2.85	4.65
14	3.76	5.26

**Table 3.** Example of a data-file containing the lowest two step-energies versus the applied magnetic field

The first column must contain the applied magnetic field, subsequent columns have to contain then the energy (in meV) of the lowest lying excited states. It is not necessary to give all excited state positions, but the program assumes that the ones which are given are the energetically lowest ones. These positions can be determined, for example, by rough fitting of all spectra as described in section 1.5 and use the excited state energies as they can be found by pressing the **Eigenstates** button (see also section 1.7).

Importing such file works analogous to importing spectroscopic data *except* that at the question “**Extracting Data from column x ?**” the answer must be “**No**”. The data is then displayed as colored circles in the GUI as shown in figure 9.

The fitting works similar as for spectroscopic data: Limits can be set in the submenu accessible by pressing the **[.;.]** button and the fitting is started with the **Fit Data** button. The results of the parameters  $g$ ,  $D$ , and  $E$  are displayed with the corresponding



**Figure 9.** The GUI after a successful fit to experimentally determined step position data.

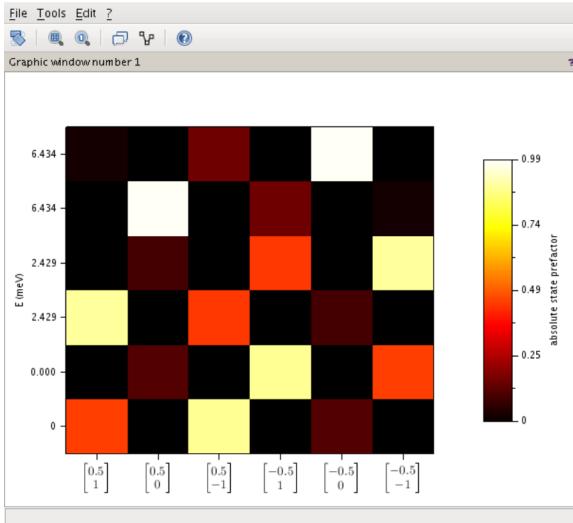
sliders and input-fields and can be toggled between the start values by pressing the  $1 \iff 2$  button. The result is shown as full lines in the GUI (see Figure 9) and can be exported with the “Save” function.

It is important to note, that the fit always assumes that the magnetic field is applied along the  $z$ -axis, i.e. along the main anisotropy axis of the spin system. If this is not the case for the experimental data, then anisotropy values  $D$  and  $E$  will result which do not obey the relation  $|D| \geq E$  and  $E \geq 0$ . The correct anisotropy values can then be determined by flipping the anisotropy axes as described in section 1.4.

### 1.7. More calculated physical quantities

The button **Eigenstates** opens a submenu which allows to select and then display some more properties of the spin system which afterward can also be exported via the save menu. Here, I will give a brief description of these functions:

**Colorplot of the States** Plots the eigenvectors of the total spin Hamiltonian written as sum in the  $m_z$  bases of the individual spins, i.e. as  $|m_z^{(1)}, m_z^{(2)}, \dots, m_z^{(3)}\rangle$ , along rows using a color code for the absolute magnitude of the component. The abscissa shows the state energy and the ordinate the components  $m_z^i$  of the base vector ordered from top to bottom (see figure 10)



**Figure 10.** Colorplot of the states for a coupled bipartite system.

For very large systems use the zoom button (the magnifying glass on top of the graph), and be aware that then only *state numbers* are plotted on the ordinate. These numbers can be converted into the  $m_z^{(i)}$  values in the scilab terminal with the command: “`State(experiment.atom,n)`”, where  $n$  is the state number of interest.

**Reduced to the Giant Spin Model** Plots the eigenstates in the base  $|S^T, m^T\rangle$  against their state-energy. The giant spin base consists of the total spin of the system  $S_T = \sqrt{\langle\psi|\hat{S}^2|\psi\rangle + \frac{1}{4}} - \frac{1}{2}$  and the total magnetic moment  $m^T = \sum_i m^i$  along the selected direction. All main directions ( $x, y, z$ ) as well as the arbitrary direction of the externally applied magnetic field can be chosen (see figure 11). The numbers in the graph are rounded-off, but the full precision is saved when the data is exported via the “Save” menu.

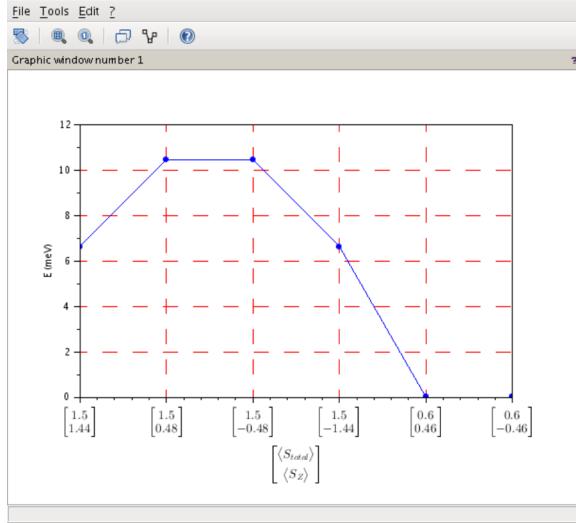
**Matrix of Eigenvectors** This button allows to directly access the eigenstates and eigenvalues of the spin system. It opens the variable editor where the eigenvectors are organized in columns.

**Negativity** The negativity  $\mathcal{N}$  is a good measure of the quantum entanglement between a member of a coupled spin system and the total spin system as long as it is build out of individual spins having  $S = 1/2$  and  $S = 1$ . It is calculated in the program by

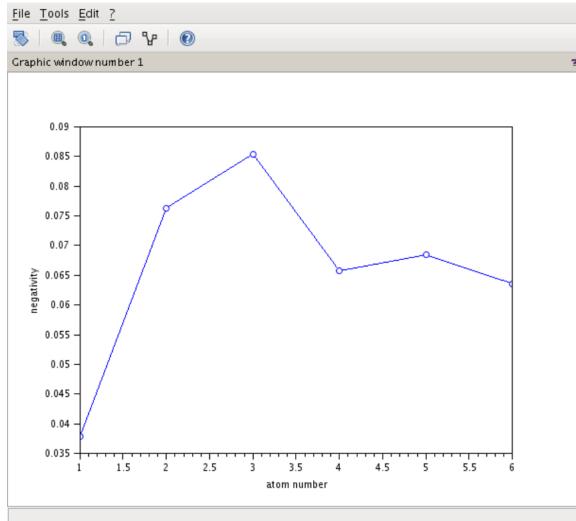
$$\mathcal{N}_i(\rho^{\Gamma_i}) = \sum_j \frac{|\lambda_j| - \lambda_j}{2}, \quad (8)$$

with  $\lambda_j$  as the eigenvalues of the partially transposed density matrix  $\rho^{\Gamma_i}$  with  $\rho$  as the total density matrix of the combined system. The partial transpose is performed on the sub-matrix  $\Gamma_i$  belonging to the  $i$ -th spin.

These function is only available on complex spin systems containing at least two



**Figure 11.** Plot of the state-energy versus eigenstate in the base of the giant spin approximation.

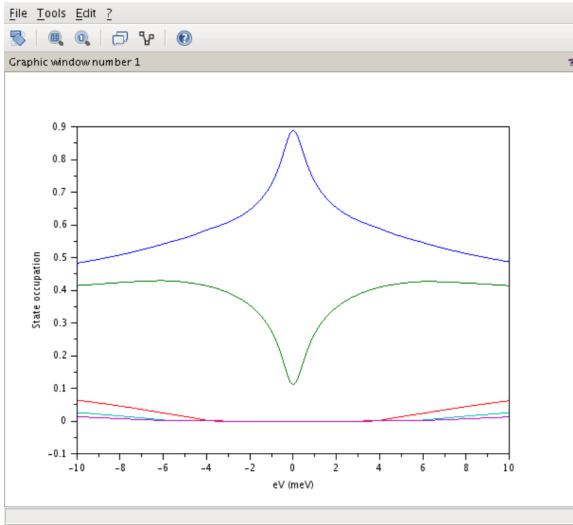


**Figure 12.** Plot of the negativity between the individual spins and the total system versus atom number for a spin system containing six coupled spins. The negativity is a measure of the quantum entanglement.

spins and displays the negativity versus atom position as shown in figure 12.

**Occupation of the States** When the differential conductance is not calculated in the zero-current limit but using rate equations, the flow of electrons change the average occupation of the eigenstates due to spin excitations and de-excitations. Furthermore, changes in the state occupations occur by spontaneous relaxations initialized by the substrate electron bath.

This submenu allows to plot the time averaged probabilities to find the system in a certain state versus the applied bias voltage as shown in Figure 13. Note, that



**Figure 13.** Plot of the state occupations versus the applied voltage for a Fe atom on Cu<sub>2</sub>N at  $T = 1$  K,  $B = 0$  T, and  $T_0^2 = 10^{-3}$  as example. At applied bias the average occupation of excited states increases non-thermal.

depending on the setting of the switch “**3rd order**” scattering processes of 2nd order only, or of 2nd and 3rd order are accounted for. The data can be saved via the “**Save**” menu.

**Entropy of the Spin System** From the above mentioned state occupations the von Neuman entropy  $S$  is calculated as:

$$S = \sum_{i=1}^n -p(i) \log(p(i)), \quad (9)$$

with  $p(i)$  as the probability to find the system in the  $i$ -th state and the summation running over the  $n$  eigenstates of the system. An example is shown in figure 14.

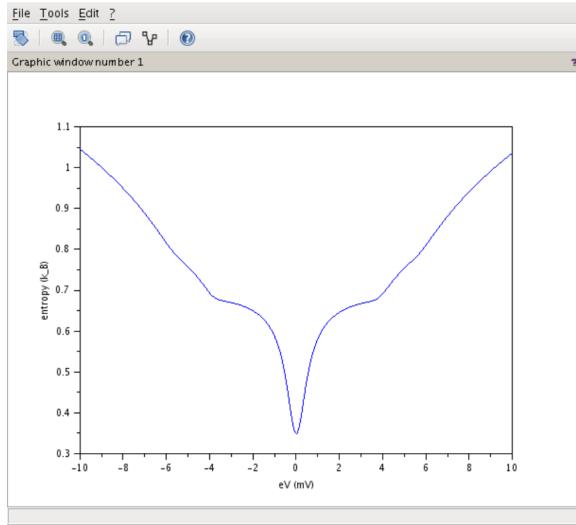
The data can be saved via the “**Save**” menu.

**Lifetime of the States** Due to the scattering with the substrate and tunneling electrons the states have a finite lifetime. When the differential conductance is calculated using rate equations, the state lifetime is calculated as the reciprocal of the sum of all scattering events which changes the spin state. The function enables to display the state lifetimes versus the applied bias as shown in figure 15 and can be saved via the “**Save**” menu.

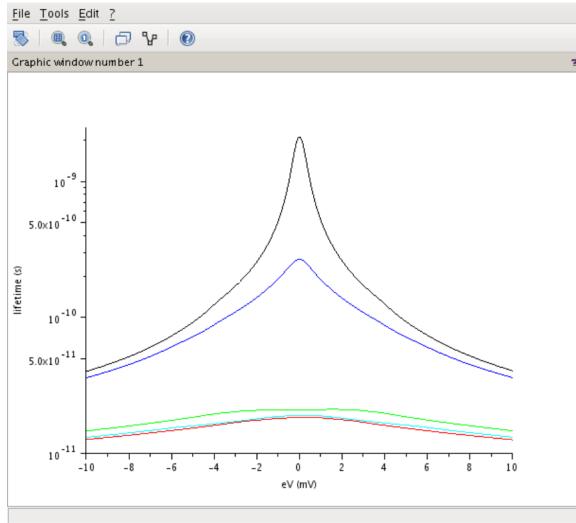
### 1.8. Setting global parameters

Some global parameters can be varied when entering this submenu by pressing the **Parameters** button. The function of these parameters are briefly described in the following:

**Max # of Eigenstates.** Limits the number eigenstates used in the calculation.



**Figure 14.** Plot of the von Neuman entropy versus the applied bias for the example shown in figure 13.



**Figure 15.** Plot of the state lifetimes versus the applied bias for the example shown in figure 13.

**Gamma** is the additional (non thermal) broadening for the log functions

**Min state occupancy** Limits the number of initial states for the scattering processes.

Its square is the minimal limit for any transition matrix elements to be evaluated.

**# of evaluations** The number of  $B$ -field values used for drawing states

**Save all data immediately** If set, all intermediately calculated data is saved. The files are stored in the standard directory of the *Scilab* installation. Files with the names “*data\_(in)\_(\_mid)\_(\_fin).dat*” for 3rd order (normal scattering order), “*data\_(in)\_(\_mid)\_(\_fin)r.dat*” for 3rd order (time reversed order), and “*data\_(in)\_(\_fin)SF.dat*” for 2nd order conductance contributions are created,

with in, mid, fin as the initial, middle, and final state number, respectively.

**Plot all spectra** If set, all intermediately calculated data will be plotted in the GUI.