SPECTRON

USER MANUAL

V.2

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Our team proudly presents SPECTRON version 2.8.x . It is the bug-fix update to the 2.7 version of SPECTRON. The number of changes from version 1.x.x includes: the kernel of the code has been completely rewritten, model excitonic systems were added. A lot of code can been optimized, numerous bugs have been fixed, a lot of work have been invested into stability. Concepts of input units and different types of density matrix dynamics were added in 2.7.x

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Darius Abramavicius: (initiator)	2003 -- 2010
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(stochastic Liouville equations)

Contents

1 History and present state

The project SPECTRON started in 2003, when Darius Abramavicius wrote an efficient modular computer code for calculation of the time domain linear and third order response functions for a given set of eigenstates. The code was easy to apply for calculation of optical signals for systems, which can be converted into a set of eigenstates. Codes of Ravindra Venkatramani and Tomas LaCour Jensen have been merged in 2004 with the help of Wey Zhuang. In 2004 the code was reoranized into a stand-alone application with a clear command-line interface. It was extensively tuned and optimized for simulations of two-dimensional photon-echo signals in vibrational polypeptide IR spectroscopy signals by Darius Abramavicius and Wei Zhuang. Wei Zhuang develped parametrization routines for vibrational frequencies. The signal part of the code was extended to simulate other types of spectroscopic signals.

In the 2005 the code was first applied to photosynthetic energy transport problems, where optical excitations are electronic and energy transport and dissipation are relevant. Redfield type relaxation equations for electronic density matrix propagation were added. The package has been used for electronic and vibrational spectroscopy signals. It was named SPECTRON.

During 2006 a lot of for bug-fixing was done. Software manual has been written. However the overall structure of the code was not suitable for extensive extensions and in 2006 the work has started for SPECTRON version 2 by Darius Abramavicius. The internal code structure was reorganized using the concepts of Object Oriented Programming breaking the code into small objects and using extensively various libraries. The files were organized into various folders with the help of Ben Robinson and Daniel Healion. New user interface was initiated by Ben Robinson based on a single central input file was created. These develpments lead to much shorter program execussion times, much easier bug-tracking, and easier code management. During 2008 the SPECTRON 1 capabilities were completely merged into SPECTRON 2 by Cyril Falvo and the new user manual was written. More options for density matrix propagation have been added starting from 2009. The concept of manually-defined physical units has been added.

The main work is now bug-fixing.

Currently the code SPECTRON performs simulation of linear and nonlinear optical signals of nonlinear oscillators and coupled oscillator complexes. The kernel of the code is the exciton Hamiltonian. Vannier, CT, and Frenkel exciton models are supported. Some specific system models are supported as well. These include:
1. C=0 Vibrations of protein backbone,
2. Amide UV excitations,
3. Generic exciton models for photosynthetic complexes.
Other types of systems are supported via generic physical models.

The code can calculate certain linear and nonlinear spectroscopy signals:
1. Absorption,

2. Circular Dichroism (CD),
3. Pump-probe,
4. photon echo,
5. double-quantum coherence signal.

This list can be extended by constructing various optical signals manually (like 3PEPS, TG, time-resolved fluorescence, narrow-band pump-probe) from the response functions, which can be calculated using SPECTRON.

Sophisticated relaxation models for the nonequilibrium density matix of excitons are available. This includes secular Redfield theory, full Redfield theory, Lindblad relaxation theory.

Refinement of lineshape simulation techniques and lineshape parameters at verious theory levels is under constant develpment.

The SPECTRON is developed under Linux OS, and in principle it can run in any unix environment where gnu compiler is available. This includes windows under CYGWIN environment. The main code is a single executable to be executed in the command-line environment. It is controlled by one or few input files specified on the command line.

Future directions:

A lot depends on the user responses.

1. Parallelization and implementation of the MPI protocol. However, we did not see real need for this at the moment. More useful approach would be OpenMP, which hides parallelization from the user and leads to transparent code execution.
2. Periodic infinite systems are currently supported only in experimental versions and not available in the release.

2 Installation and running examples

Needed development packages and libraries:

gcc	(4.*)
c++	(4.*)
libstdc++6	(4.*)
gfortran	(4.*)
gnu make	(3.8.0)

Libraries required to build the code (included)

blas	(3.*)
lapack	(3.*)
fftw3	(3.*)
newmat	(11)

Main steps to compile a binary using a shell (bash):
extract

```
tar -zxf spectron-***.tar.gz
```
change directory into the spectron folder
```
cd spectron-***
```
run
```
./configure
```
then
```
make
```

The executable is created in `./bin` directory. To clean build folders, run
```
make cleanall
```

The program is executed from a command-line shell:

```
<path-to-spectron>/bin/spectron2 <options> -i input_file
```

Basic options are:
```
-i filename
```
specifies the input filename,
```
-v
```
turns on output of supplementary intermediate information (verbose mode).

Additional tuning of how the code is built is modified via
```
make.top.in
```
and
```
make.extralibs
```

In the begining of `make.top.in` there are definitions
```
USER_INC_DIR= .
USER_LIB_DIR= .
```
These may be modified to add additional include file or library folders:
```
USER_INC_DIR= /<my folder of include files>
USER_LIB_DIR= /<my folder of library files>
```
These may be used when having separate fftw or other libraries.

An important option is
```
DEBUG_BUILD = TRUE  #FALSE
```
By selecting TRUE, the code (excluding third-party libraries) will be built with debugging information. This is useful for testing or tuning the code. By selecting FALSE, the code will be built with speed optimizations. This is useful for extensive simulations since it speeds up the code considerably.

A compiler for the code may be selected. For the default gnu compiler the options are:
```
DC_CC           = gcc
DC_CPP          = g++
DC_F77          = gfortran
DC_F90          = gfortran
CC              = gcc
CPP             = g++
CRR             = cpp
F77             = gfortran
```

```
F90                = gfortran
LD_CC              = gcc
LD_CPP             = g++
LD_F77             = gfortran
LD_F90             = gfortran
```

Note that currest SPECTRON code includes blas, lapack, fftw and newmat libraries. By default these will be compiled and installed locally for spectron when building the SPECTRON code. In order to switch off this compilation and use default OS or previously pre-built libraries, modify `make.extralibs` file by deleting or commenting out the relevant lines.

Complete cleanup of the spectron folder is performed by executing
./clean-all

3 Basic usage and functionality

SPECTRON code calculates certain linear and non-linear spectroscopic signals. The code uses one or a set of input files as an interface. No interactive usage is available.

The main input file is supplied on a command line using an option

```
-i <filename>
```

The main input file structure is as follows. Different sections start with `$XX` sign and end with `$END`.

```
--------------------------------
$REGISTRATION

< signal1 >
< signal2 >
...
< list of requested signals >

$END

$SYSTEM

< characterization of system properties>

$END

$BATH

< characterization of environment >

$END
```

```
$<signal1>

< signal1 properties >

$END

$<signal2>

< signal1 properties >

$END
--------------------------------------
```

In some special cases the environment section may be not needed. Other sections are necessary.

Currently possible signals are:
LA – linear absorption,
CD – circular dichroism,
KI – rephasing photon echo (2D),
KII – non-rephasing photon echo (2D),
KIII – double-quantum coherence signal (2D),
KIIIA – double-quantum coherence signal (2D - different projection),
PP – pump-probe (2D).
TDLR – Time domain linear response function (1D).
TDRS – Time domain third order response functions I, II and III (3D).
These signals must be listed in REGISTRATION section to turn them on.

The systems are either generic or specific. Generic systems are characterized by energy levels and transition amplitudes between these levels. These level properties are given as an additional input files. More specific systems represent certain models and are switched on by specific keywords. Additional information of such systems are again listed in the main input file or accessory files.

One section is necessary for each experimet. One may have many experiment sections. Only those that are specifield in the REGISTRATION section, are activated.

4 Relevant physical units

Angstrom 1 Å = 10^{-10} m

The speed of light c = $2.9979*10^{8}$ m/s = 2997.9 Å/fs = $2.9979*10^{-5}$ cm/fs

The electron charge e =$1.602*10^{-19}$ C= 1e

Borh Magneton $m_b=\frac{e\hbar}{2mc}$ = $3.0935*10^{-32}$ Cm = $1.9308*10^{-3}$ eÅ.

The following units are used internally in the code.

Energy is equivalently used as frequency using wavenumber representation. The wavenumber is $\kappa=1/\lambda$, or inverse wavelength. The wavenumber is usually given in reciprocal centimeters. For instance the green 500 nm wavelength light has wavenumber 20000 cm^{-1}. This corresponds to $\nu=c/\lambda$ = 599.5 THz oscillation frequency of electromagnetic field or 2.48 eV energy. 1 eV of energy is equivalent to 8065.545 cm^{-1}.

Distance is given using angstroms [Å] or nanometers [nm]. 1 m = 10^{10} Å, 1 nm = 10 Å. The natural units in the code are angstroms and all distances are converted into these.

Time is given in femtoseconds [fs].
Rates or **timescales** is sometimes used to characterize decay process. The conversion between two is based on relation $\exp(i\omega t-\gamma t)\equiv\exp(i 2\pi\nu t-t/\tau)$. The timescale of a decay process γ is $\tau=1/\gamma$. Using [fs] for timescale and [cm^{-1}] for rate we have relation
$\tau_{fs}=(1/(2\pi c_{cm/fs}))1/\gamma_{cm^{-1}}=5308.8/\gamma_{cm^{-1}}$.

Transition electric dipole μ is defined using operator $\hat{\mu}=q\hat{r}$. That is the coordinate representation. The natural unit is then electron charge times angstrom [eÅ]. Additionally, debye [Deb] may be used: 1 [Deb] = 0.2082 [eÅ]. The electric dipole has the same units as the Bohr magneton [BM] defined above. The conversion 1 [BM] = 1.9308*10^{-3} [eÅ] is then relevant. Alternatively sometimes gradient representation (nabla) may be used for the electric transition characterization: $\hat{\mu_{\nabla}}=\hat{\nabla}$. Then [Å^{-1}] should be used. The conversion from $\hat{\mu_{\nabla}}$ into $\hat{\mu}$ is $\hat{\mu}$ [eÅ] = 6.1459*10^{4} / E[cm^{-1}] * $\hat{\mu_{\nabla}}$ [Å^{-1}]. Here E is the transition energy.

Transition magnetic dipole m is defined using operator $\hat{m}=\frac{e}{2m}(\hat{r}\times\hat{p})$. The natural units are [eÅ^{2}/fs] . Let me define another representation: $\hat{m}=c\,\hat{m}_c$, where $\hat{m}_c=\frac{e}{2mc}(\hat{r}\times\hat{p})$. This quantity has the same units as the electric dipole. So it may be given by [eÅ] or by [Deb] or by [BM]. I get relation $\hat{m}$ [eÅ^{2}/fs] = 2997.9 $\hat{m}_c$ [eÅ]. And in terms of Debye $\hat{m}$ [eÅ^{2}/fs] = 0.2082*2997.9 $\hat{m}_c$ [Deb]. Or $\hat{m}$ [eÅ^{2}/fs] = 1.9308*10^{-3}*2997.9 $\hat{m}_c$ [BM] .

Transition quadrupole q is defined using operator $\hat{q}^{\chi\psi}=\frac{e}{2}\hat{r}^{\chi}\hat{r}^{\psi}$. The natural units are [eÅ^{2}] . Other derived units are [Deb Å], [Deb nm], [BM Å] and [BM nm].

Summary of conversions

E [cm^{-1}]	=	8065.545		E	[eV]
E [cm^{-1}]	=	8.065545		E	[meV]
E [cm^{-1}]	=	33.357		E	[THz]
γ [cm^{-1}]	=	5308.8	/	τ	[fs]
μ [eÅ]	=	0.2082		μ	[Deb]

μ [eÅ] = $1.9308*10^{-3}$ μ [BM]
μ [eÅ] = $(6.1459*10^{4}$ / E[cm^{-1}]) μ_{∇} [$\mathrm{Å}^{-1}$]
q [$\mathrm{eÅ}^{2}$] = 0.2082 q [Deb Å]
q [$\mathrm{eÅ}^{2}$] = 2.082 q [Deb nm]
q [$\mathrm{eÅ}^{2}$] = $1.9308*10^{-3}$ q [BM Å]
q [$\mathrm{eÅ}^{2}$] = $1.9308*10^{-2}$ q [BM nm]
m [$\mathrm{eÅ}^{2}$/fs] = 2997.9 m_c [eÅ]
m [$\mathrm{eÅ}^{2}$/fs] = 624.16 m_c [Deb]
m [$\mathrm{eÅ}^{2}$/fs] = 5.7883 m_c [BM]

5 Command-line options

The command-line options follow the executable upon execution. Short and long verions of options are supported. Some options have arguments.

```
short     long           argument
-v        --verbose      x
```
verbose mode: prints some extra output on the screen
```
-h        --help         x
```
prints some help information
```
-i        --input        v
```
specifies the main input file
```
-r        --rands        v
```
sets the “seed” of the random number generation
```
-u        --units        v
```
specifies the units of imput parameters

Available unit combinations in SPECTRON input

`local`

(default)

energy	[cm^{-1}]
distance	[Å]
el dipole	[eÅ]
m dipole	[$\mathrm{eÅ}^{2}$/fs]
el quadrupole	[$\mathrm{eÅ}^{2}$]
time	[fs]

`de_nm_cm`

energy	[cm^{-1}]
distance	[nm]
el dipole	[Deb]
m dipole	[Deb]
el quadrupole	[Deb nm]
time	[fs]

`de_an_cm`

energy	[cm^{-1}]

distance	[Å]
el dipole	[Deb]
m dipole	[Deb]
el quadrupole	[Deb Å]
time	[fs]

`bm_nm_ev`

energy	[ev]
distance	[nm]
el dipole	[Bm]
m dipole	[Bm]
el quadrupole	[Bm nm]
time	[fs]

`bm_an_ev`

energy	[ev]
distance	[Å]
el dipole	[Bm]
m dipole	[Bm]
el quadrupole	[Bm Å]
time	[fs]

`db_an_cm`

energy	[cm^{-1}]
distance	[Å]
el dipole	[Deb]
m dipole	[Bm]
el quadrupole	[Deb Å]
time	[fs]

`db_an_ev`

energy	[ev]
distance	[Å]
el dipole	[Deb]
m dipole	[Bm]
el quadrupole	[Deb Å]
time	[fs]

`db_nm_ev`

energy	[ev]
distance	[nm]
el dipole	[Deb]
m dipole	[Bm]
el quadrupole	[Deb nm]
time	[fs]

`ia_an_ev`

energy	[ev]
distance	[Å]

el dipole	[Å^{-1}] – (gradient representation)
m dipole	[Bm]
el quadrupole	[eÅ^{2}]
time	[fs]

`ia_an_cm`

energy	[cm^{-1}]
distance	[Å]
el dipole	[Å^{-1}] – (gradient representation)
m dipole	[Bm]
el quadrupole	[eÅ^{2}]
time	[fs]

`de_nm_th`

energy	[THz]
distance	[nm]
el dipole	[Deb]
m dipole	[Deb]
el quadrupole	[Deb nm]
time	[fs]

`bm_nm_th`

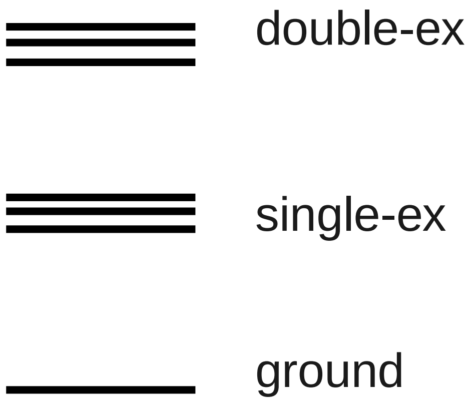
energy	[THz]
distance	[nm]
el dipole	[BM]
m dipole	[BM]
el quadrupole	[BM nm]
time	[fs]

Please note that these options are still under development and may not work in many cases so it is always safer to use default units.

6 Generic simple systems

In the following the components of the main input file are described for various system setups. Generic systems are characterized by a set of energy levels and transition amplitudes between them. The energy levels must fall into certain manifolds. The ground state is always assumed to have energy 0. In equilibrium only a single such state is occupied. All other states are accessible only via optical transitions. The single-exciton manifold is connected to the ground state. The double-exciton manifold is connected to the single-exciton manifold. All units in the generic system are standart (corresponds to `-u local`). Others units are not supported.

A. *System Made of Known Energy Levels*



In this model the system is assumed as a set of energy levels. The energy levels should fall into certain manifolds or bands. The signle ground state is separated and has energy equal to 0. The single-exciton band is shifted from the ground state by a value close to optical excitation energy. The band may consist of an arbitrary number of states. Electric and magnetic transition dipoles as well as electric quadrupoles may connect the single-exciton states with the ground state. Energy transport through exciton population relaxation is supported in this manifold. This amount of information is used for linear signals such as absorption and CD.

A double-exciton information is additionally necessary for the nonlinear signals. The double-exciton manifold may consist of an arbitrary number of states as well. Electric and magnetic transition dipoles, and electric transition quadrupoles can be given to describe transition amplitudes between the single- and the double-exciton states. The double-exciton state excitation directly from the ground states is not supported.

Supported keywords.

ORIENTATION **F**_str

RANDOM (default) unoriented system in the lab frame. Complete 3D orientational averaging is performed when calculating optical signals. The model corresponds to isotropic ensemble (gas phase or solution).
ALONG_Z - z axis is fixed, averaging is performed for rotation only around z. The model represents partially oriented ensemble.
FIXED – all axes are fixed. No averaging is performed.

NUMMODES **N**_int

(required) the number of states in singly-excited manifold

ES_NUMST **N**_int

(required) the total number of states (including the ground state)

ES_EVALS **F**_str #[T1]

(required) the filename of the list of eigenstate energies in reciprocal centimeters with respect to the ground state in increasing order. The file includes the ground state. Its energy is 0. File type is T1. Number of entries = **ES_NUMST**

ES_EDIPS **F**_str #[T2]

(required) the filename of the list of transition dipoles between the states. 1st and 2nd columns are the state indices, then x, y, z values. The number of rows is not fixed: zero-value transition dipoles can be skipped.

ES_QTENS **F**_str #[T9]

the filename of the transition quadrupoles. 1st and 2nd columns are the state indices, then xx, yy, zz, xy, xz, yz. xy=yx type symmetrization is imposed.

ES_MDIPS **F**_str #[T2]

the filename of the transition magnetic dipole. 1st and 2nd columns are the state indices, then x, y, z as for electric dipoles.

CONST_DEPHASING **X**_real #[cm^{-1}]

Lorentzian linewidth (FWHM = 2X) of all optical transitions. This is the simplest line-broadening model that can be used almost in all simulations.

ES_DEPHASINGS **F**_str #[T4]

the filename of the matrix of exciton dephasing rates (energy units) between various exciton states. The file contains a three-column matrix. First two columns are state indices. The last column is the dephasing value between the two states. State ordering is equivalent to **ES_EVALS**.

TRANSPORT **N**_int

This flag when **N**>0 turns on population transport. Populations rates must then be either supplied from a file or allowed to calculate.

TRANSPORT_RATES **F**_str #[T4]

the filename of the matrix of population transport rates in the single-exciton manifold. They must be given in units of fs^{-1}. The diagonal of the file contains the negative lifetime of the state, corresponding to the column/row number. The numbers above diagonal are the rates from the higher to the lower states and the numbers below the diagonal are the rates from lower to higher states. State ordering is equivalent to **ES_EVALS**. The file only the rates between singly-excited states *and the ground state*. No doubly-excited states are included.

REDFIELD_RATES **F**_str

the filename of the complex Redfield relaxation super-matrix for single-exciton space population-coherence dynamics. This matrix does not include the ground state. This is the most complete Markovian model for the describing dynamics of the single-exciton manifold. Other dephasings should be specified as requested by certain signals. The file format is equivalent to the one described in **PRINT_REDFIELD_M.** Snapshots of the operator can be used when using **NUM_SHOTS**: the sanpshots are then separated by 'D' character as the first element on line (from word “Done”); the following content of the line is ignored.

ES_LAMBDA **F**_str #[T8]

the filename of the matrices of system-bath couplings for the diagonal fluctuations (including the ground state for consistency) to different bath modes (more sophisticated model than **CONST_DEPHASING**). The lineshapes and linewidths are calculated. The size is **ES_NUMST***x***ES_NUMST**. The system-bath couplings, $\lambda_{ab,m}$, corresponds to the spectral density $C''_{ab}(\omega)=\sum_m \lambda_{ab,m} J_m(\omega)$, derived from the correlation function $C_{ab}(t)\equiv\frac{1}{\hbar^2}\langle\varepsilon_a(t)\varepsilon_b(0)\rangle=\int\frac{d\omega}{2\pi}e^{-i\omega t}(1+\coth(\beta\hbar\omega/2))C''_{ab}(\omega)$. The number of matrices is equal to the number of bath modes. This option requires additional **$BATH...$END** section present in the input file.

ES_K_LAMBDA **F**_str #[T8]

the filename of the matrices of system-bath couplings for the off-diagonal fluctuations (singly-excited states+ the ground state for consistency) to different bath modes (more sophisticated model than **TRANSPORT_RATES**). The transport rates are calculated from the model. The size is **ES_NUMST***x***ES_NUMST**. The system-bath couplings, $\kappa_{ab,m}$, corresponds to the spectral density $\bar{C}''_{ab}(\omega)=\sum_m \kappa_{ab,m} J_m(\omega)$, derived from the correlation function $\bar{C}_{ab}(t)\equiv\frac{1}{\hbar^2}\langle J_{ab}(t)J_{ab}(0)\rangle=\int\frac{d\omega}{2\pi}e^{-i\omega t}(1+\coth(\beta\hbar\omega/2))\bar{C}''_{ab}(\omega)$. The number of matrices is equal to the number of bath modes. This option requires additional **$BATH...$END** section present in the input file.

A sample section of three-level system could look like

```
$SYSTEM
  NUMMODES          1
  ES_NUMST          3
  ES_EVALS          <filename>
  ES_EDIPS          <filename>
  CONST_DEPHASING   100
$END
```

This type of setup can be used together with **NUM_SHOTS** in techniques to calculate signal by adding disorder in the input files. In such case, the different “snapshots” of the system dynamics must be recorded in the input files one-after-another continuously. Comment characters may be used to separate different snapshots.

B. *An excitonic aggregate (Frenkel model)*

This is the core system model for coupled charge-neutral sites (oscillators) interacting via dipolar interactions. The oscillators may be two-level or three-level oscillators. Only single-exciton manifold is needed for the linear signals. The double-exciton manifold is constructed automatically. Only-single-exciton information is required for the system of two-level molecules. Additional anharmonicity information is needed for the three-level molecules. The additional anharmonicity consists of anharmonicity of energies and the anharmonicity of transition dipoles. The excitonic model is defined by strict relation between the number of the single-exciton and the double-exciton states.

Supported keywords

ORIENTATION **F**_str

check section 6A.

NUMMODES **N**_int

(required) the number of coupled oscillators. Must be larger or equal than 1. If equal to 1, then only one oscillator is considered. This case is allowed.

INP_HAM_L_ **F**_str #[T3]

(required) the filename of the zero-order Hamiltonian matrix. The off diagonal part of the matrix represents real-space Frenkel exciton quadratic couplings (exciton resonance interactions). The diagonal of the matrix are the energies of the singly-excited molecules. Size of the matrix is **N**x**N**.

INP_DIP_L_ **F**_str #[T5]

(required) the filename of the electric transition dipole for each oscillator. The three columns are X, Y and Z coordinates. The order of the dipoles is the same as in **INP_HAM_L_**.

INP_COO_L_ **F**_str #[T5]

the filename of the transition origin coordinates for each oscillator. The three columns are X, Y and Z coordinates. The order of the dipoles is the same as in **INP_HAM_L_**.

INP_QAD_L_ **F**_str #[T6]

the filename of the electric transition quadrupole for each oscillator. The tensors are ordered as in **INP_HAM_L_**. Different columns are xx, yy, zz, xy, xz, yz components. xy=yx type symmetrization is imposed.

INP_MAG_L_ **F**_str #[T5]

the filename of the transition magnetic dipole for each oscillator. The three columns are X, Y and Z coordinates. The order of the dipoles is the same as in **INP_HAM_L_**.

ELECTRONIC **N**_int

The switch which chooses between two-level or three-level coupled oscillator models. The default corresponds to three-level coupled oscillators. Nonzero **N** switches to two-level oscillators.

ANHARMONICITY **X**_real #[cm^{-1}]

Shift of doubly-excited state energies from harmonic regime for three-level coupled-oscillator system. All oscillator overtones will get the same shift from harmonic value specified by **X**.

INP_ANH_L_ **F**_str #[T3]

the filename of the shift of double-exciton state energies from the harmonic model by Δ_{mn} . It may be used as for three-level oscillatos as for two-level oscillators. In case of two-level oscillators the diagonal is discarded. The interpretation is as follows: the energy of the doubly-excited state when oscillators *m* and *n* are excited is $\varepsilon_m+\varepsilon_n+\Delta_{mn}$. The size of the matrix is **NUMMODES***x***NUMMODES**. The keyword replaces **ANHARMONICITY.**

EXC_HAM2_ANH_COUPL **F**_str

F_str is the file name containing a matrix $A_{mn,kl}$ all non-harmonic properties, coupling and energy shifts, with respect to harmonic case, for double-excitons. The keyword replaces both **ANHARMONICITY** and **INP_ANH_L_.** This matrix is added on top to the double-exciton block, constructed from the single-exciton manifold. It can be used with two-level or three-level coupled oscillators. In case of two-level oscillators all overtone properties (if given) are ignored. Only non-zero values may be specified. Each row in the file reflects one element of the matrix. There are 5 columns in each row. The first four columns are indices of oscillators starting from zero. The order of oscillators is the same as in **INP_HAM_L_.** The last number os the value of the anharmonicity in energy units. Types of anharmonic properties:

1. Anharmonicity of overtone states *f=(mm):* $A_{mm,mm}$,
2. Anharmonicity of combination states *f=(mn):* $A_{mn,mn}$, $m\neq n$,
3. the coupling shift between a combination band *f=(mn)* $m\neq n$ and a combination band *f'=(kl)* $k\neq l$ from its harmonic approximation $A_{mn,kl}$,
4. couplings between overtones *f=(mm)* and *f'=(nn):* $A_{mm,nn}$, $m\neq n$,
5. coupling shift between overtone *f=(mm)* and combination band *f'=(kl)* $k\neq l$: $A_{mm,kl}$.

This anharmonicity matrix may be used only in SOS signals.

INP_D_2_L_ **F**_str

the filename of the electric transition dipole anharmonic correction $\mu^{(2)}$. It may be used either in form $\mu_m^{(2)}\hat{B}_m^+\hat{B}_m\hat{B}_m$ or in more complicated $\mu_{mnk}^{(2)}\hat{B}_m^+\hat{B}_n\hat{B}_k$ form. This form is controlled by a keyword **FORM_D_2_L_** . The file structure differs for two different forms. For $\mu_m^{(2)}\hat{B}_m^+\hat{B}_m\hat{B}_m$ the input file consists of three columns, which are X, Y and Z components. Each line represents one oscillator. The order of the dipoles is the same as in **INP_HAM_L_**. For the form $\mu_{mnk}^{(2)}\hat{B}_m^+\hat{B}_n\hat{B}_k$ the file consists of six columns. The first three columns are *m*,*n* and *k* and then the corresponding dipole (X, Y and Z components) is given. This dipole anharmonicity currently can be used only in SOS-based signals.

FORM_D_2_L_ **N**_int

A bool value (0 = off or 1 = on) switches between two forms of the transition dipole anharmonicity. The default (0) corresponds to $\mu_m^{(2)}\hat{B}_m^+\hat{B}_m\hat{B}_m$ form. The value 1 corresponds to $\mu_{mnk}^{(2)}\hat{B}_m^+\hat{B}_n\hat{B}_k$ form.

REDUCTING_HAM **F**_str

The Hamiltonian describing the two exciton manifold, is generate automatically from the one exciton Hamiltonian and the non linear couplings. If the one exciton Hamiltonian is block diagonal, the two exciton block will be as well. Depending on the specific spectroscopic technique used, not all the blocks are probe (this is especially true for two color experiments). This keyword is designed to reduced the size of the second block and save computational time.
Restriction: this keyword is valid **only** for SOS calculation. The current version only support three level system and is not valid with the EXC_HAM2_ANH_COUPL keyword.
F_str is the input file containing the block information of the system.
Input file for the REDUCTING_HAM keyword. The BLOCK1 part describe how the one exciton Hamiltonian is divided into blocks. The BLOCK2 part describe how the two exciton Hamiltonian should be constructed. For example the first block is generate by a combination of states from the first block of the one exciton Hamiltonian. The second block is generate by a combination of states from the first and second block of the one exciton Hamiltonian, etc...

```
-------------
BLOCK1     nblock1
1     nstates1    1 ... nstates1
2     nstates2    nstates1+1  ... nstates1+nstates2
...
nblock1
BLOCK2     nblock2
1  1
1  2
```

```
2  2
...
nblock2
-------------
```

SB_COUPLING **X**_real #[cm-1]

The simple model of system-bath interaction. A single number on the input is the system-bath coupling strength λ. The model is that each oscillator is coupled to identical local bath by the same strength; these local baths are uncorrelated. The bath is characterized by a single stochastic coordinate – a single spectral density. In the real space we have the following nonzero correlation functions

$C(t)\equiv\frac{1}{\hbar^2}\langle\varepsilon_n(t)\varepsilon_n(0)\rangle=\int\frac{d\omega}{2\pi}e^{-i\omega t}(1+\coth(\beta\hbar\omega/2))C''(\omega)$ and $C''(\omega)=\lambda J(\omega)$, where $J(\omega)$ is a dimensionless odd function defined from 0 to infinity. The model is advanced compared to **CONST_DEPHASING** since it allows to calculate population transport rates and thus includes temperature-dependent lineshape. More complex models are available in specific system models.

INP_LINDBLAD_PARAMETRS **F**_str

the filename of the Lindblad operator coefficients. Can be strictly used only for an excitonic model. However, the model is defined in the basis of single-exciton eigenstates. The model which is used is that the Lindblad parameters are defined as $\hat{L}=\sum_{ab}u_{ab}\hat{B}_a^+\hat{B}_b$, where *a* and *b* are the single-exciton eigenstates and *B* are creation/annihilation operators. Then we define correlation coefficients $c_{ab,cd}=\langle u_{ab}^* u_{cd}\rangle$. One may assume different types of correlations. The fully uncorrelated case is when only “diagonal” elements are non-zero $c_{ab}^{(c)}=\delta_{ac}\delta_{bd}c_{ab,cd}$. This is controlled by a keyword **LINDBLAD_UNCORRELATED**. Using Lindblad operators allows to calculate all dephasing and relaxation rates for an excitonic system for all manifolds. So this model excludes all system-bath coupling models based on Redfield theory. This may be used only together with **SOS_PRO** type signals. Other **SOS** or **QP** signals can not use this Lindblad model. The file format is as follows. In the case of the uncorrelated coefficients $c_{ab}^{(c)}$ is given in the input file as a square matrix. In case correlated coefficients case the super-matrix $c_{ab,cd}$ is given as a set of square matrices for indices *cd* (*d* inside *c*); index *b* is looping inside *a.*

LINDBLAD_UNCORRELATED **N**_int

The integer value define the correlation state of the Lindblad correlation coefficients:

0 = correlated case; here the matrix $c_{ab,cd}=\langle u_{ab}^* u_{cd}\rangle$ is given as a set of square sub-matrices in a datafile **INP_LINDBLAD_PARAMETRS.**

1 = uncorrelated case (default); here the matrix $c_{ab}^{(c)}=\langle u_{ab}^{*}u_{ab}\rangle$ is given as a triangular data matrix in file **INP_LINDBLAD_PARAMETRS.**
For more info read about **INP_LINDBLAD_PARAMETRS.**
2 = partially correlated case implying weak-coupling limit and real correlations; here the following restrictions are applied:
$\langle u_{ab}u_{cd}\rangle=\langle u_{cd}u_{ab}\rangle$,
$\langle u_{ab}u_{cd}\rangle(\exp(-\varepsilon_b/kT)+\exp(-\varepsilon_d/kT))=\langle u_{ba}u_{dc}\rangle(\exp(-\varepsilon_c/kT)+\exp(-\varepsilon_a/kT))$.
Matrix $c_{ab,cd}^{(x)}=\langle u_{ab}u_{cd}\rangle$ is represented as $c_{ab,cd}^{(x)}=\cos(\alpha_{ab,cd})\chi_{ab}\chi_{cd}$. χ_{ab} are given by relating single-exciton dephasing and population relaxation matrices, while on the input file the correlation coefficients $\cos(\alpha_{ab,cd})$ are specified.On the input file one gives two matrices: The triangular matrix of $\cos(\alpha_{aa,bb})$ for coherence transfer. Note that diagonal $\cos(\alpha_{aa,aa})=1$ and is not used. The second is square matrix $\cos(\alpha_{aa,ab})$ coupled coherences and populations. Its diagonal is discarded as well. Other types of correlations are neglected.

INP_RELAXATION_MATRIX **F**_str **C**_str (under construction)

F_str is the filename of the complete set of relaxation rates of Markovian relaxation model. Can be strictly used only for an excitonic model. These rates are given in the basis of single-exciton eigenstates and their product states. The order of single-exciton eigenstates is in increasing eigenstate energy. This may be used only together with **SOS_PRO** type signals.
The file contains relaxation matrices of the following set of equations:

$$\dot{G}=-i h^B G+R^B G \quad for\, \rho_{e,g};[N\times N]$$

$$\dot{G}^{(Y)}=-i h^Y G^Y+R^Y G^Y \quad for\, \rho_{(e_2e_1),g};[N^2\times N^2]$$

$$\dot{G}^{(N)}=-i h^N G^N+R^N G^N \quad for\, \rho_{e_2,e_1};[N^2\times N^2]$$

$$\dot{G}^{(Z)}=-i h^Z G^Z+R^Z G^Z \quad for\, \rho_{(e_3e_2),e_1};[N^3\times N^3]$$

all product states $(e_2e_1)\wedge(e_1e_2)$ are included. The rates are given in the order specified by **C**_str:
B – denotes that only R^B is given
BY – the set R^B , R^Y is given,
BN – the set R^B , R^N is given,
BNZ – the set R^B , R^N , R^Z is given
BYZ – the set R^B , R^Y , R^Z is given and
BYNZ – the full set R^B , R^Y , R^N , R^Z is given. R^B Is given as a square matrix: columns are lower indices and rows are higher indices (same holds everywhere else). For two states we have:
[0,0] [0,1]
[1,0] [1,1]
R^Y and R^N are given as square matrices with the following order of elements
[(0,0),(0,0)] [(0,0),(0,1)] [(0,0),(1,0)] [(0,0),(1,1)]
[(0,1),(0,0)] [(0,1),(0,1)] [(0,1),(1,0)] [(0,1),(1,1)]

[(1,0),(0,0)] [(1,0),(0,1)] [(1,0),(1,0)] [(1,0),(1,1)]
[(1,1),(0,0)] [(1,1),(0,1)] [(1,1),(1,0)] [(1,1),(1,1)]

R^Z is given with the following order of elements

[(0,0,0),(0,0,0)] [(0,0,0),(0,0,1)] ...[(0,0,0),(1,1,1)]
[(0,0,1),(0,0,0)] [(0,0,1),(0,0,1)] ...[(0,0,1),(1,1,1)]

[(1,1,1),(0,0,0)] [(1,1,1),(0,0,1)] ...[(1,1,1),(1,1,1)]

The spectral broadenings may be specified either using **CONST_DEPHASING** or **ES_DEPHASINGS**. Note that these are specified for the eigenstates, not for real-space coupled oscillators. **TRANSPORT** may be used as well: in this case the transport rates must be given either using **TRANSPORT_RATES** keyword, or read from file with **REDFIELD_RATES** (all these are for eigenstates), or must be calculated using **SB_COUPLING**. It is also important that eigenstate properties are properly used in SOS type signal simulations. For QP type calculations all necessary options and assumptions and possible error messages must be carefuly considered.

This type of setup can be used together with **NUM_SHOTS** in techniques to calculate signal using inhomogeneous averagings. In such case, the different “snapshots” of the system dynamics must be recorded in the input files one-after another continuously.

The energy-level and th excitonic models are very versatile models and are basic ingredientis in most other more sophisticated models. Simulations of spectroscopic signals rely on these two models. All specific system models are transformed into one of these models. The SOS simulation techniques usually proceed from energy-level model. The QP simulation techniques usually start with the exciton model and then make an intermediate model, where all properties are given in terms of single-exciton properties and their scatterings.

C. Generic trajectories (only for SOS approaches)

This system representation relies on previous models. Either energy-level approach or excitonic generic model can be used. The key concept here is that due to environment the system parameters (energy levels etc.) fluctuate. Correlation functions of these fluctuations determine spectral line broadenings. The fluctuating trajectories of generic parameters as used in generic models above can be used on input and then the correlation functions can be obtained directly in SPECTRON.

At the moment only fluctuating trajectories of Hamiltonian energy parameters can be used. It is assumed that fluctuating transition dipoles are not correlated with the fluctuating transition frequencies. The transition dipole averaged amplitudes are eventually used.

The Hamiltonian trajectories are essentially employed to get motional narrowing effects using the cumulant expansion techniques. The method is correct when fluctuations are small and the mean or the reference Hamiltonian can be well-defined (under construction).

The basic system setup is the same as the generic models described above. Instead of a single Hamiltonian in input files specified via either **INP_HAM_L_** or **ES_EVALS** , the tranjectories of Hamiltonians must be used: the Hamiltonians of different snapshots are goven one after another. The time separation between different snapshots must be equal.

Additional to generic systems, new keywords are as follows:

GENERATE_LS_FUNCT **N**_int

Nonzero N turns on calculation of lineshape functions from the fluctuating Hamiltonian trajectory files for SOS_CGF simulations. The Hamiltonian given on an input file must contain a trajectory.

TRAJECTORY_NP **N**_int

N is number of points in the fluctuating trajectory of the Hamiltonian.

TRAJECTORY_TS **X**_real [fs]

Timestep in the fluctuating trajectory of the Hamiltonian (generic time units).

TRAJECTORY_TRANSITIONS **N**_int

Nonzero N adds averaging over fluctuating transition dipoles; these are treated as uncorrelated with the fluctuations of energies. The transition dipole files must contain a trajectory.

FLUCTUATION_BASIS **N**_int

Nonzero N specifies type of basis sets used in the calculation of fluctuating trajectories:
N=1 generates energy gap correlations (approximate – more stable: assumes semiclassical approximation of the correlation functions, I. e. that the correlation functions are symmetric around zero).
N=2 generates eigen-energy cross-correlations (exact for diagonal fluctuations: do not assume semiclassical approximation for fluctuations).

Additional specification of single-exciton block (number of states, etc.) and double-exciton block (anharmonicities, etc) are necessary. If anharmonicities are used, they must contain trajectories as well.

The calculation proceeds as follows. The first time the Hamiltonian trajectory is read and the average Hamiltonian is obtained. It is then used as a reference Hamiltonian. Its eigenvalues and eigenvectors are calculated. The trajectory is then read the second time. The fluctuating eigenstate energies and their couplings are obtained with respect to the reference Hamiltonian by transforming each snapshot Hamiltonian to the reference basis set. The fluctuation trajectories are written to binary intermediate files.

The intermediate binary files are read and relevant correlation functions are then calculated. Different correlation functions are used for different basis according to **FLUCTUATION_BASIS**. The correlation functions are then used to build the lineshape functions of optical transitions.

The fluctuating inter-state Hamiltonian elements (couplings) may be used to calculate population transport matrix by using Markovian approximation. At the moment it is not possible to separate fast and slow fluctuations. For that various trajectory windows may be manually used.

D. Fluctuating Hamiltonian (NEP)

This is the core system for a fluctuating Frenkel exciton hamiltonian to be used with NEP simulation model. This is only valid when used with the calculating method NEP. Theoretical formalism is detailed in C. Falvo, B. Palmieri and S. Mukamel, JCP, 130, 184501 (2009). If you are using this methodology please cite this paper. The following experiments are available : LA, KI, KII and KIII. Using NEP, the optical response is computed for only one initial condition and one orientation. Proper average over initial conditions and orientations must be realized externally. The model is described in
$SYSTEM
...
$END
section. Next is the list of keywords.

NUMMODES **N**_int

(required) the number of coupled oscillators. Must be larger or equal than 1. If equal to 1, then only one oscillator is considered. This case is allowed.

INP_HAM_L_ **F**_str #[T3]

(required) the filename of Hamiltonian matrix in reciprocal centimeters. The off diagonal part of the matrix represents real-space Frenkel exciton quadratic couplings (exciton resonance interactions). The diagonal of the matrix are the energies of the singly-excited molecules. The file is a **binary** file composed of **NUMMODES*(NUMMODES+1)/2*TRAJECTORY_NP floats**.

INP_DIP_L_ **F**_str #[T5]

(required) the filename of the transition dipole for each oscillator in Debye. The three columns are X, Y and Z coordinates. The order of the dipoles is the same as in **INP_HAM_L_**. The file is a **binary** file composed of **NUMMODES*3*TRAJECTORY_NP floats**.

INP_ANH_L_ **F**_str #[T3]

the filename of the shift of double-exciton state energies from the harmonic model by Δ_{mn}. The interpretation is as follows: the energy of the doubly-excited state when oscillators *m* and *n* are excited is $\varepsilon_m+\varepsilon_n+\Delta_{mn}$. The file is a **binary** file composed of **NUMMODES*(NUMMODES+1)/2*TRAJECTORY_NP floats**.

TRAJECTORY_NP **N**_int

TRAJECTORY_NP is number of points in the fluctuating trajectory of the Hamiltonian.

TRAJECTORY_TS **X**_real [fs]

Timestep in the fluctuating trajectory of the Hamiltonian.

PROPAGATION_ORDER **N**_int

To propagate the wavefunction, the Hamiltonian is expanded in the excitonic coupling. **PROPAGATION_ORDER** change the order of expansion. Currently available is 0 (no coupling), 1 and 2.

COUPLING_SCALE **X**_real

Scale the excitonic coupling by the factor **COUPLING_SCALE**.

MEAN_FIELD **N**_int

Use the mean field approximation (value 0 or 1)

7 Physical models of open systems

Specific applications of the generic systems are tuned in this section. The SPECTRON code is done is such way that specific physical systems is like an envelope over the generic systems. The signal calculation routines see and interact only with the generic systems. The specific application models described in this section perform automatic setup of the generic systems.

Specific systems are chosen during runtime with a keyword **SYSTEM_KEYWORD**. In this way specific system is selected and its creation is initiated. Each specific system may be build in its own way. It may be written by any group not involved in the mainstream code production. In principle the SPECTRON group does not control different specific systems.

The other type of the ingredient is the surrounding environment. Its properties may be defined in a separate section `$BATH ... $END`. The thermal bath is described by its spectral density resembling various fluctuation correlation functions. The bath may be characterized by several types of spectral densities or stochastic oscillators. These may be coupled to different system points and so multi-mode stochastic system-bath model may be realized.

A. Bath

The bath is represented by a set of stochastic modes characterized by specific dimensionless spectral densities as continuous functions. Three types of the spectral densities are hard-coded: the overdamped Brownian oscillator (OBO) with the system-bath spectral density $C''_m(\omega)=2\lambda_m\frac{\omega\Lambda_m}{\omega^2+\Lambda_m^2}$, the Ohmic spectral density with the spectral density $C''_m(\omega)=\frac{\omega\lambda_m}{\omega_{mc}}\exp(-|\omega|/\omega_{mc})$ and the Lorentzian underdamped bath $C''_m(\omega)=\frac{\omega_m^4}{\lambda_m}\frac{\omega\gamma_m}{(\omega^2-\omega_m^2)^2+\omega^2\gamma_m^2}$. m indicates the bath stochastic coordinate. The system-bath coupling is the system property and therefore we separate it from the bath characterization. In the code we characterize the bath by dimensionaless spectral densities $J_m(\omega)=2\frac{\omega\Lambda_m}{\omega^2+\Lambda_m^2}$, $J_m(\omega)=\frac{\omega}{\omega_{mc}}\exp(-|\omega|/\omega_{mc})$ and $J_m(\omega)=\frac{\omega_m^2\omega\gamma_m}{(\omega^2-\omega_m^2)^2+\omega^2\gamma_m^2}$ respectively.

Other type of the spectral density can be specified using a data file containing a numeric function $J_m(\omega)$ of energy (or frequency). The bath is defined using the same units as the system, i. e. eV, meV, cm^{-1} , THz for the energy units, fs for time units. These are set by a command-line option `-u <units>`. The temperature is given in Kelvin.

In the SPECTRON code the same bath object is also used to calculate correlation functions, spectral densities and lineshape functions using fluctuating trajectories on the input. Several keywords are used to describe such properties. The are given in separate section

```
$BATH
...
$END
```

in the main input file. The following keywords are relevant:

`BATH_MODEL` **F**_str

the character string selecting a certain bath model:
`MM_Brownian_spectral_density` – the Overdamped Brownian Oscillator model (default).
`MM_Ohmic_spectral_density` – the multimode Ohmic bath model.
`MM_Lorentzian_spectral_density` – the multimode Lorentzian spectral density model
`MM_Continuous_spectral_density` – the most flexible model: the spectral density must be given on the file by `SPECTRAL_DENSITIES` keyword.

OSCILLATORS_NUM **N**_int

the number of bath stochastic coordinates. Default is 1.

TEMPERATURE **X**_real

the bath temperature (Kelvin). Applies for all bath models. Different baths with different temperatures cannot be specified. All bath stochastic coordinates have the same temperature.

FREQUENCY **X**_real

The effective characteristic frequency in energy units of the bath stochastic coordinate for the single-mode bath model. It is supported for the Ohmic and for Lorentzian bath (parameter ω_m or ω_c).

TIMESCALE **X**_real

The effective timescale τ in femtoseconds of the bath stochastic coordinate for the single-mode bath model. For the Overdamped Brownian model it is Λ^{-1} . For cummulant expansion calculation using fluctuation Hamiltonian trajectories this keyword specifies the cutoff used for the calculated function *g(t)*: for $t<\tau$ we use the calculated *g(t)*, fo r $t>\tau$ *g(t) = g(* τ *)+k*(t-* τ *)*. Here *k = dg/dt* at τ value.

OSCILLATORS_FREQS **F**_str

the file name of the effective frequencies of the multimode bath when requested by a certain bath model. It is needed for the Ohmic and Lorentzian baths. The file consists of a column of frequencies in energy units.

OSCILLATORS_TIMESCALES **F**_str

the file name of the effective timescales of the multimode bath when requested by a certain bath model. It is needed for the Overdamped Brownian oscillator model. See **TIMESCALE**.

SPECTRAL_DENSITIES **F**_str #[T1]

the file name of the spectral density function: Either a single or a set of spectral densities $J_m(\omega)$ can be specified. $J_m(\omega)$ Is given from 0 to some largest frequency with a constant frequency step. The file consists of a single column of numbers. The first number is the number of points in the first spectral density. The second number is the frequency step. The following numbers are the values of the spectral density as a function of frequency staring from zero with the specified frequency step. If **OSCILLATORS_NUM** is larger than 1, the second and the third spectral densities are appended to the same file.

SMOOTHING **F**_str

type of smoothing when calculating spectral densities and the lineshape functions from the fluctuationg trajectories. The frequency-domain spectral density is converted into time domain using Fourier transformation. A predefined function of time is multiplied to the quantum time correlation function thus equivalent to the convolution in the frequency domain. Two possible smoothing functions can be selected:

Gaussian – $\exp\left(-\left(t/TimeScale\right)^2/2\right)$
Lorentzian - $\exp\left(-|t|/\tau\right)$.
τ is defined using **TIMESCALE** keyword.

OUT_CORRELATION **N1**_int **N2**_int **F**_str

outputs the classical correlation function for the transition N1 and N2 to the file F. If N2 = -1 (N1=-1) all transitions from N1 (N2) are printed.

OUT_GFUNCTION **N1**_int **N2**_int **F**_str

output the g function for the transition N1 and N2 to the file F. If N2 = -1 (N1=-1) all transitions from N1 (N2) are printed.

B. Physical system definition

Basic system is initialized in the $SYSTEM section. Only one type of system can be initiated during a single execussion of the code. The system cannot be changed in the middle. The system type is defined as follows:

```
$SYSTEM
SYSTEM_KEYWORD Excitonic_Disordered_ens__
...
$END
```

In the following we describe different systems, which can be given together with the `$BATH ... $END` to describe a physical model.

C. Disordered excitonic complex (aggregate of coupled two-/three-level oscillators)

Tis model is more advanced compared with the generic model. It has the possibility of calculating inter-molecular interactions, adding disorder and has various sophisticaltions of system-bath interactions. It represents a set of weakly coupled oscillators. These can be molecules, vibrations, etc. The input units are controlled by `-u <units>` command line argument.

SYSTEM_KEYWORD **Excitonic_Disordered_ens__**

NUMMODES **N**_int

the number of coupled oscillators or molecules or vibrations. Only one optical transition per oscillator is allowed. If more than one transition in realistic molecule is relevant, they must be represented by different oscillators.

INP_HAM_L_ **F**_str #[T3]

the filename of the Hamiltonian matrix in energy units. The off diagonal part of the matrix represents real-space exciton quadratic couplings (exciton resonance interactions). The diagonal of the matrix are the energies of the singly-excited oscillators. Size of the matrix is **N**x**N**. The triagonal matrix must be given on the input.

INP_DIP_L_ **F**_str #[T5]

the filename of the **transition** dipole moments for each oscillator. The three columns are X, Y and Z coordinates. Different rows correspond to different oscillators. The order of the dipoles is the same as in file **INP_HAM_L_**. These dipoles may be used to calculate inter-molecular resonant interactions together with **CALCULATE_J.**

INP_DIP_1X **F**_str #[T5]

the filename of the **permanent** electric dipoles of singly-excited oscillators in Debye. The three columns are X, Y and Z coordinates. The order and file format is the same as in **INP_DIP_L_**. These dipoles may be used to estimate quartic intermolecular interactions between excited oscillators together with **CALCULATE_K**. This interaction is relevant for third order nonlinear signals.

INP_QAD_L_ **F**_str #[T6]

the filename of the transition quadrupole for each oscillator. Each row in the file follows

XX XY XZ YY YZ ZZ

pattern. Each row then represents the quadrupole moment of each oscillator. The rows are ordered as in **INP_HAM_L_**.

INP_COO_L_ **F**_str #[T5]

the filename of the transition origin coordinates for each oscillator. The three columns are X, Y and Z coordinates. The order of the dipoles is the same as in **INP_HAM_L_**.

INP_MAG_L_ **F**_str #[T5]

the filename of the transition magnetic dipole for each oscillator. The three columns are X, Y and Z coordinates of the imaginary part of the magnetic moment (the real parts are assumed to be 0). The order of the dipoles is the same as in **INP_HAM_L_**.

DISORDER_INTRA_DIAG_GAUSS **X**_real

intra-aggregate transition energy disorder: the disorder is added to each oscillator by shifting its transition energy with a Gaussian random number with variance **X**. A new random number is generated for each oscillator. This model is relevant when repeating signal simulation for many times and making a statistical average by **NUM_SHOTS** is various **$<technique> ... $END** sections.

DISORDER_INTRA_DIAG_GAUSS_F **F**_str

intra-aggregate transition energy disorder: the disorder is added to each oscillator by shifting its transition energy with a Gaussian random number with variance **X**. A new random number is generated for each oscillator. This model is relevant when repeating signal simulation for many times and making a statistical average by **NUM_SHOTS** is various **$<technique> ... $END** sections. On the input is a file name containing disorder variances for each oscillator (site). The order of numbers is the same as of hamiltonian elements.

DISORDER_INTER_DIAG_GAUSS **X**_real

inter-aggregate transition energy disorder: the disorder is added to each oscillator by shifting its transition energy with a Gaussian random number with variance **X**. A new random number is generated for each aggregate. The oscillators in the same aggregate attain the same random shift. This model is relevant when repeating signal simulation for many times and making a statistical avrerage by **NUM_SHOTS** is various **$<technique> ... $END** sections.

CALCULATE_J **N**_int

Nonzero **N** turns on calculation of J couplings using dipole-dipole interaction formula. This requires to specify as excitonic transition dipoles, **INP_DIP_L_**, as transition coordinates, **INP_COO_L_**, as diagonal transition energies, **INP_ENE_DI**. **INP_HAM_L_** should **not** be used.

INP_ENE_DI **F**_str #[T1]

F is the file name containing a column of diagonal elements of the excitonic single-exciton Hamiltonian (diagonal transition energies) used with **CALCULATE_J**

CALCULATE_K **N**_int

Nonzero **N** turns on calculation of K (quartic) couplings using dipole-dipole interaction formula between permanent transition dipoles. This requires to supply as excitonic permanent dipoles of singly-excited molecules, **INP_DIP_1X**, as transition coordinates, **INP_COO_L_**; three-level molecules require specifying **INP_AND_DI** as well.

INP_ANH_DI **F**_str #[T1]

F is the file name containing a column of diagonal elements of the excitonic diagonal anharmonicities (energy differences between actual diagonal doubly-excited overtone energies and their harmonic values); used together with **CALCULATE_K** for three-level molecules. For two-level molecules this information should not be used.

SYSTEM_BATH_COUPLING **X**_real

System-bath interaction strength λ . The model is used that each oscillator is coupled to its own statistically independent stochastic bath oscillator. Different bath oscillators are independent. Thus only one spectral density is needed to specify. The **$BATH ... $END** section must be used to define that stochastic bath spectral density (a single mode bath oscillator). Each system oscillator is then coupled to that bath coordinate by the same strength λ . In the real space we have the following nonzero correlation functions

$C_n(t) \equiv \frac{1}{\hbar^2}\langle \varepsilon_n(t)\varepsilon_n(0)\rangle = \int \frac{d\omega}{2\pi} e^{-i\omega t}(1+\coth(\beta\hbar\omega/2))C''(\omega)$ and then $C''(\omega)=\lambda J(\omega)$.

SYSTEM_BATH_COUPLING_EQUIVALENT_SITES **F**_str #[T1]

This model extends the one used by **SYSTEM_BATH_COUPLING.** Instead of single spectral density here we assume $C''(\omega)=\sum_m \lambda_m J_m(\omega)$ and different $J_m(\omega)$ are given as different stochastic coordinates in **$BATH ... $END** section. **F** is the file of the coupling strengths between system oscillators and different modes of local-bath, λ_m . All system oscillators are equivalent and statistically independent. However the couplings strengths to different baths is different. The couplings are in energy units. The model cannot be used together with **SYSTEM_BATH_COUPLING**.

SYSTEM_BATH_COUPLING_MM **F**_str #[T7]

This model extends the one used by **SYSTEM_BATH_COUPLING_EQUIVALENT_SITES.** In this model the sites are not equivalently coupled to different bath oscillators. So some oscillators (sites) may be coupled to one type bath, while other sites to different type bath. All system oscillators are statistically independent. Single-mode and well as multi-mode baths are supported. **F** is the file of the coupling strengths matrix λ_{nm} of oscillators -to- multi-mode local-bath couplings. The coupling between system oscillator and the bath modes are unique and are listed in the file in energy units. The size of the matrix is **OSCILLATORS_NUM**×**NUMMODES**. Different rows corresponds to different baths (stochastic coordinates) and the columns represent different system oscillators (sites). This model is given by spectral density $C''_n(\omega)=\sum_m \lambda_{nm} J_m(\omega)$.

SYSTEM_BATH_COUPLING_MM_CORRELATED **F**_str #[T8] the filename of the strength matrix of oscillators -to- multi-mode local-bath couplings. Similar to SYSTEM_BATH_COUPLING_MM but cross-correlations between different oscillators are not zero: SYSTEM_BATH_COUPLING_MM is a special case for only diagonal system-bath interactions. The units are [cm^{-1}]. This model represents $C_{nn'}(t)\equiv\frac{1}{\hbar^2}\langle\varepsilon_n(t)\varepsilon_{n'}(0)\rangle=\int\frac{d\omega}{2\pi}e^{-i\omega t}(1+\coth(\beta\hbar\omega/2))C''_{nn'}(\omega)$ with $C''_{nn'}(\omega)=\sum_m\lambda_{nn',m}J_m(\omega)$.

D. Square (cubic) lattice aggregate (finite 1D, 2D or 3D system; aggregate of coupled two-/three-level oscillators): extends excitonic random aggregate

This model is an extension of the specific excitonic system. Instead of specifying an arbitrary geometry, this model builds linear, square or cubic setup of sites. Geometrical properties must be defined in the input file.

SYSTEM_KEYWORD **Excitonic_Disordered_ens__**

LATTICE_DIMENSIONALITY **N**_int

This keyword allows choosing 1, 2, or 3 dimensional square lattice.

LATTICE_LENGTH_X **N**_int

number of oscillators in X dimension

LATTICE_LENGTH_Y **N**_int

number of oscillators in Y dimension (not used if LATTICE_DIMENSIONALITY = 1)

LATTICE_LENGTH_Z **N**_int

number of oscillators in Z dimension (not used if LATTICE_DIMENSIONALITY = 1, 2)

LATTICE_CONSTANT_X **X**_real

lattice constant in length units in X dimension

LATTICE_CONSTANT_Y **X**_real

lattice constant in length units in Y dimension (not used if LATTICE_DIMENSIONALITY = 1)

LATTICE_CONSTANT_Z **X**_real

lattice constant in length units in Y dimension (not used if LATTICE_DIMENSIONALITY = 1, 2)

LATTICE_ZEROTH_DIPOLE **X**_real **X**_real **X**_real

Transition dipole vector of the initial oscillator (at origin 0,0,0). All other transition dipoles will be generated from this initial vector by a certain transformation defined below.

LATTICE_CONTROLLER **F**_str

Defines how transition dipoles are created from the one at the origin. Possible values:

- transformed_dipoles_with_f_<code> - a vector field transformation is performed as predefined by <code> (a character code). Possible codes:
  repeat – just repeats the initial vector.
- random_dipoles – all dipoles in the lattice will be random with the length of the initial dipole.
- fluctuated_dipoles – fluctuation is introduced in the predefined dipole: This can extend method "transformed_dipoles_with_f_" as fluctuated_dipoles_transformed_dipoles_with_f_<code>.

LATTICE_MEAN_TRANSITION_ENERGY **X**_real

Mean (central) transition energy of lattice oscillators

LATTICE_DIP_FLUCTUATION_FACTOR **X**_real # (0<X<1)

Introducing additional fluctuations in the transition dipoles. The original vector is ***a*** and its length is *L*. I take a random unit-length 3D vector ***r*** (it points into random direction) and I create a new vector $\mathbf{n}=((1-X)*\mathbf{a}/L+X*\mathbf{r})*L$, which I assign to the lattice site. When *X=0*, ***n***=***a***, and there is no disorder in transition dipoles. They are all equivalent in the lattice. When *X=1*, the all transition dipoles habe completely random directions with the constant length *L*.

COUPLING_CUTOFF_DIST **X**_real

Distance from which the coupling between dipoles is not calculated and is set to 0.

Almost all features of the excitonic special system can be used here. Some derived available features are useful:

SYSTEM_BATH_COUPLING
SYSTEM_BATH_COUPLING_EQUIVALENT_SITES
DISORDER_INTRA_DIAG_GAUSS
DISORDER_INTER_DIAG_GAUSS

E. Cylindrical 1D finite chiral system; aggregate of coupled two-/three-level oscillators: extends excitonic random aggregate

This is the extension of the excitonic system, where automatic creation of cylindrical Frenkel excitonic system is implemented. The cylinder can contain up to 5 walls. Each wall contains a specified number of rings translated along z coordinate. Ring areas are perpendicular to the z axis. The following keywords specify this system.

SYSTEM_KEYWORD **Excitonic_Cyllinders_ens__**

NUMBER_OF_WALLS **N**_int

Number of walls in the cylinder (up to 5 is allowed). Different cylinders have the same symmetry axis, so that these cylinders penetrate each other. By default the walls are loosely (randomly) tuned with respect to each other unless specified otherwise. The idea behind this is that the cylinders are assumed very long and so the relative orientation should be sampled randomly to represent realistic mesoscopic systems.

NEXT_WALL **N**_int

N>0 switches the active wall index to the next (simple incrementation). In this way the parameters of all walls can be given one wall after another. It is impossible to return to previous wall. So all parameters of a wall must be given in the same block.

NUMBER_OF_RINGS **N**_int

Gives the number of rings in the active wall.

RING_DIAMETER **X**_real #[Å]

Diameter of the ring in the active wall.

NUM_SITES_PER_RING **N**_int

Gives the number sites per ring in the active wall. Sites in the ring are distributed symmetrically along the ring perimeter.

RING_ROTATION_Z **X**_real #[deg]

The rotation angle in degrees between two adjacent rings in the active wall.

RING_TRANSLATION_Z **X**_real #[Å]

The translation distance between two rings in the active wall.

FIXED_WALLS **N**_int

N>0 turns off feature of random cylinder inter-orientation. It is then defined by the FIXING_VECTOR. The building of the cylinder proceeds by creating a ring of units by placing **NUM_SITES_PER_RING** sites around the ring; then creating **NUMBER_OF_RINGS** rings, twisting them by **RING_ROTATION_Z** around **z** axis (with respect to each other) and shifting them vertically by **RING_TRANSLATION_Z**. All walls are created in this way.

FIXING_VECTOR **X**_real **X**_real **X**_real #[Å]

Defines the starting point from which the cylinder is being built for each wall. The building in (x,y,z) coordinate system starts from (**rho**,0,0**)+FIXING_VECTOR**, where **\rho** is the diameter/2.

FIRST_DIPOLE **X**_real **X**_real **X**_real #[D]

Defines the transition dipole in Debyes of the first site for each wall. The cylinder is being built by rotation/translation operations. The coupling between the sites is given by the dipole-dipole interaction unless specified by **DISTRIBUTED_CHARGES**

RING_ENERGY **X**_real #[cm^{-1}]

Average energy of the ring in the active wall.

RING_INHOMOGENEITY **X**_real #[cm^{-1}]

Average energy inhomogeneity (diagonal Gaussian disorder) of the ring in the active wall.

DIPOLE_FLUCTUATION_CODE **F**_str

r – allows adding fluctuations to the dipole vectors in each site (leads to off-diagonal disorder). The fluctuation to original vector **v** is introduced according to $\boldsymbol{v}_n = l(a\boldsymbol{r}+(1\text{-}a)\boldsymbol{v}/l)$, where l=|$\boldsymbol{v}$| and $\boldsymbol{r}$ is the random unit-length vector, and $0<a<1$ is a real number. a is given by **DIPOLE_FLUCTUATION_MAGNITUDE**

DIPOLE_FLUCTUATION_MAGNITUDE **X**_real

Magnitude of the dipole fluctuation for the active wall (see **DIPOLE_FLUCTUATION_CODE**).

DISTRIBUTED_CHARGES **N**_int

N>0 turns on the model where each site is represented by a pair of positive and negative charges to calculate the inter-site couplings by Coulomb formula.

SITE_DIPOLAR_CHARGE **X**_real #[e]

Charge assigned to each site (positive and negative have the same value) in the elementary charges (goes together with **DISTRIBUTED_CHARGES**).

SITE_DIPOLAR_SEPARATION **X**_real #[Å]

Separation between the positive and the negative charges for each site. Their placement is decided according to dipole direction. Used together with **DISTRIBUTED_CHARGES**.

MEDIUM_DIELECTRIC_CONSTAN **X**_real

The relative dielectric contant of the medium. This number goes as denominator in calculation of the inter-site couplings.

Derived available features:

SYSTEM_BATH_COUPLING
SYSTEM_BATH_COUPLING_EQUIVALENT_SITES

F. Infinite periodic Frenkel exciton model (only for QP approches)

This model represents infinite molecular crystal-like structures. The infinite system size is realized through cyclic boundary conditions. The unit of the sytem is a lattice which may contain certain set of oscillators. The unite lattice can be replicated in *x*, *y*, or *z* directions, which simulates either one- or two- or three-dimensional infinite crystal. The infinite problem is reduced by applying spatial Fourier transformation into the momentum space what introduces the lattice wavevector (or k-space). The sampling of *k*-space then defines the accuracy of simulations. The following keywords describe building of the lattice model. The following keywords define the system

SYSTEM_KEYWORD **Excitonic_Infinite_System_**

INF_DIMENSIONALITY **N**_int

The dimensionality of the infinite system. It may be 1, 2 or 3. 1 is associated with *x* axis, 2 is associated with (*xy*) plane and 3 is for (*xyz*) space.

INF_COUPLING_LENGTH **N**_int

The inter-cell coupling length in the cell number. The inter-cell interactions between N neighbours are included in all dimensions.

INF_LATTICE_CONSTANT_X **X**_real

Lattice constant in length units in the lowest dimension.

INF_LATTICE_CONSTANT_Y **X**_real

Lattice constant in length units in the *y* dimension.

INF_LATTICE_CONSTANT_Z **X**_real

Lattice constant in length units in the highest dimension.

INF_NUMBER_K **N**_int

sampling number of the momentum space. If N=100, 100 points are used to divide 2\pi interval of the momentum space in each dimension.

INF_CELL_TYPE **F**_str

A keyword defining how the unit cell is generated. Possible values:
1D-cylinder - defines the onedimensional cylinder according to a finite cylinder model described in subsection E.
ND-square-F – defines an 1, 2 or 3-dimensional square lattice of Frenkel excitonic model as described in subsection C.

G. Transition property mapping (for vibrational or electronic excitations)

This library is designed to describe the mapping of the frequency, the anharmonicity and the transition dipole of vibrational modes through the electrostatic field using MD trajectories. In principle this can be used for any system where the electrostatic interaction play the main role. The current version does not support the mapping of the couplings but a new version is under work.

Units used in the library

distance : angstroms
transition dipole : debye
Frequencies : wavenumber
Electrostatic parameters : atomic unit

SYSTEM_KEYWORD **VIB_MAPPING**

NUMMODES **N**_int

Total number of modes which need to be mapped

NUM_LOCAL_MAPS **N**_int

Total number of maps used in the system, the minimum is one. One map can be used by multiple modes.

NUMATOMS **N**_int

Total number of atoms in the system. This should be fixed during the simulations so no grand-canonical simulations

NUMRES **N**_int

Total number of residues in the system.

BOXSIZE **X**_real **X**_real **X**_real #[Å]

Dimension of the simulation box.
Restriction: only orthorhombic box are supported in the current version.

XSTFILE **F**_str

When the simulation box is fluctuating, the library can read a NAMD XST file containing the box information.
Restriction: only orthorhombic box are supported in the current version.
Should not be used with BOXSIZE keyword.

TRAJECTORY_FORMAT [PDB/DCD]

Format of the MD simulation trajectory. Only PDB and DCD have been tested, XYZ is also available but hasn't been tested.

TRAJECTORY_FILE **F**_str

File of the MD simulation trajectory, the format should be given by TRAJECTORY_FORMAT keyword.

TOPOLOGY_FORMAT [PSF]

Format of the file containing the topology information of the MD simulation. Currently only PSF is supported.

TOPOLOGY_FILE **F**_str

File containing the topology information of the MD simulation. The format should be given by TOPOLOGY_FORMAT keyword.

MAP_FILE **F**_str

File containing all the maps informations.

MODE_FILE **F**_str

File containing all the modes informations.

STARTSTEP **N**_int

Starting snapshot from the MD trajectory to generate the calculation.

SKIPSTEP **N**_int

Skipping N steps in the MD trajectory between each calculations

INITIALWRAP **N**_int

some MD simulations doesn't wrap the molecules in the box. This keyword does it at the beginning of the calculation of each snapshot
INITIAL_WRAP = 0 (default) no initial wrapping.
INITIAL_WRAP = 1 wrapping of the system

EFIELD_CUTOFF **X**_real #[Å]

For cutoff electric field calculation this keyword defined the cutoff value. For Ewald based (full Ewald and PME) calculation this keyword is used to divide long range and short range interactions. For cutoff calculation and PME the cutoff should be smaller than half of the box size since only the minimum distance interaction are taken into account. For full Ewald calculation the result does not depend on the value of the cutoff (with a specified tolerance) but it should be adjusted to minimize the calculation costs.

EWALDSUM **N**_int

EWALDSUM=0 (default) not using the full Ewald calculation
EWALDSUM=1 using the full Ewald calculation
The full ewald calculation assume the that box is neutral and the boundary conditions are a vanishing potential a the infinity and no macroscopic dipole
Restriction: In conflict with PME

PME **N**_int

PME=0 (default) not using the PME calculation
PME=1 using the PME calculation
The PME calculation assume the that box is neutral and the boundary conditions are a vanishing potential a the infinity and no macroscopic dipole
Restriction: In conflict with EWALDSUM

PMEORDER **N**_int

order of the interpolation used in the PME calculation. The interpolation used currently is Lagrange interpolation

PMEGRID **N**_int **N**_int **N**_int

Size of the grid used to interpolate the charge in the PME calculation. Typically this should be slightly bigger than the box size (in Å)

EWALDTOLERANCE **X**_real

Tolerance for the potential fluctuation in the PME and full Ewald calculations. Used to define the ewald parameter. Typical value is 10^{-6}

JCOUPL_CUTOFF **X**_real #[Å]

cutoff used to calculate the dipole dipole coupling. The cutoff should be smaller than half of the box size.

Map file

input file containing the map information. Each map is specified in a different section. Each section should contains the following information : a part containing basic information about the map, a file giving the map data, an atoms list part which define a local coordinate system and a parameter list part.

```
-------------
$MAPNAME
```

```
        NATOM            3
        NPARAM           3
        ORDER            2
        MD_COORD         0

        FILE          map.out

        ATOM    1      C      -0.123064  -0.033747   0.000000
        ATOM    2      O       1.063723   0.252917   0.000000
        ATOM    3      O      -1.126233   0.895891   0.000000

        PARAM   1      X        0.000000   0.000000   0.000000
        PARAM   2      Y        0.000000   0.000000   0.000000
        PARAM   3      Z        0.000000   0.000000   0.000000

$END
```

The following keywords are used to describe a map.

NATOM **N**_int

Number of atoms describing the map (minimum 3). Theses atoms are used to defined a local referential. In the current version the first atom is used to set the translation (comparing with the MD simulation), the second and third atoms are used to set the rotations. (Developer note : a Powell minimization should be used to set this local coordinate, in the future ... maybe). In the current version defining more than 3 atoms are useless.

NPARAM **N**_int

Number of parameters defining the map.

ORDER **N**_int

The order of the map. The current version support up to the second order in the electrostatic field. First order means that the exciton parameters are linear in each electrostatic parameters, second order means that the exciton parameters are quadratic in each electrostatic parameters.

MD_COORD [0/1]

MD_COORD = 0 the parameters are computed at the coordinate X,Y,Z specified in the PARAM keywords.

MD_COORD = 1 the parameters are computed at the MD trajectory coordinate of the atom specified in the PARAM keywords.

FILE **F**_str

the file which contains the value of each coefficient.

ATOM **N**_int **C**_char **X**_real **Y**_real **Z**_real

specification of an atom. N is the atom number, C is a character which designate the atom (never really used), X,Y,Z are the coordinates in the local frame.

PARAM **N**_int **C**_string **X**_real **Y**_real **Z**_real

Specification of a parameters using MD_COORD=0. N is the parameter number, C is string characterizing the parameter and X,Y,Z are coordinate where the parameter is computed. The list of actual parameters name is U, X, Y, Z, XX, YY, ZZ, XY, XZ, YZ, XXX, YYY, ZZZ, XYY, XXY, XXZ, XZZ, YZZ, YYZ, XYZ.
U is the electrostatic potential (assuming U=0 at the infinity and no macroscopic dipole). X is Ex=-dU/dX the electrostatic field in the x direction (in the local frame), Y is Ey=-dU/dY, Z is Ez=-dU/dZ, XX is Exx=-d2U/dX/dX ....

PARAM **N**_int **C**_string **A**_int

Specification of a parameters using MD_COORD=1. N is the parameter number, C is string characterizing the parameter and A is the atom number (in the map file) where the calculation should be done.

GRID_SAMPLING [0/1]

Instead of calculating the electrostatic parameters by an analytic formula, GRID_SAMPLING use a grid given by the file GRID_FILE of size GRID_SIZE on which the electrostatic field is computed analytically for each points, then the derivatives of the potential are generated up to the GRID_ORDER (max 3).

GRID_FILE **F**_str #[T5]

File containing the grid definition

GRID_SIZE **N**_int

how many points are defining the grid

GRID_ORDER **N**_int

max order of the derivatives of the electrostatic parameters (GRID_ORDER <= 3)

Mode file format:

input file containing all the mode information. In the current version only two part are available the mode part and the exclusion part

```
-------------
MODE        1       MAP1        04  05  06
MODE        2       MAP1        12  13  14
MODE        3      MAP2         21  22  23

EXCLUD      1      8        2 3 4 5 6 7 8
EXCLUD      2      8      10 11 12 13 14 15 16 17
EXCLUD      3      10     19 20 21 22 23 24 25 26 27 28
-------------
```

Each mode field is defined by a number (first integer), the name of the map used, and a list of atoms (same numbers as in the topology file). The order of the atoms corresponds to the definition of the map.

Each exclusion field is defined by a number (the mode number), the number of atoms to exclude from the electrostatic calculations and the list of atoms. Note: in the full Ewald and PME calculation the exclusion is done only in the central box, the surroundings box contains all atoms.

Map coefficient file

input file containing the coefficient of a map. This file consist of 7 columns.

```
-------------
 0   0      1728.00       -16.00     -0.21593     -0.01202      0.00000
 0   1     -2026.48        95.15      0.00000      0.00000      0.00000
 0   2     -1202.22       -28.36      0.00000      0.00000      0.00000
 0   3         0.00         0.00      0.00000      0.00000      0.00000
 1   1    -17900.00     -1931.25      0.00000      0.00000      0.00000
 1   2     -8662.50     19656.25      0.00000      0.00000      0.00000
 1   3         0.00         0.00      0.00000      0.00000      0.00000
 2   2     30568.75      5456.25      0.00000      0.00000      0.00000
 2   3    -16587.50      7606.25      0.00000      0.00000      0.00000
 3   3    -16587.50      7606.25      0.00000      0.00000      0.00000
-------------
```

the first and second column designated which parameters the coefficient refers to. 0 0 means the zero order value, 0 1 means first order of the first parameters, 2 2 means second order of the second parameter. The other columns designated the coefficient in the following order: frequency, anharmonicity, transition dipole x, transition dipole y and transition dipole z.

H. Tight Binding Electron-Hole Model

All intermolecular interactions are calculated using Coulomb formulas. The model is derived from the tight-binding semiconductor model. However it is developed for an arbitrary excitonic system where CT excitons are relevant. Long-range charge transfer is available as well through electron transport between CT states. Calculation of bi-exciton states is painfull. Exciton scattering representation must be used instread. However it is still very time-consuming to calculate exciton scattering matrix. More efficient approach of direct numerical propagation should be considered in some cases. However, we do not have an efficient computer code for this purpose. Hopefully I will write this code some day. Only generic units are supported at the moment.

SYSTEM_KEYWORD Excitonic_Disordered_CT

NUMSITES **N**_int

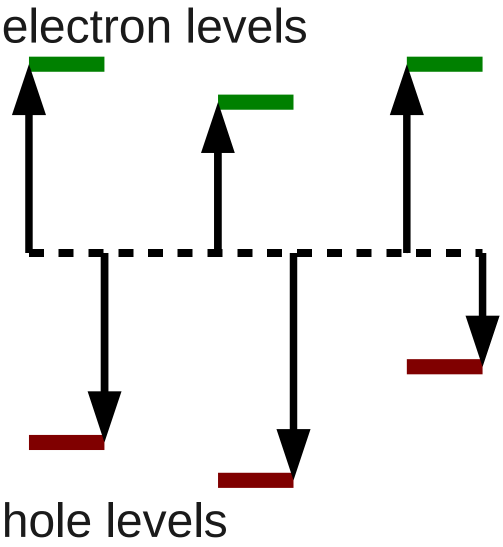
Total number of sites (atoms, molecules) where electron or hole reside

COO_S **F**_str

The file name of site coordinates; This is a three-column vector. Each row represents the site coordinates in **X**\tab**Y**\tab**Z** format. The number of rows must be equal to **NUMSITES**.

HAM_E **F**_str

The filename of electron energy levels; energies of electron molecular orbitals *h* $h_{nn}^{(e)}$. Energy axis is directed up as shown by arrown on picture on the right. Requires **HAM_H**. The file is a single-column vector of energies. Each row represents a site index. The number of rows must be equal to **NUMSITES**. This parameter together with **HAM_H** is used to calculate transition energies of Frenkel excitons and of electron-hole pairs. The transition energy of a Frenkel exciton is calculated by $h_{nn}^{(e)}+h_{nn}^{(h)}+V^{(S)}$. $V^{(S)}$ is a manually introduced energy shift defined by **ENERGY_EH_STABILIZATION** and may be induced by the electron-hole interaction energy being on the same site. The transition energy of an electron-hole CT exciton when electron is on site n_e and hole is on site n_h is calculated by $h_{n_e n_e}^{(e)}+h_{n_h n_h}^{(h)}+V_{n_e n_h}^{(eh)}(r_{n_e},r_{n_h})+V_0^{(eh)}/(\epsilon R_0^{eh})$. In this way the electron and hole potential surfaces are correctly reproduced. Also for additional information see the particle-interaction keywords below.



HAM_H **F**_str

The file name of hole energy levels; energies of hole molecular orbitals $h_{nn}^{(h)}$. Energy axis is directed down as shown by arrows on the picture on the right. Requires **HAM_E**. The file is a single-column vector of energies. Each row represents a site index. The number of rows must be equal to

NUMSITES. For more information see electron site energies above.

HAM_EXC **F**_str

The file name of known exciton transition energies e_n on each site. This model is incomplete because it is impossible to decide about energies of holes and electrons from the specification of excitons only. However the assumption is made that $h_{nn}^{(e)}=e_n/2$ and $h_{nn}^{(h)}=e_n/2$. The file is a single-column vector of energies. Each row represents a site index. The number of rows must be equal to **NUMSITES**. For more information see electron site energies above.

EN_HOPPING_E **X**_real

Electron hopping energy. The model is used as follows $h_{mn,m\neq n}^{(e)}=h_0^{(e)}\exp(-|r_m-r_n|/l_e)$. The **EN_HOPPING_E** is the parameter $h_0^{(e)}$. Requires **DECAY_L_WF_E**.

EN_HOPPING_H **X**_real

Hole hopping energy. The model is used as follows $h_{mn,m\neq n}^{(h)}=h_0^{(h)}\exp(-|r_m-r_n|/l_h)$. The **EN_HOPPING_H** is the parameter $h_0^{(h)}$. Requires **DECAY_L_WF_H**.

DECAY_L_WF_E **X**_real

Electron hopping radius. The model is used as follows $h_{mn,m\neq n}^{(e)}=h_0^{(e)}\exp(-|r_m-r_n|/l_e)$. The **DECAY_L_WF_E** is the parameter l_e . Requires **EN_HOPPING_E**.

DECAY_L_WF_H **X**_real

Hole hopping radius. The model is used as follows $h_{mn,m\neq n}^{(h)}=h_0^{(h)}\exp(-|r_m-r_n|/l_h)$. The **DECAY_L_WF_H** is the parameter l_h . Requires **EN_HOPPING_H**.

DIP_EH **F**_str

The file name of transition dipoles for electon-hole pair excitations. The file contains a five-column vector. Each row represents a certain electron hole pair. The first column is the electron site index, the second column is the hole site index, the third, fourth and fifth columns are **X**\tab**Y**\tab**Z** values of the transition dipole. In this way electron-hole pairs (CT excitons) as well as Frenkel excitons can be optically active. **DIP_EH** cannot be used with **DIP_X**. The number of rows is not important. Only non-zero transition dipoles can be given.

DIP_X **F**_str

The file name of transition dipoles for Frenkel excitons. The file contains a three-column vector. Each row represents a certain site. The three columns are **X**\tab**Y**\tab**Z** values of the transition dipole. In this model the

Frenkel excitons can be optically active. Electroh-hole pairs (CT excitons) are dark. The number of rows must be equal to **NUMSITES**. **DIP_X** cannot be used with **DIP_EH**.

STRENGTH_U_0EE **X**_real

Electron-electron interaction energy factor. The model is used as follows

$V_{mn}^{(ee)}=\left\{\begin{matrix}\frac{V_0^{(ee)}/\epsilon}{|r_m-r_n|},|r_m-r_n|>R_0^e\\ \frac{V_0^{(ee)}/\epsilon}{R_0^e},|r_m-r_n|\leq R_0^e\end{matrix}\right\}$, where by default $V_0^{(ee)}=\frac{q_e^2}{4\pi\epsilon_0}$ and R_0^e = 5Å.

The **STRENGTH_U_0EE** allows to change the value of parameter $V_0^{(ee)}$. ϵ is a medium dielectric constant defined by **MEDIUM_DIELECTRIC_CONSTANT**.

LENGTH_U_0EE **X**_real

Electron-electron interaction energy parameter. See above definition of the interaction energy. The **LENGTH_U_0EE** allows to change the value of parameter R_0^e .

STRENGTH_U_0HH **X**_real

Hole-hole interaction energy factor. The model is used as follows

$V_{mn}^{(hh)}=\left\{\begin{matrix}\frac{V_0^{(hh)}/\epsilon}{|r_m-r_n|},|r_m-r_n|>R_0^h\\ \frac{V_0^{(hh)}/\epsilon}{R_0^h},|r_m-r_n|\leq R_0^h\end{matrix}\right\}$, where by default $V_0^{(hh)}=\frac{q_e^2}{4\pi\epsilon_0}$ and R_0^h = 5Å.

The **STRENGTH_U_0HH** allows to change the value of parameter $V_0^{(hh)}$. ϵ is a medium dielectric constant defined by **MEDIUM_DIELECTRIC_CONSTANT**.

LENGTH_U_0HH **X**_real

Hole-hole interaction energy parameter. See above definition of the interaction energy. The **LENGTH_U_0HH** allows to change the value of parameter R_0^h .

STRENGTH_U_0EH **X**_real

Electron-hole interaction energy factor. The model is used as follows

$V_{mn}^{(eh)}=\left\{\begin{matrix}-\frac{V_0^{(eh)}/\epsilon}{|r_m-r_n|},|r_m-r_n|>R_0^{eh}\\ -\frac{V_0^{(eh)}/\epsilon}{R_0^{eh}},|r_m-r_n|\leq R_0^{eh}\end{matrix}\right\}$, where by default $V_0^{(eh)}=\frac{q_e^2}{4\pi\epsilon_0}$ and R_0^{eh} = 5Å. The **STRENGTH_U_0EH** allows to change the value of parameter $V_0^{(eh)}$.

ϵ is a medium dielectric constant defined by **MEDIUM_DIELECTRIC_CONSTANT**.

LENGTH_U_0EH **X**_real

Electron-hole interaction energy parameter. See above definition of the interaction energy. The **LENGTH_U_0EH** allows to change the value of parameter R_0^{eh} .

LENGTH_U_0FF **X**_real

Förster type dipole-dipole interaction energy parameter. This interaction energy is necessary to describe excitonic interactions between Frenkel excitons. Dipole-dipole interaction formula is used (the coupling is F^{dd}) based on Frenkel exciton transition dipole values. The interaction is scaled by ϵ , is a medium dielectric constant defined by **MEDIUM_DIELECTRIC_CONSTANT**. The model is used as follows $V_{mn}^{(F)}=\begin{Bmatrix} F^{dd}(\mu_m,\mu_n,r_m,r_n),|r_m-r_n|>R_0^F \\ 0,|r_m-r_n|\le R_0^F \end{Bmatrix}$, where by default R_0^F = 5Å. The **LENGTH_U_0FF** allows to change the value of parameter R_0^F .

ENERGY_EH_STABILIZATION **X**_real

Electron-hole stabilization energy at zero distance. It enters into calculation of a Frenkel exciton transition energy. The transition energy of a Frenkel exciton is always $h_{nn}^{(e)}+h_{nn}^{(h)}+V_{nn}^{(S)}$. The **ENERGY_EH_STABILIZATION** tunes the $V_{nn}^{(S)}$ parameter. By default $V_{nn}^{(S)}=0$.

MEDIUM_DIELECTRIC_CONSTANT **X**_real

Specifies the relative medium dielectric constant ϵ . This parameter scales all interaction energies.

This system framework can in principle be used with the constant dephasing (**CONST_DEPHASING**) to observe various resonances is spectroscopic signals. However calculation of dephasing parameters and of relaxation rates is impossible with this information.

The following microscopic bath models are for the purpose of calculating dephasing and relaxation rates and spectral linewidths. Two bath models are available. They cannot be used both at the same time.

The polaronic system-bath coupling model

The model assumes that the Frenkel excitons are weakly coupled to the environment. The coupling in principle doeas not change strongly from site to site because the permanent dipoles of Frenkel excitons at various sites are zero. The electron-hole pairs induce strong permanent charges separated between the molecules. As the distance between an electron and a hole increase the polarization cloud is formed. At long electron-hole separation distances the electron and hole form their own polarization clouds and thus the bath influence does not change at varying the distance. We assume that the system-bath coupling of CT excitons is $d_{mn}^{CT}=d_0^{CT}[1-\exp(-|r_m-r_n|/R_p)]$. According to this expression the system-bath coupling of a CT state is zero for the Frenkel excitons and grows up to a constant value when separation distance is large. The frenkel excitons may be coupled to a multimode bath via a set of coupling constants $d_{mm,1}^F$, $d_{mm,2}^F$ ...

The bath for such model must be explicitly specified. The important property is that at least two bath modes must be given: the last bath mode is always assigned to the CT excitons. Other than the last modes are assumed to be the Frenkel exciton modes. All CT and Frenkel state fluctuations are uncorrelated. Bote that the bath is defined in the **$BATH** section. Keywords specifying this system-bath model are as follows

POLARON_BATH_COUPLING **X**_real

Specifies the d_0^{CT} constant. Only single bath coordinate may be dedicated to the CT states.

POLARON_RADIUS **X**_real

Specifies the R_p constant.

EXCITON_BATH_COUPLING **X**_real

Specifies the $d_{mm,1}^F$ constant: same value for all sites. Only single bath coordinate is used for Frenkel excitons. All sites are coupled to bath equally. The sites are uncorrelated. Two bath oscillators must be used. The first one is then for Frenkel excitons, the second is for CT excitons. Cannot be used with **EXCITON_BATH_COUPLING_MM.**

EXCITON_BATH_COUPLING_MM **F**_str

Specifies the filename where matrix of $d_{mm,\alpha}^F$ is stored. Many stochastic bath oscillators can be used. For ***N*** oscillators given by **OSCILLATORS_NUM** (in **$BATH** section) ***N-1*** oscillators are dedicated to the Frenkel exciton description and the last ***N***'th oscillator is coupled to the CT excitons. The matrix is given as follows. Let there be M sites. The first set of M numbers are $d_{mm,1}^F$, the following set is $d_{mm,2}^F$, etc up to ***N-1*** sets. The organization of the numbers is not important but is recommended that each set should be given as a separate row; then different bath coordinates are represented by different rows, different sites – as different columns. Cannot be used with **EXCITON_BATH_COUPLING.**

The orbital system-bath coupling model

The model is based on atomic (molecular) orbitals. Each electron and hole site fluctuates on its own. This translates into correlated fluctuations of the Frenkel and CT excitons. In the exciton representation the relevant quantities are the correlation functions $C^{xx}_{nm,kl}=\tilde{h}^{x}_{mn}(t)\tilde{h}^{x}_{kl}(0)$; x denotes the exciton representation. Now assuming that the Coulomb interaction energy does not fluctuate we may have $\tilde{h}^{x}_{m_1 m_{2,} n_1 n_2}=\tilde{h}^{e}_{m_1 n_1}\delta_{m_2 n_2}+\tilde{h}^{h}_{m_2 n_2}\delta_{m_1 n_1}$. Additionally here we assume that the electron and hole hopping elements are very small and we neglect them. So we get fluctuations of only electron and hole energy levels. We then get $\tilde{h}^{x}_{m_1 m_{2,} n_1 n_2}=\delta_{m_1 n_1}\delta_{m_2 n_2}(\tilde{h}^{e}_{m_1 m_1}+\tilde{h}^{h}_{m_2 m_2})$ and I get only correlations of excitonic transition energies: $C^{xx}_{mn,kl}(t)=\delta_{m_1 n_1}\delta_{k_1 l_1}\delta_{m_2 n_2}\delta_{k_2 l_2}(c^{ee}_{m_{1,} k_1}(t)+c^{eh}_{m_{1,} k_2}(t)+c^{he}_{m_{2,} k_1}(t)+c^{hh}_{m_{2,} k_2}(t))$. So no fluctuations of couplings are involved. This model is possible to use with NEE and CGF. The spectral densitiy coefficients corresponding to these correlation functions must be specified in an input file as matrices λ^{ee} , λ^{hh} and λ^{eh} . Note that $\lambda^{eh}_{mn}=\lambda^{he}_{nm}$ so only λ^{eh} is specified. λ^{ee} and λ^{hh} are symmetric matrices so only triangular forms is needed on the input. λ^{eh} Is not symmetric, so it must be specified as a square matrix.

The bath for such model must be explicitly specified using the **$BATH** section. An arbitrary number of bath oscillators is possible. Keywords specifying this system-bath model are as follows

ORBITAL_BATH_COUPLING_MM **F**_str

> Specifies the filename where three matrices λ^{ee} , λ^{eh} and λ^{hh} are stored for each bath oscillator sequentially. Many stochastic bath oscillators can be used as specified by **OSCILLATORS_NUM** in **$BATH** section. The first is triangular λ^{ee} matrix, then square λ^{eh} matrix and then triangular λ^{hh} matrix. If there is second bath oscillator, we have again λ^{ee} , λ^{eh} and λ^{hh} matrices but now with respect to the second oscillator. There are so many λ^{ee} , λ^{eh} and λ^{hh} triplets as bath oscillators.

I. Protein Excitonic model; DichroCalc parametrization

This model has been tested and used for UV absorption, LD and CD calculation of proteins based on their PDB files. This section is just an interface to DichroCalc library developed by Benjamin M. Bulheller (J. D. Hirst research group at University of Nottingham, Nottingham, UK). All usage for nonlinear signals is highly experimental and should be performed only with high level of scpeticism. During the calculation the Dichrocalc library is called to construct the single-exciton Hamiltonian, i. e. transition energies, couplings and electric/magnetic transition dipoles. In principle this information may be used to construct the bi-exciton manifold by assuming some model for the bi-exciton interactions. At the moment a hard-core boson model is assumed. Charge-transfer (CT) states are not interfaced and should not be used. The following keywords directly reflect command-line options when calling dichrocalc standalone executable. For their meaning and for basic usage please read DichroCalc manual first in dichrocalc/doc folder. Units conversion should not be used since DichroCalc uses predefined set of units corresponding to db_an_cm.

SYSTEM_KEYWORD DichroCalc

DICHROCALC_INPUT **F**_str

Main input file for the DichroCalc library. Corresponds to -i command line option of DichroCalc.

DICHROCALC_PARAMETERS **F**_str

The folder of DichroCalc parameter files. Corresponds to -p command line option of DichroCalc.

DICHROCALC_VERBOSE **N**_int

Verbose option: 1 = true, 0 = false. Corresponds to -v command line option of DichroCalc.

DICHROCALC_DEBUG **N**_int

Debug level. Corresponds to -d command line option of DichroCalc.

DICHROCALC_PRINTVEC **N**_int

Create .vec file (for absorbance/LD): 1 = true, 0 = false. Corresponds to --vec command line option of DichroCalc.

DICHROCALC_PRINTPOL **N**_int

Create .pol file (transition polarizations): 1 = true, 0 = false. Corresponds to --pol command line option of DichroCalc.

DICHROCALC_PRINTMAT **N**_int

Create .mat file (matrix, eigenvectors, eigenvalues): 1 = true, 0 = false. Corresponds to --mat command line option of DichroCalc.

8 SIGNALS

Various optical signals can be calculated using SPECTRON package. The properties of optical fields involved are characterized in specific section of the main input file. The title of this section must coincide with the entry in the **$REGISTRATION ... $END** section. For instance if one has

```
$REGISTRATION
  LA
$END
```

then the section

```
$LA
  ...
```

$END
is required to describe the properties of the linear absorption spectrum. The most important parameters are those specifying range of excitation frequencies, number of points in the spectrum.

Signal names, titles and binary codes:

Linear absorption	LA	1
Linear response function	TDLR	2
Third order response function	TDRS	3
Circular dichroism	CD	4
Pump-probe	PP	5
2D photon echo rephasing	KI	6
2D photon echo non-rephasing	KII	7
2D double quantum coherence [(2,3) representation]	KIII	8
2D double quantum coherence [(1,2) representation]	KIIIA	9

A. Setup of excitation fields

This section describes some generic optional parameters which can be used in any experiment setup described by their section.

CEN_FREQ1 **X**_real #[cm^{-1}]
Central optical frequency of field 1 in multi-color setup.

CEN_FREQ2 **X**_real #[cm^{-1}]
Central optical frequency of field 2 in multi-color setup.

CEN_FREQ3 **X**_real #[cm^{-1}]
Central optical frequency of field 3 in multi-color setup.

CEN_FREQ4 **X**_real #[cm^{-1}]
Central optical frequency of field 4 in multi-color setup.

WID_FREQ1 **X**_real #[cm^{-1}]
Optical field bandwidth of field 1 in multi-color setup.

WID_FREQ2 **X**_real #[cm^{-1}]

Optical field bandwidth of field 2 in multi-color setup.

WID_FREQ3 **X**_real #[cm^{-1}]

Optical field bandwidth of field 3 in multi-color setup.

WID_FREQ4 **X**_real #[cm^{-1}]

Optical field bandwidth of field 4 (signal) in multi-color setup.

OPT_POL1 **X**_real **X**_real **X**_real #(a.u.)

Optical polarization of field 1 in X Y Z representation.

OPT_POL2 **X**_real **X**_real **X**_real #(a.u.)

Optical polarization of field 2 in X Y Z representation.

OPT_POL3 **X**_real **X**_real **X**_real #(a.u.)

Optical polarization of field 3 in X Y Z representation.

OPT_POL4 **X**_real **X**_real **X**_real #(a.u.)

Optical polarization of field 4 (signal) in X Y Z representation.

OPT_WAV1 **X**_real **X**_real **X**_real #(a.u.)

Optical wavevector of field 1 in X Y Z representation.

OPT_WAV2 **X**_real **X**_real **X**_real #(a.u.)

Optical wavevector of field 2 in X Y Z representation.

OPT_WAV3 **X**_real **X**_real **X**_real #(a.u.)

Optical wavevector of field 3 in X Y Z representation.

OPT_WAV4 **X**_real **X**_real **X**_real #(a.u.)

Optical wavevector of field 4 (signal) in X Y Z representation.

PULSE_ENVELOPES_G **X**_r **X**_r **X**_r **X**_r **X**_r **X**_r **X**_r **X**_r #(cm^{-1})

Adds finite Gaussian pulse envelopes in frequency domain (finite bandwidth of a field). The values are as follows: central frequency of pulse 1, pulse width 1 (standart deviation), central frequency of pulse 2, pulse width 2, central frequency of pulse 3, pulse width 3, central frequency of pulse 4, pulse width 4.

Requires ADD_PULSE_ENV 1

PULSE_ENVELOPES_L_INTERPOLATED **X X X X *W* N F**

Adds finite pulse envelopes in frequency domain of arbitrary spectral shape. The values: **X** - central frequency of pulse 1, 2, 3, 4, allocated pulse width ***W*** (same for all pulses), **N** - number of points, defining a pulse shape, **F** - name of the data file of the pulse shapes. The shape is given as a data set covering range from (-***W****/2)* to (+***W****/2*-***W****/****N****) with a step* ***W****/****N****;* the data are equally spaced. The required value at a certain frequency is calculated using linear interpolation between data values. The file **F** is one column data set (file type 1). The file contains 8x**N** ordered sets as follows.

1 pulse spectral shape real part (N values), imaginary part (N values),
2 pulse spectral shape real part (N values), imaginary part (N values),
3 pulse spectral shape real part (N values), imaginary part (N values),
4 pulse spectral shape real part (N values), imaginary part (N values).

Note that the data contain not the amplitude but separately real and imaginary parts. The data corresponds to the amplitude only when the imaginary part is set to zero.

Requires `ADD_PULSE_ENV     1`

`ADD_PULSE_ENV` **N**_int

Turns on the option, which allows using finite pulse bandwidths in any other technique.

`FAKE` **N**_int

Nonzero N skips generation of the signal (used for system-only inspection)

B. Linear absorption technique

This section describes contol of the linear absorption technique. The linear absorption is switched on by

```
$REGISTRATION
LA
$END
```

A separate

```
$LA
...
$END
```

section is then necessary. The following are keywords of this section

`INI_FREQ` **X**_real #[cm^{-1}]

Initial frequency from which the looping over frequency proceeds.

FIN_FREQ **X**_real #[cm^{-1}]

Final frequency until the looping over frequency proceeds; The actual final frequency value is **FIN_FREQ-(FIN_FREQ-INI_FREQ)/NUM_FREQ**

NUM_FREQ **N**_int

Number of points in the frequency interval.

NUM_SHOTS **N**_int

Number of repeated calculations (needed with system disorder).

OPT_POL **X**_real **X**_real **X**_real #[a.u.]

Absolute polarization of fields (useful only for oriented systems).

CAL_METHOD **F**_str

SOS_CGF_F – simple sum-over-eigenstates approach with the lineshapes functions (time-domain + FFT) defined through cumulant techniques; population lifetimes included.
SOS_PRO_ES – sum-over-eigenstates approach, which uses nonsecular Redfield relaxation matrix; coherence transfer available.
SIM – sum-over-eigenstates approach, which uses constant dephasing/relaxation matrices.
QP – (default) simple sum-over-eigenstates approach together with the Markovian limit for lineshapes (sum over Lorentzians in the frequency domain).

OUT_FILE **F**_str

filename for the signal. Default is “sig-la”. The file contains two-column data set: frequency and absoprtion strength (a.u.)

C. Circular dichroism (CD) technique

This section describes contol of the circular dichroism signal. The CD is switched on by

```
$REGISTRATION
CD
$END
```

A separate

```
$CD
...
$END
```

section is then necessary. The following are keywords of this section

INI_FREQ **X**_real #[cm^{-1}]

Initial frequency from which the looping over frequency proceeds.

FIN_FREQ **X**_real #[cm^{-1}]

Final frequency until the looping over frequency proceeds; The actual final frequency value is **FIN_FREQ-(FIN_FREQ-INI_FREQ)/NUM_FREQ**

NUM_FREQ **N**_int

Number of points in the frequency interval.

NUM_SHOTS **N**_int

Number of repeated calculations (needed with system disorder).

CAL_METHOD **F**_str

SOS_CGF_F – simple sum-over-eigenstates approach with the lineshapes functions (time-domain + FFT) defined through cumulant techniques; population lifetimes included.

SOS_PRO_ES – sum-over-eigenstates approach, which uses nonsecular Redfield relaxation matrix; coherence transfer available.

SIM – sum-over-eigenstates approach, which uses constant dephasing/relaxation matrices.

QP – (default) simple sum-over-eigenstates approach together with the Markovian limit for lineshapes (sum over Lorentzians in the frequency domain).

OUT_FILE **F**_str

filename for the signal. Default is “sig-cd”. The file contains two-column data set: frequency and absoprtion strength (a.u.)

D. KI, KII and PP techniques (same options)

This section describes contol of the non-linear two-dimensional technique. These techniques are swithed on by

```
$REGISTRATION
KI
KII
PP
$END
```

Only one of them may be selected. A separate section describing each of them is then necessary. For instance for KI techniques one needs to have

```
$KI
...
$END
```

The following are keywords of these sections

INI_FREQ1 **X**_real #[cm^{-1}]

Initial frequency of Ω_1 from which the looping over frequency proceeds.

Note that this frequency is negative for KI

FIN_FREQ1 **X**_real #[cm^{-1}]

Final frequency of Ω_1. Note that this frequency is negative for KI

NUM_FREQ1 **N**_int

Number of points in the frequency interval.

INI_FREQ3 **X**_real #[cm^{-1}]

Initial frequency of Ω_3 from which the looping over frequency proceeds.

FIN_FREQ3 **X**_real #[cm^{-1}]

Final frequency of Ω_3.

NUM_FREQ3 **N**_int

Number of points in the frequency interval.

DEL_TIME2 **X**_real #[fs]

Delay time t_2.

NUM_SHOTS **N**_int

Number of repeated calculations (needed with system disorder).

CAL_METHOD **F**_str

SIM – simple sum-over-eigenstates technique with constant dephasing/relaxation parameters.
SOS_CGF_F – simple sum-over-eigenstates approach with the lineshapes functions (time-domain + FFT). Exact when transport is off. Transport is treated by factorizing the Doorway-Window functions unsing the secular propagation.
SOS_CGF_G – Same as CGF but the Doorway-Window functions are not factorized; slow bath dynamics may be included.
SOS_CGF_C – Same as CGF_G but includes dynamic Stokes shift.
SOS_PRO_ES – Uses Markovian Redfield propagation beyond secular limit for all density matrix intervals. The solution is in exciton basis set.
SOS_PRO_LS – Uses Markovian Redfield propagation beyond secular limit for all density matrix intervals. The solution is in Redfield basis set (may be faster).
QP – Uses exciton quasiparticle representation for double-excitations and Markovian limit for lineshapes.

OUT_FILE **F**_str

filename for the signal. Default file-names are sig-k1, sig-k2, sig-pp, for the three signals.

E. KIII technique

This section describes contol of the non-linear double-quantum coherence (KIII) technique ($\Omega_2\,\Omega_3$) represntation. It is switched on by

```
$REGISTRATION
KIII
$END
```

A separate

```
$KIII
...
$END
```

section is then necessary. The following are keywords of this section

`INI_FREQ2` **X**_real #[cm^{-1}]

Initial frequency of Ω_2 from which the looping over frequency proceeds.

`FIN_FREQ2` **X**_real #[cm^{-1}]

Final frequency of Ω_2.

`NUM_FREQ2` **N**_int

Number of points in the frequency interval.

`INI_FREQ3` **X**_real #[cm^{-1}]

Initial frequency of Ω_3 from which the looping over frequency proceeds.

`FIN_FREQ3` **X**_real #[cm^{-1}]

Final frequency of Ω_3.

`NUM_FREQ3` **N**_int

Number of points in the frequency interval.

`DEL_TIME1` **X**_real #[fs]

Delay time t_1.

`NUM_SHOTS` **N**_int

Number of repeated calculations (needed with system disorder).

`CAL_METHOD` **F**_str

`SIM` – simple sum-over-eigenstates technique with constant dephasing/relaxation parameters.

`SOS_CGF_F` – simple sum-over-eigenstates approach with the lineshapes functions (time-domain + FFT). Exact when transport is off. Transport is treated by factorizing the Doorway-Window functions unsing the secular propagation.

`SOS_CGF_G` – Same as `CGF` but the Doorway-Window functions are not

factorized; slow bath dynamics may be included.
SOS_CGF_C – Same as CGF_G but includes dynamic Stokes shift.
SOS_PRO_ES – Uses Markovian Redfield propagation beyond secular limit for all density matrix intervals. The solution is in exciton basis set.
SOS_PRO_LS – Uses Markovian Redfield propagation beyond secular limit for all density matrix intervals. The solution is in Redfield basis set (may be faster).
QP – Uses exciton quasiparticle representation for double-excitations and Markovian limit for lineshapes.

OUT_FILE **F**_str
filename for the signal. The default name is “sig-k3”.

F. KIIIA technique

This section describes contol of the non-linear double-quantum coherence (KIII) technique ($\Omega_1 \Omega_2$) represntation. It is switched on by

```
$REGISTRATION
KIIIA
$END
```

A separate

```
$KIIIA
...
$END
```

section is then necessary. The following are keywords of this section

INI_FREQ1 **X**_real #[cm^{-1}]
Initial frequency of Ω_1 from which the looping over frequency proceeds.

FIN_FREQ1 **X**_real #[cm^{-1}]
Final frequency of Ω_1.

NUM_FREQ1 **N**_int
Number of points in the frequency interval.

INI_FREQ2 **X**_real #[cm^{-1}]
Initial frequency of Ω_2 from which the looping over frequency proceeds.

FIN_FREQ2 **X**_real #[cm^{-1}]
Final frequency of Ω_2.

NUM_FREQ2 **N**_int
Number of points in the frequency interval.

DEL_TIME3 **X**_real #[fs]

Delay time t_3.

NUM_SHOTS **N**_int

Number of repeated calculations (needed with system disorder).

CAL_METHOD **F**_str

SIM – simple sum-over-eigenstates technique with constant dephasing/relaxation parameters.

SOS_CGF_F – simple sum-over-eigenstates approach with the lineshapes functions (time-domain + FFT). Exact when transport is off. Transport is treated by factorizing the Doorway-Window functions unsing the secular propagation.

SOS_CGF_G – Same as CGF but the Doorway-Window functions are not factorized; slow bath dynamics may be included.

SOS_CGF_C – Same as CGF_G but includes dynamic Stokes shift.

SOS_PRO_ES – Uses Markovian Redfield propagation beyond secular limit for all density matrix intervals. The solution is in exciton basis set.

SOS_PRO_LS – Uses Markovian Redfield propagation beyond secular limit for all density matrix intervals. The solution is in Redfield basis set (may be faster).

QP – Uses exciton quasiparticle representation for double-excitations and Markovian limit for lineshapes.

OUT_FILE **F**_str

filename for the signal. Default is “sig-k3a”.

G. *TDRS technique*

This section describes contol of the simulation of complete set of non-linear time-domain response finctions. This simulation is switched on by

```
$REGISTRATION
TDRS
$END
```

A separate

```
$TDRS
...
$END
```

section is then necessary. Only SOS – type simulation is allowed. The following are keywords of this section

INI_TIME1 **X**_real #[fs]

Initial time of t_1 from which the looping over time delays proceeds.

INI_TIME2 **X**_real #[fs]

Initial time of t_2 from which the looping over time delays proceeds.

INI_TIME3 **X**_real #[fs]

Initial time of t_3 from which the looping over time delays proceeds.

FIN_TIME1 **X**_real #[fs]

Final time of t_1 to which the looping over time delays proceeds.

FIN_TIME2 **X**_real #[fs]

Final time of t_2 to which the looping over time delays proceeds.

FIN_TIME3 **X**_real #[fs]

Final time of t_3 to which the looping over time delays proceeds.

NUM_TIME1 **N**_int

Number of points in the time interval.

NUM_TIME2 **N**_int

Number of points in the time interval.

NUM_TIME3 **N**_int

Number of points in the time interval.

NUM_SHOTS **N**_int

Number of repeated calculations (needed with system disorder).

CAL_METHOD **F**_str

SIM – simple sum-over-eigenstates technique with constant dephasing/relaxation parameters.

SOS_CGF_F – simple sum-over-eigenstates approach with the lineshapes functions (time-domain + FFT). Exact when transport is off. Transport is treated by factorizing the Doorway-Window functions unsing the secular propagation.

SOS_CGF_G – Same as CGF but the Doorway-Window functions are not factorized; slow bath dynamics may be included.

SOS_CGF_C – Same as CGF_G but includes dynamic Stokes shift.

SOS_PRO_ES – Uses Markovian Redfield propagation beyond secular limit for all density matrix intervals. The solution is in exciton basis set.

SOS_PRO_LS – Uses Markovian Redfield propagation beyond secular limit for all density matrix intervals. The solution is in Redfield basis set (may be faster).

QP – Uses exciton quasiparticle representation for double-excitations and Markovian limit for lineshapes.

OUT_FILE **F**_str

name of the signal file

OUT_TYPE **F**_str
Type of the output information:
ASCII – simple text file
BIN – binary file.

Allows using
REC_OSCILLATIONS **N**_int

Additional required options include
CEN_FREQ1 **X**_real #[cm^{-1}]
CEN_FREQ2 **X**_real #[cm^{-1}]
CEN_FREQ3 **X**_real #[cm^{-1}]
CEN_FREQ4 **X**_real #[cm^{-1}]
WID_FREQ1 **X**_real #[cm^{-1}]
WID_FREQ2 **X**_real #[cm^{-1}]
WID_FREQ3 **X**_real #[cm^{-1}]
WID_FREQ4 **X**_real #[cm^{-1}]

H. TDLR technique

This section describes contol of the simulation of the linear time-domain response function. This simulation is switched on by

```
$REGISTRATION
TDLR
$END
```

A separate

```
$TDLR
...
$END
```

section is then necessary. Only SOS – type simulation is allowed. The following are keywords of this section

INI_TIME1 **X**_real #[fs]
Initial time of t_1 from which the looping over time delays proceeds.

FIN_TIME1 **X**_real #[fs]
Final time of t_1 to which the looping over time delays proceeds.

NUM_TIME1 **N**_int
Number of points in the time interval.

NUM_SHOTS **N**_int

Number of repeated calculations (needed with system disorder).

CAL_METHOD **F**_str

SOS_CGF_F – simple sum-over-eigenstates approach with the lineshapes functions (time-domain + FFT) defined through cumulant techniques; population lifetimes included.
SOS_PRO_ES – sum-over-eigenstates approach, which uses nonsecular Redfield relaxation matrix; coherence transfer available.
SIM – sum-over-eigenstates approach, which uses constant dephasing/relaxation matrices.
QP – (default) simple sum-over-eigenstates approach together with the Markovian limit for lineshapes (sum over Lorentzians in the frequency domain).

OUT_FILE **F**_str

name of the signal file

OUT_TYPE **F**_str

Type of the output information:
ASCII – simple text file
BIN – binary file.

Allows:
REC_OSCILLATIONS

Additional required fields:

CEN_FREQ1	**X**_real	#[cm^{-1}]
CEN_FREQ2	**X**_real	#[cm^{-1}]
WID_FREQ1	**X**_real	#[cm^{-1}]
WID_FREQ2	**X**_real	#[cm^{-1}]

9 Appendix: Extensions and tuning for advanced simulations

A. Some fine-tuning of signal calculations

(all signal sections)

DIAGRAM_R1 **N**_int

N=0 turns off R1 Feynman diagram is SOS.

DIAGRAM_R2 **N**_int

N=0 turns off R2 Feynman diagram is SOS.

DIAGRAM_R3 **N**_int

N=0 turns off R3 Feynman diagram is SOS.

DIAGRAM_R4 **N**_int

N=0 turns off R4 Feynman diagram is SOS.

ADD_PULSE_ENV **N**_int

N>0 allows using pulse envelopes in signal calculations.

WAV_CI **N**_int

N>0 allows calculating responses to first order in wavevector (these are chirality-induced techniques.

REC_OSCILLATIONS **N**_int

N>0 does not shift response function optical oscillation frequencies. Can be used with TDRS and TDLR

B. KI, KII and PP advanced extensions

$PP section

SIG_TYPE **F**_str

T2W3 – Specifies calculation of two dimensional (τ,Ω) signal, where τ≡t_2 and Ω≡ Ω_3 ; t_1=0. This setup simulates the narrow-band pump – broad band probe signal when τ is the delay time between pump and probe pulses and Ω is the probe frequency. Finite pulse parameters should be used for pump probe as follows:
CEN_FREQ1, CEN_FREQ2 should be used as pump central frequency;
CEN_FREQ3, CEN_FREQ4 should be the center of probe frequency band;
WID_FREQ1, WID_FREQ2 should be pump linewidth; WID_FREQ3, WID_FREQ4 should cover the probe bandwidth.
Ranges of (τ,Ω) are defined using INI_FREQ3, FIN_FREQ3, NUM_FREQ3 for Ω; and INI_TIME2, FIN_TIME2, NUM_TIME2 for τ (see below).
INI_FREQ1, FIN_FREQ1 are encouraged to use for selecting excitation bandwidth in SOS. DEL_TIME2 should not be used.

INI_TIME2 **X**_real #[fs]

Initial time for t_2 interval in fs.

FIN_TIME2 **X**_real #[fs]

Final time for t_2 interval in fs.

NUM_TIME2 **N**_int

Number of points in t_2 interval.

$KI or $KII section

VARIATION_3D **N**_int

Nonzero N makes calculation of 3D signal (Ω_3,t_2,Ω_1). Range of t_2 is controlled through INI_TIME2, FIN_TIME2, NUM_TIME2 (see below); this setup is useful for tracking time evolution of a selected crosspeak.

INI_TIME2 **X**_real #[fs]
Initial time for t_2 interval in fs.

FIN_TIME2 **X**_real #[fs]
Final time for t_2 interval in fs.

NUM_TIME2 **N**_int
Number of points in t_2 interval.

C. Output of intermediate system quantities to STDOUT

SPECTRON code has many internal intermediate quantities. Some of them can be printed on the terminal output. These must be turned on globally using “-v” command-line option; otherwise they are ignored.

These options must be given in the

```
$SYSTEM
...
$END
```

section.

PRINT_POPULATION_M **N**_int
Nonzero N: prints population transport matrix (if available) in inverse picoseconds; square matrix.

PRINT_REDFIELD_M **N**_int
Nonzero N: prints Redfield operator (Only single-exciton manifold; no ground state) as it is stored inside (if available); can be used as a platform for REDFIELD_IN_FILE.

Format:
The full Redfield matrix is R_{mnkl}. The code stores only nonzero elements. Therefore the output consists of two parts. The first part tells how many (kl) pairs there are for a pair (mn). The second part gives the values (real and imaginary) for given (mnkl) indices:
For instance for a dimer with secular approximation we would have

```
#first part:
0       0       2
0       1       1
1       0       1
```

```
1	1	2
#Second part:
0	0	0	0	a	0
0	0	1	1	b	0
0	1	0	1	c	d
1	0	1	0	e	f
1	1	0	0	g	0
1	1	1	1	h	0
Done
```

Where a b c e g h are real parts of the rates and d f are imaginary parts (the population rates are real)

The Complete Redfield relaxation rate would generate (secular part precedes other elements as highlighted; that is not necessary, but it is how its generated):

```
0	0	4
0	1	4
1	0	4
1	1	4
0	0	0	0	a	0
0	0	1	1	b	0
0	0	0	1	xr	xi
0	0	1	0	xr	xi
0	1	0	1	c	d
0	1	0	0	xr	xi
0	1	1	0	xr	xi
0	1	1	1	xr	xi
1	0	1	0	e	f
1	0	0	0	xr	xi
1	0	0	1	xr	xi
1	0	1	1	xr	xi
1	1	0	0	g	0
1	1	1	1	h	0
1	1	0	1	xr	xi
1	1	1	0	xr	xi
Done
```

PRINT_DOS **N**_int

Nonzero N: prints density of single-exciton states (DOS) if available.

PRINT_EVALUES **N**_int

Nonzero N: prints single-exciton eigenvalues (if available)

PRINT_EVECTORS **N**_int

Nonzero N: prints single-exciton eigenvectors (if available)

PRINT_EL_DIPOLES_1 **N**_int

Nonzero N: prints single-exciton transition dipoles (if available)

PRINT_SM_TRUNCATION_INFO **N**_int

Nonzero N: prints various information of the scattering matrix related to truncation (if available).

PRINT_HAM_1 **N**_int

Nonzero N: prints single-exciton real space Hamiltonian.

PRINT_INVPR_1 **N**_int

Nonzero N: prints single-exciton eigenstates real space inverse participation ratios: $\xi_e^{(1)}=[\sum_n \psi_{n,e}^4]^{-1}$.

PRINT_ANHARM **N**_int

Nonzero N: prints full energy anharmonicity matrix.

PRINT_EIGENVALUES_2 **N**_int

Nonzero N: prints double-exciton eigen-energies.

PRINT_EIGENVECTORS_2 **N**_int

Nonzero N: prints double-exciton real space wavefunctions (PRSE basis set).

PRINT_INVPR_2 **N**_int

Nonzero N: prints double-exciton real space inverse participation ratios (PRSE basis): $\xi_f^{(2)}=[\sum_{m,n}^{m\geq n} \Psi_{(mn),f}^4]^{-1}$.

PRINT_EIGENVECTORS_2_PESE **N**_int

Nonzero N: prints double-exciton wavefunctions in the basis of product-of-single-exciton-eigenstates (PESE basis set).

PRINT_INVPR_2_PESE **N**_int

Nonzero N: prints double-exciton inverse participation ratios in the basis of product-of-single-exciton-eigenstates (PESE basis set) $\xi_f^{(2)}=[\sum_{m,n}^{m\geq n} \Psi_{(mn),f}^4]^{-1}$.

PRINT_PRSE_PESE_TRANSF **N**_int

Nonzero N: prints double-exciton transformation matrix from real-space representation to product-of-single-exciton-eigenstates (PRSE-to-PESE basis).

D. *Fine-tuning of system properties*

Calculating of single-exciton DOS can be tuned using:

CALCULATE_DOS_NUM_BINS **N**_int

N>0 specifies number of “bins” used in calculation of single-exciton density of states (DOS) in the interval from lowest-energy to the value shifted up by CALCULATE_DOS_BIN_SIZExCALCULATE_DOS_NUM_BINS.

CALCULATE_DOS_BIN_SIZE X_real [cm^{-1}]

X specifies width of a single “bin” in DOS calculations.

Fine tuning of the exciton scattering in QP representation is performed using:

TRUNCATION_MAGNITUDE **X**_real

Approximation level for the NEE scattering matrix. 0<X<1. Several levels of truncation are available:
1. the scattering matrix is truncated based on exciton overlap. The exciton pairs which overlap less than X are neglected.
2. single-exciton states which have transition oscillator strengths smaller than X*max, are neglected.
3. Exciton pairs which are not connected by “third” exciton are neglected.
These properties are controlled additionally by TRUNCATION_ALL_TRANSITIONS and TRUNCATION_ALL_CONNECTIONS.

MEAN_FIELD_APPROX **N**_int

When N>0 the scattering matrix is calculated within the Mean Field Approximation. This works currently for finite systems of soft/hard core bosons.

TRUNCATION_ALL_TRANSITIONS **N**_int

N>0 does not perform truncation based on transition amplitudes (see TRUNCATION_MAGNITUDE)

TRUNCATION_ALL_CONNECTIONS **N**_int

N>0 does not truncation based on “third” excitons connecting the initial and final exciton pairs (see TRUNCATION_MAGNITUDE).

SCATTERING_FREQ_I **X**_real #[cm^{-1}]

Initial frequency of the scattering matrix (when automatic calculation does not work for some reasons).

SCATTERING_FREQ_F **X**_real #[cm^{-1}]

Final frequency of the scattering matrix (when automatic calculation does not work for some reasons).

SCATTERING_FREQ_N **N**_int

Number of points in the frequency window of the scattering matrix (when automatic calculation does not work for some reasons).

SCATTERING_MATRIX2_IM_SH **N**_int

Nonzero N requests calculation of the scattering matrix with imaginary shifts (more correct for time-domain NEE signals)

PRECALCULATE_SM **N**_int

ZERO N requests calculation of the scattering matrix “on the fly”. This is more correct than precalculating the scattering matrix (nonzero N), however the calculations may be extremely slow.

SCATTERING_MEMORY_LIMIT **N**_int

Sets the limit for the computer memory space allocated for the single scattering matrix. This is useful for a computer to keep “alive”. The specification is as follows:
N = n**G**: n gigabytes (n - integer)
N = n**M**: n megabytes
N = n**k**: n kilobytes

READ_IN_SM **F**_str

Requests output of the scattering matrix (and all supporting material) to a binary file. This may be later used with WRITE_OUT_SM keyword to read and use this information by spectron code for future calculations (in the case precalculation of the scattering matrix takes a lot of time. Several snapshots may simply appended to the file.
F_str is the file name

WRITE_OUT_SM **F**_str

Reads the scattering matrix (and all supporting material) from a binary file created using WRITE_OUT_SM keyword.
F_str is the file name

Fine tuning of the exciton transport

REDFIELD_RWA **N**_int

ZERO N turns off the rotating-wave approximation in Redfield relaxation operator for transport.

REDFIELD_RWA_WIDTH **X**_real #[cm^{-1}]

Imposes a finite window for the RWA approximation in the Redfield relaxation operator for transport (used for mixing of populations and coherences).

REDFIELD_REDUCED **N**_int

ZERO N turns off the SECULAR approximation in Redfield relaxation operator for transport.

WF_OVERLAPS_EXTENT **X**_real

The coefficient (<1), which used to speed-up calculation of the Redfield relaxation tensor: inside some summations the products of wavefunctions $\sum_n \psi_{e_4 n} \psi_{e_3 n} \psi_{e_2 n} \psi_{e_1 n} < X$ are neglected.

REDFIELD_WITH_PURE_DEPHASING **N**_int

ZERO N turns off the limitation of the Redfield relaxation operator, which neglects the pure dephasing. N=0 includes the pure dephasing.

Control/tuning of the dephasing parameters for quasi-infinite systems

EXCITON_COHERENCE_SIZE **X**_real

Phenomenological constant in units of lattices, where realistic excitons are expected to be delocalized. The constant is used to tune the transport rates, which vanish for infinitely delocalized excitons.

INF_USE_K0_DEPHASINGS **N**_int

Nonzero N requests using of dephasing constant at the zero momentum for all other momenta.

INF_USE_0_DEPHASING **N**_int

Nonzero N requests using of dephasing constant of the first exciton state at zero momentum for all other single-exciton states.

10 Appendix: source file types

The following fist of data representation on a text file is used in the SPECTRON code unless specified separately.

Type 1:

Single column of numbers ordered by increasing value. Trajectory (if needed) is given by appending “snapshots” to the file with no separators.

```
-------------
0
14000
16000
29000
```

```
29800
30200
-------------
```

Type 2:

Five columns of numbers. Used to represent matrices of vectors. Usually first two columns are matrix index and the remaining three columns are the values of X, Y and Z coordinates.

```
-------------
0       1       1.0     1.0     1.0
0       2       1.0     0.0     0.0
1       3       2.0     0.0     0.0
1       4       0.0     2.0     0.0
1       5       0.0     0.0     2.0
2       3       2.0     0.0     2.0
2       4       0.0     2.0     0.0
2       5       2.0     0.0     2.0
-------------
```

Type 3:

Triangular scalar matrix usually representing symmetric square matrix.

```
------------
0
0       100
0       -20     100
0       30      30      500
0       30      30      50      500
0       30      30      50      50      500
-------------
```

Type 4:

Square scalar matrix for non-symmetric matrices.

```
------------
0       0       0
0       -0.01 0.03
0       0.01    -0.03
-------------
```

Type 5:

Three columns of numbers. Used to represent ordered list of vectors. Usually the three columns are the values of X, Y and Z coordinates.

```
-------------
1.0    1.0    1.0
1.0    0.0    0.0
2.0    0.0    0.0
0.0    2.0    0.0
0.0    0.0    2.0
2.0    0.0    2.0
0.0    2.0    0.0
2.0    0.0    2.0
-------------
```

Type 6:

Six columns of numbers. Used to represent ordered list of symmetric second-order three-dimensional tensors. Usually the six columns are the values of components XX, YY, ZZ, XY, XZ, YZ.

```
-------------
1.0    1.0    1.0    1.0    1.0    1.0
1.0    0.0    0.0    1.0    1.0    1.0
2.0    0.0    0.0    1.0    1.0    1.0
0.0    2.0    0.0    1.0    1.0    1.0
0.0    0.0    2.0    1.0    1.0    1.0
2.0    0.0    2.0    1.0    1.0    1.0
0.0    2.0    0.0    1.0    1.0    1.0
2.0    0.0    2.0    1.0    1.0    1.0
-------------
```

Type 7:

A general square (MxN) matrix. In the example the matrix is (3x6).

```
-------------
1.0    1.0    1.0    1.0    1.0    1.0
1.0    0.0    0.0    1.0    1.0    1.0
2.0    0.0    0.0    1.0    1.0    1.0
-------------
```

Type 8:

A set of T3 matrices. Separator is non-essential.

```
------------
0
0      100
```

```
0       -20    100
#
0
0       100
0       -20    100
#
0
0       100
0       -20    100
#
0
0       100
0       -20    100
-------------
```

Type 9:

Eight columns of numbers. Used to represent the matrix of symmetric second-order three-dimensional tensors. Usually the first two columns are the indices of the transitions between the states and six remaining columns are the values of components XX, YY, ZZ, XY, XZ, YZ.

```
-------------
0      1      1.0    1.0    1.0    1.0    1.0    1.0
0      2      1.0    0.0    0.0    1.0    1.0    1.0
0      3      2.0    0.0    0.0    1.0    1.0    1.0
1      4      0.0    2.0    0.0    1.0    1.0    1.0
2      4      0.0    0.0    2.0    1.0    1.0    1.0
3      4      2.0    0.0    2.0    1.0    1.0    1.0
1      5      0.0    2.0    0.0    1.0    1.0    1.0
2      5      2.0    0.0    2.0    1.0    1.0    1.0
-------------
```

11 Appendix: SPECTRON binary header

If binary signal output is used (currently available for TDLR and TDRS) all binary files start with a specific header. The binary SPECTRON header is as follows. It contains the following set of (char) characters
`'S','P','E','C','T','R','O','N',':','2','.','x',':','S',':',#,`
where # is the signal code. Twenty 0-value chars follow. The header size on the 32 bit linux gnu compiler is 36 byte.

12 Appendix: signal representation (simulated data files)

The simulated results are given in text format (ASCII, binary in some specific cases).

1D signals (LA and CD) are two-column data sets. The first column is the frequency (or wavelength), the second column is the relevant intensity.

1D response function (TDLR) is written either in binary or the ASCII formats. An ASCII representation is a four-column data set. The first column is the time index, the second – the time in fs, the third and fourth is the real and imaginary value of the response function at this delay time. The BIN format is created as follows. First the binary header is created. Then Then the value of **INI_TIME1** is written [sizeof(double)], **FIN_TIME1** is written [sizeof(double)], and **NUM_TIME1** is written [sizeof(int)]; in the following the memory block of complex values corresponding to the response function time-dependent values is written using

```
f->write(&sig[0],(NUM_TIME1)*sizeof(complex<double>));
```

The generated file size is

```
(NUM_TIME1)*sizeof(complex<double>)+
2*sizeof(double)+
sizeof(int)+
36*sizeof(char).
```

2D signals (PP, KI, KII, KIII) are represented as 6-column data sets in ASCII format. The signal is characterized by a higher-order coordinate (y axis) and a lower-order (x axis) coordinate. The first two columns are indices of points in 2D space. The first column – the higher-order index, the second column – the lower-order index. The third and fourth columns are actual frequency (wavelength) values corresponding to these indices in the same order. The fifth and sixth columns are the real and imaginary part of the signal at these frequencies. The frequencies in decreasing order are Ω_3, Ω_2, and Ω_1.

3D signals (TDRS) may be written in ASCII or binary representation. The ASCII output is written into 6 files: the first file with --i extension has six columns and contains the three time indices of t_3 t_2 and t_1 and the actual values of t_3, t_2 and t_1. The next file has --1 extension has two columns and contains the real and imaginary values of the $\boldsymbol{k_I}$ response function. The order of the values is the same as in --i file. The next file has --2 extension, has two columns and contains the real and imaginary values of the response function $\boldsymbol{k_{II}}$. The order of the values is the same as in --i file. The next file has --3 extension, has two columns and contains the real and imaginary values of the response function $\boldsymbol{k_{III}}$. The order of the values is the same as in --i file. The next file has --4 extension, has two columns and contains the real and imaginary values of the response function $\boldsymbol{k_{IV}}$. The order of the values is the same as in --i file. The last file has no extension. It combines all the results together for convenience. It has fourteen columns. The first six columns are the same as in --i file. The next two are those of --1 file and so on. The binary output is written into four files. These files correspond to four parts of the response function ($\boldsymbol{k_I}$, $\boldsymbol{k_{II}}$, $\boldsymbol{k_{III}}$, and $\boldsymbol{k_{IV}}$). Their format is identical so only one of the files will be described. The file starts with the binary-file SPECTRON header. Then the value of **INI_TIME3** is written [sizeof(double)], **FIN_TIME3** is written [sizeof(double)], **NUM_TIME3** is written [sizeof(int)]; then the value of **INI_TIME2** is written [sizeof(double)], **FIN_TIME2** is written [sizeof(double)], **NUM_TIME2** is written [sizeof(int)]; then the value of **INI_TIME1** is written [sizeof(double)], **FIN_TIME1** is written [sizeof(double)], **NUM_TIME1** is written [sizeof(int)]; after that follow the values of the response function [sizeof(complex<double>]: inner-most looping is over t1, then t2 and finally t3. This is achieved by

```
for(int i3=0; i3<NUM_TIME3; i3++)
for(int i2=0; i2<NUM_TIME2; i2++)
{
     f->write(&sig[i3][i2][0],(NUM_TIME1)*sizeof(complex<double>));
}
```

This format is used for all four response functions.