

# EXP-T

a relativistic multireference coupled cluster program

v 1.8.1

User manual

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# 1 Introduction

The EXP-T program package is designed for high-precision modeling of molecular electronic structure using the relativistic Fock space coupled cluster method (FS-RCC). Features and program components are listed in Sec. 1.1 and 1.2.

The authors will be grateful for any comments or suggestions:

[exp-t-program@googlegroups.com](mailto:exp-t-program@googlegroups.com)

<https://groups.google.com/d/forum/exp-t-program>

## 1.1 Features of EXP-T

The EXP-T package does not include subroutines for solving the (Dirac-) Hartree-Fock equations and subsequent four-index transformation, so molecular integrals have to be imported from third party electronic structure packages. Currently EXP-T is interfaced to the DIRAC program package [1, 2], thus getting access to the wide variety of Hamiltonians and property operators implemented therein.

Electronic structure models available in EXP-T:

- single-point energy calculations with any point groups and (nearly) all Hamiltonians, implemented in DIRAC (4c-DC, X2Cmmf, 2c-ECP, non-relativistic);
- ground state energy calculations (the  $0h0p$  sector): CCSD, CCSD(T), CCSDT-n (n=1,2,3), CCSDT models;
- the FS-CCSD method for excited states is implemented for the  $0h1p$ ,  $1h0p$ ,  $1h1p$ ,  $0h2p$ ,  $2h0p$ ,  $0h3p$ ,  $1h2p$  Fock space sectors;
- FS-CC models for excited states accounting for triples (CCSDT-n (n=1,2,3), CCSDT) are implemented for the  $0h1p$ ,  $1h0p$ ,  $1h1p$ ,  $0h2p$ ,  $2h0p$ ,  $0h3p$  Fock space sectors.

The summary of all electronic structure models implemented in the EXP-T program system is given in the table:

FS sector	CCSD	CCSD+T(3)	CCSDT-1	CCSDT-2	CCSDT-3	CCSDT
$0h0p$	+	+	+	+	+	+
$0h1p$	+	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>
$1h0p$	+	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>
$1h1p$	+	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>
$0h2p$	+	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>
$2h0p$	+	–	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>
$0h3p$	+	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>
$1h2p$	<i>t</i>	–	–	–	–	–

*“+” – implemented, “–” – not implemented, “t” – currently being tested*

Features for property calculations and analysis of wavefunctions:

- analytic density matrices and property calculations (including  $\mathcal{T}$ -odd operators) for the ground-state CCSD and CCSD(T) models;
- finite-field [3] and direct [4] approaches to transition moments calculations;
- quasidiabatization of SO-coupled states and extraction of spin-orbit matrix elements [5].
- “quasi-natural” spinors (NS) and natural transition spinors (NTS) for non-trivial Fock space sectors;

- one-electron properties via the interface to the OneProp program by L. V. Skripnikov [6].

Features to deal with the intruder state problem:

- “dynamic” energy denominators shifts as a solution of the intruder-state problem [5];
- Padé extrapolation to the zero-shift limit [7];
- intermediate Hamiltonian technique for incomplete main model spaces (IH-IMMS) [8];

Features for high-performance calculations:

- OpenMP parallelization (for shared-memory systems);
- parallel calculations on NVIDIA GPUs using the CUDA platform [9].

## 1.2 Program components

`expt.x`            Input processing + all CC calculations.

`heffman.x`        Manipulations with effective Hamiltonian matrices: Padé extrapolations, finite-field transition moments calculations, quasidiabatization of SO-coupled states.

`expt_transform_natorb.x`

Transformation of “quasi-natural” spinors to the AO basis.

`expt_diatomic.x`

Rotational-vibrational levels and properties of diatomic molecules.

`expt2pam.x`      Tool for convenient basis set and pseudopotential input.

`expt2spectrum.py`

Tool for convenient extraction of calculated information on transitions and spectra from EXP-T output files.

## 1.3 Citation

We kindly ask you to acknowledge any use of the EXP-T program system that results in published material using the following citation:

A. V. Oleynichenko, A. Zaitsevskii, E. Eliav. Towards high performance relativistic electronic structure modelling: the EXP-T program package. *Commun. Comput. Inf. Sci.* 1331, 375 (2020). doi: [10.1007/978-3-030-64616-5\\_33](https://doi.org/10.1007/978-3-030-64616-5_33)

In addition, credit must be given to the corresponding papers which describe the implementation and the underlying methodological developments:

- Triples in the low Fock space sectors: [10]
- The  $0h3p$  Fock space sector: [11]
- Finite-field transition matrix elements (general): [3]

- Finite-field transition matrix elements (the  $0h0p \rightarrow 1h1p$  excitations): [12]
- Spin-orbit coupling calculations: [5]
- Dynamic denominator shifts (real): [5]
- Dynamic denominator shifts (imaginary, or their real simulation): [13]
- Padé extrapolation of effective Hamiltonian series: [7]
- Intermediate Hamiltonian for incomplete main model spaces (IH-IMMS): [8]
- Direct method of transition matrix elements calculations: [4]

## 1.4 Credits

EXP-T is based on ideas and design solutions of the suite of FS-CC programs written by Ephraim Eliav and Uzi Kaldor.

## 2 Installation from source code

### 2.1 Compiling EXP-T

EXP-T is currently oriented at Unix-like operating systems.

Tools required for compiling the EXP-T package from source code:

- C and Fortran compilers. Currently supported compiler systems are

`gcc/gfortran` GNU compilers

`icc/ifort` Intel compilers

- `cmake` (version 3.0.2 or higher) and `make` utilities:

<https://cmake.org/>

<https://www.gnu.org/software/make/>

Optional dependencies:

- Implementation of the BLAS/LAPACK linear algebra libraries (OpenBLAS [14] or Intel MKL [15] are recommended);
- NVIDIA drivers and CUDA Toolkit are required to perform parallel calculations on GPU:  
<https://www.nvidia.com/Download/index.aspx?lang=en-us>  
<https://developer.nvidia.com/cuda-toolkit>

Download the EXP-T source code as a `*.tar.xz` file and unpack it:

```
tar xvf expt-X.Y.Z.tar.xz
```

Go to the EXP-T home directory, create the `build` directory and make it the current working dir:

```
mkdir build
```

```
cd build
```

Compilation (*Intel compilers*):

```
CC=icc FC=ifort cmake ..
```

```
make
```

Compilation (*GNU compilers*):

```
CC=gcc FC=gfortran cmake ..
```

```
make
```

We recommend specifying compilers explicitly (since the default C compiler may be something other than `gcc`).

The CMake utility will try to locate BLAS/LAPACK libraries on your computer and link them to the project. If there are no pre-installed libraries on your machine, the internal OpenBLAS will be compiled and linked to EXP-T.

When using Intel MKL together with GNU compilers, you will probably need to explicitly specify the path to the MKL home directory by setting the environment variable `MKLROOT`. For example:

```
export MKLROOT=/opt/intel/mkl
```

In case of successful compilation, the executable file `expt.x` will appear in the `build` directory.

*We strongly recommend that compilation is followed by testing (see Sect 2.4).*

*Do not forget to add the directory containing the binaries to the `PATH` environment variable!*

### 2.1.1 Compiling on Mac OS X

The default C compiler for Mac OS X is `clang`; this compiler was not tested, so we strongly recommend to use `gcc` instead:

```
CC=gcc FC=gfortran cmake ..  
make
```

We strongly recommend not to use GNU compilers installed with Homebrew. Instead, download the GNU compilers suitable for your version of Mac OS X from:

<http://hpc.sourceforge.net/>

In order to use a BLAS/LAPACK implementation other than the one attached to the EXP-T package, you can use the following manual:

<https://pheiter.wordpress.com/2012/09/04/howto-installing-lapack-and-blas-on-mac-os/>

However, the Netlib implementation described there can perform several times slower than the OpenBLAS implementation included in EXP-T.

## 2.2 Compiling with CUDA

*Compilation of EXP-T does not require the user to have a CUDA-compatible GPU device. If the CUDA toolkit is missing, the CUDA code will simply be excluded from the compilation process.*

EXP-T is adapted for parallel calculations on NVIDIA GPUs (the CUDA technology [9]).

Notes:

1. At the moment, the OpenMP+CUDA hybrid model as well as multi-GPU support is not implemented. Only one GPU can be used for calculations.
2. non-professional GPUs for gaming are not suitable for CUDA calculations (except for Kepler cards).
3. CUDA code in EXP-T was tested only for CUDA 9.1 and 10.0.
4. Only Intel and GNU compilers were tested for compatibility with CUDA.

To compile EXP-T with CUDA:

1. Make sure your graphics card supports CUDA. CUDA-compatible GPUs are listed here:  
<https://developer.nvidia.com/cuda-gpus>
2. Install proprietary NVIDIA drivers (not the nouveau driver!).  
<https://www.nvidia.com/Download/index.aspx?lang=en-us>.  
For Linux you can find drivers in your distribution's repository.
3. Install CUDA toolkit  
<https://developer.nvidia.com/cuda-downloads>  
or from distribution's repository.
4. Make sure that all drivers and CUDA toolkit are installed and work correctly. Compile the test suite in the `samples` directory of the CUDA home directory and run some of them. The most important are the tests employing the CUBLAS linear algebra library.
5. Compile EXP-T as described in Sec. 2.1. All CUDA tools will be located automatically by CMake.
6. Make sure that the results produced by EXP-T do not depend on the use of CUDA.

## 2.3 Troubleshooting

This section describes the most common problems which can occur during the compilation process. In case of any questions or problems, please don't hesitate to contact us. Don't forget to attach the output file (in case of problems with calculations) or the file with the output of the `make VERBOSE=1` command (in case of problems with compilation).



Google Groups:

<https://groups.google.com/d/forum/exp-t-program>

E-mail:

[exp-t-program@googlegroups.com](mailto:exp-t-program@googlegroups.com)

### 2.3.1 Outdated version of CMake

We highly recommend using CMake version 3.0.2 or higher, otherwise, problems may occur when building the internal OpenBLAS. The following command will show what version of CMake is installed:

```
cmake --version
```

If CMake version is lower than 3.0.2, download the binary distribution from their official website <https://cmake.org/download/>. After installation do not forget to add the directory containing the CMake binary files to the `PATH` environment variable.

*Installation of CMake binary files does not require root privileges.*

## 2.4 Testing

Test suite is located in the `test` directory. The testing system is written in the Python programming language (must be pre-installed on your machine). Either Python 2 or Python 3 can be used.

In order to run the testing suite, run the following command:

```
make test
```

## 3 Running EXP-T

*See Sec. 6 for a description of an additional utility programs included in the EXP-T package.*

A typical coupled cluster calculation consists of two sequential steps:

1. SCF and integral transformation within DIRAC (Sect. 3.1);
2. CC calculation within EXP-T (Sect. 3.2).

### 3.1 Precomputing spinors and molecular integrals: the DIRAC step

*The interface to DIRAC was tested only for the DIRAC17, DIRAC18 and DIRAC19 releases.*

DIRAC stores transformed molecular integrals in the following binary files:

MRCONEE    information about SCF calculation, symmetry, occupation numbers, one-electron integrals;  
MDCINT     symmetry-unique nonzero two-electron integrals;  
MDPROP     one-electron property integrals.

Run DIRAC and save the files containing the transformed integrals to the working directory using the `--get` option:

```
pam --noarch --mol=<mol-file> --inp=<inp-file> --get="MRCONEE MDCINT MDPROP"
```

If DIRAC starts in parallel mode (MPI), it is necessary to choose the “scheme 4” transformation algorithm. By default, DIRAC uses the “scheme 6” algorithm which produces multiple MDCINT files [16] and currently EXP-T requires that all integrals are stored in a single file. In order to accomplish this, add the following lines to the DIRAC input file:

```
**MOLTRA  
.SCHEME  
4
```

To calculate properties, transition moments and intensities without resorting to the finite-field scheme property integrals transformed to the basis of molecular spinors are also required. We recommend explicitly asking DIRAC to calculate and transform these integrals by adding the `.PRPTRA` keyword together with the list of the required property operators to DIRAC input files:

```
**MOLTRA  
.PRPTRA  
. . . . .  
**PROPERTIES  
.DIPOLE
```

*If the molecular-mean-field X2C Hamiltonian (X2Cmmf) was used at the DIRAC stage, one **must** specify the `x2cmmf` flag in the EXP-T input file! (see also page 23).*

### 3.2 Coupled cluster calculation: the EXP-T step

Run an EXP-T job using the following command:

```
expt.x [options] <input-file>
```

The EXP-T output (including error messages) is flushed to the UNIX standard output (`stdout`). Use the output redirection operator “`>`” in case of long time calculations:

```
nohup expt.x <input-file> > <output-file> &
```

Examples of DIRAC and EXP-T input files are given in Sec. 5.

### 3.3 Command-line arguments

Use the `expt.x --help` command to print a list of available command-line arguments:

Usage: `expt.x [OPTION...] <input-file>`

`expt --` A Fock-Space Multireference Relativistic Coupled-Cluster Program

<code>-n, --no-clean</code>	Do not clean scratch directory on exit (use this option to keep cluster amplitudes etc)
<code>-s, --scratch=PATH</code>	Path to scratch directory (default: <code>./scratch</code> )
<code>-, --help</code>	Print this help list and exit
<code>--usage</code>	Print a short usage message and exit
<code>-V, --version</code>	Print program version and exit

Mandatory or optional arguments to long options are also mandatory or optional for any corresponding short options.

Please report bugs to `<exp-t-program@googlegroups.com>`.

## 4 Input files syntax and keywords

*See Sec. 6 for the description of additional utility programs included in the EXP-T package.*

*The input file format may change in future versions.*

The EXP-T input file contains a list of instructions. Each instruction is placed on a separate line and consists of a keyword and a list of arguments. Single-line comments start with '#' and continue until the end of the line. Input is case insensitive. Examples of EXP-T input files are given in Sec. 5. Molecular geometry, basis set etc have to be described only once in the DIRAC input files at the molecular integrals calculation stage (not in EXP-T input files).

The detailed description of the keywords used in the EXP-T input file is provided below. For convenience, keywords are grouped into several sections. The order of instructions in the input file can be arbitrary.

### *General settings*

**title** optional comment.

Syntax: **title** <quoted-string>

Default: no title

Example: **title** "my first ccsc calculation"

**arith** allows one to force EXP-T to use the complex arithmetic everywhere.

Syntax: **arith** **complex**

**print** print level.

Syntax: **print** ( **low** || **medium** || **high** || **debug** || <quoted-string> )

where <quoted-string> can be:

"**eff config**" effective configurations of spinors for each electronic state;

"**model vectors**" expansions of model vectors in terms of model determinants;

"**model space**" information about model space determinants.

One is allowed to combine several **print** instructions.

Default: **print medium**

Example:

**print low**

**print "eff config"**

**degen\_thresh** energy levels are considered as degenerate if the energy gap between them is lower than **degen\_thresh**.

Syntax: **degen\_thresh** <real thresh>

Units: atomic

Default: 1e-8

**spinor\_labels** manual assignment of symbolic names (labels) of specific spinors (orbitals). Symbolic name is printed together with spinor symmetry and energy. This option can be useful when studying composition of electronic states.

Syntax:

```
spinor_labels
. . .
<integer spinor-number> <string spinor-label>
. . .
end
```

Default: disabled.

Example: labels of atomic spinors:

```
spinor_labels
2  2s_1/2
3  2p_1/2
4  2p_3/2
5  2p_3/2
end
```

## *Model*

**sector** specifies the target Fock space sector. To the moment the  $0h0p$ ,  $0h1p$ ,  $1h0p$ ,  $1h1p$ ,  $0h2p$ ,  $2h0p$ ,  $0h3p$ ,  $1h2p$  FS sectors are implemented ( $h$  – holes,  $p$  – particles).

Syntax: **sector** <integer H>h<integer P>p

Default: **sector**  $0h0p$  (vacuum)

**model** CC model (approximation to the cluster operator).

Syntax: **model** ( **ccs** || **ccd** || **ccsd** || **ccsd(t)** || **ccsd+t(3)** || **ccsdt-1** || **ccsdt-2** || **ccsdt-3** || **ccsdt** )

Default: **model** **ccsd**

Notes:

- Keywords **ccsd(t)** and **ccsd+t(3)** are equivalent.
- The codes implementing the CCSD+T(3), CCSDT-n and CCSDT models in the non-trivial sectors and all CC models in the  $0h3p$  sector are experimental (currently being tested), to be used with care.
- The current implementation of the CCSD(T) model for the  $0h0p$  sector is not very computationally efficient.
- The CCS and CCD models are implemented simply by setting all  $T_2$  (CCS) or  $T_1$  (CCD) amplitudes to zero, this does not make computation faster, and exist primarily for the purposes of testing and debugging.

**occ** spinor occupation numbers. This keyword can be used to setup calculations with a “high-spin” vacuum state [17]. This keyword is alternative to the **occ\_irreps** keyword (see below).

Syntax: **occ** <list of the 0 and 1 digits separated by spaces>

Default: occupation numbers are read from MO integrals files

Example: 5 electrons and 10 spinors:

```
occ 1 1 0 0 0 1 1 1 0 0
```

*CC calculations with high-spin vacuum states were tested for the 0h0p FS sector only.*

*It is rather convenient to use the **dirac\_mointegral\_export** routine [18] from the DIRAC package to generate string with occupation numbers.*

**occ\_irreps** overall number of electrons in each irrep. Overall irrep occupations are ignored if occupation numbers of individual spinors are given (by the **occ** keyword, see above). Names of irreps are listed in Appendix C.

Syntax: **occ\_irreps** <pairs irrep:occ>

Example: occupation numbers for the ground triplet state of the O<sub>2</sub> molecule:

```
# for gerade irreps:
```

```
occ_irreps [1/2g+]:3 [1/2g-]:2 [3/2g+]:0 [3/2g-]:1
```

```
# for ungerade irreps:
```

```
occ_irreps [1/2u+]:2 [1/2u-]:2 [3/2u+]:1 [3/2u-]:1
```

Default: occupation numbers are read from MO integrals files.

## Active space

**nacth/nactp** active (i. e. valence) space specification (by the overall number of active spinors, regardless of their symmetry). This method of configuring the active space is recommended.

- **nacth** – number of highest occupied spinors (*active holes*)
- **nactp** – number of lowest virtual spinors (*active particles*)

It is convenient to setup the active space by the **nacth/nactp** keywords when exploring electronic states of molecules in a range of geometries (potential energy surfaces, transition moment functions etc). Using the **nacth/nactp** keywords one can specify either overall number of active spinors (holes or particles) or number of active spinors in each irreducible representation.

Syntax: **nacth** <integer dim>

**nactp** <integer dim>

*or*

**nacth** <pairs irrep:number-of-spinors>

**nactp** <pairs irrep:number-of-spinors>

Default: **nacth** 0, **nactp** 0 (no active spinors).

Example: consider the low-lying electronic states of the La atom. Those are dominated by the  $6s^n 5d^m$  configurations, generating even electronic states. So it seems reasonable to include the  $6s_{1/2}$ ,  $6d_{3/2}$  and  $6d_{5/2}$  atomic spinors of the La<sup>3+</sup> cation into the active space and achieve target electronic states in the 0h3p Fock space sector. In order to make the input file easy to

read, one can use two sequential `nactp` directives, one for the “negative” projections of  $m_j$ , and one for the “positive” ones:

```
nactp [1/2g+]:3 [3/2g+]:2 [5/2g+]:1
```

```
nactp [1/2g-]:3 [3/2g-]:2 [5/2g-]:1
```

One can extend the scope of achievable electronic states by inclusion of the  $6p$  and  $4f$  spinors:

```
nactp [1/2u+]:4 [3/2u+]:3 [5/2u+]:2 [7/2u+]:1
```

```
nactp [1/2u-]:4 [3/2u-]:3 [5/2u-]:2 [7/2u-]:1
```

**active** active (i. e. valence) space specification by energy range. Active spinors must have one-electron energies lying in the range  $\varepsilon_i \in [\varepsilon_{min}; \varepsilon_{max}]$  (regardless of their symmetry). Setting the active space using the `active energy` instruction is convenient only for atomic calculations.

Syntax: `active energy <real eps_min> <real eps_max>`

Default: no active spinors

Example: `active energy -1.0 5.0`

## *Intermediate Hamiltonian for incomplete main model spaces (IH-IMMS)*

Intermediate Hamiltonian technique for incomplete main model spaces (IH-IMMS) can be used to achieve convergence of iterative solution of CC equations. The first paper [8] on the IH-IMMS method concerns only the special case of atomic systems. Structure of incomplete model spaces for molecules is simpler than for the special case of atoms; recent molecular applications with detailed discussions on IH-IMMS for molecules can be found in [4] (the ThO molecule) and [19] (the AcF molecule).

The basic idea of the method is to split the whole model space into the “main” and “intermediate” subspaces. Slater determinants  $|\Phi_M\rangle$  which span the main model space must be chosen to describe the bulk of wavefunctions of target electronic states. FS-CC equations for amplitudes corresponding to excitations from main determinants remain unchanged. In contrast, equations for amplitudes from intermediate (“buffer”) determinants  $|\Phi_I\rangle$  are solved with shifted energy denominators to suppress the intruder state problem. For each cluster amplitude corresponding to the excitation  $I \rightarrow K$  from  $|\Phi_I\rangle$  a shift parameter  $S_{IK}$  is calculated as:

$$S_{IK} = \bar{E}_0 - E_I,$$

where  $E_I$  stands for the energy of the  $|\Phi_I\rangle$  model-space determinant and  $\bar{E}_0$  stands for the some “frontier” energy. This value is used to calculate a shift for energy denominator corresponding to a cluster amplitude using one of the formulas (4)–(7). All model space determinants  $|\Phi_M\rangle$  with energy  $E_M \leq E_0$  are considered as main ones. Determinants  $|\Phi_I\rangle$  with energy  $E_I > E_0$  are intermediate.

By default, IH-IMMS is disabled. IH settings are specified using the complex instruction `ih_imms`:

```
ih_imms
  <option-1>
  <option-2>
  <option-3>
  . . .
end
```

To set up the IH-IMMS calculation:

1. split the set of active spinors into several subspaces. In the current version of EXP-T only spinor energies can be used to select these subspaces;

2. define model Slater determinants which will be considered as the “main” ones. Sets of “main” determinants are defined via the numbers of particles (holes) in each spinor subspace;
3. (optional) define the “frontier” energy  $\overline{E}_0$ . By default, frontier energy is calculated automatically.

The use of IH-IMMS for the simple case of the carbon atom is considered in details in Sect. 5.4.

The following keywords can be used inside the `ih_imms` block:

**sectors** list of Fock space sectors in which the IH-IMMS technique will be applied. This keyword is mandatory.

Syntax: `sectors <list-of-sector-labels>`

Default: no target FS sectors.

Example: `sectors 0h1p 0h2p`

**subspace** defines subspace of active spinors with energies  $\varepsilon \in [\varepsilon_{\min}, \varepsilon_{\max}]$ . Subspaces are used to define composition of main model space determinants via the `main_occ` keyword. One should use several `subspace` options in the input file to define more than one subspace of active spinors. This keyword is mandatory, at least one subspace must be specified.

Syntax: `subspace energy <real emin> <real emax>`

Default: no subspaces are defined.

Example: `subspace energy -1.0 -0.5`

**main\_occ** defines subspace of main model space determinants. The argument of this option contains the number of particles (holes) in the 1st, 2nd, ... subspaces of active spinors. One should use several `main_occ` options in the input file to define more than one subspace of main model space determinants. This keyword is mandatory, at least one subspace of determinants must be specified.

Syntax: `main_occ <list-of-integers>`

Default: no main model spaces are defined.

Example: imagine that we have to define model space determinants with 2 electrons on active spinors belonging to the 1st spinor subspace, 1 electron on spinors from the 2nd subspace and 0 electrons on the other active spinors (such a model determinant belongs to the *0h3p* sector). The proper option is as follows:

```
main_occ 2 1 0
```

**shift\_type** which formula for denominator shift should be used for cluster amplitudes associated with “intermediate” model space determinants. See also description for the `shifttype` keyword (Page 22).

Syntax: `shift_type ( none || real || realimag || imag || taylor )`

Default: `shift_type realimag`

**npower** attenuation parameter used in the shifting formula (see Eq. (4)–(7)).

Syntax: `npower <int n>`

Default: `npower 5`



**scale** scaling factor for the shift parameter  $S$ :

$$S \rightarrow S' = \alpha S$$

Syntax: **scale** <real factor>

Default: **scale** 1.0 (no scaling)

**frontier\_energy** “frontier” energy  $\overline{E}_0$  used to calculate shift for the given (intermediate) determinant.

Syntax: **frontier\_energy** <real energy>

Default: frontier energy is evaluated automatically as the maximum energy of main model space determinants:

$$\overline{E}_0 = \max_{\Phi_M \in \text{main}} E_M, \quad E_M = \langle \Phi_M | H_0 | \Phi_M \rangle.$$

## *Properties*

**analyt\_prop** analytic calculation of coupled cluster expectation values of arbitrary property operators (including  $\mathcal{T}$ -odd ones). Matrix elements of property operators must be stored in the DIRAC’s MDPROP unformatted file.  $\Lambda$ -equations, analytic density matrix and properties are currently available only for the  $0h0p$  sector (vacuum state) and the CCSD and CCSD(T) models.

Syntax: **analyt\_prop** <property-name>

Default: disabled.

Example: calculation of x,y,z-components of the dipole moment.

**analyt\_prop** XDIPLEN

**analyt\_prop** YDIPLEN

**analyt\_prop** ZDIPLEN

**density** calculation of analytic density matrix in the  $0h0p$  sector. Prints occupation numbers of CC natural orbitals. Analytic density matrices are currently implemented for the CCSD and CCSD(T) models.

Syntax: **density** 0h0p

Default: disabled.

**hermit** perform symmetric orthogonalization of model vectors. Orthogonalized model vectors are used only to calculate properties and approximate density matrices; matrices of effective Hamiltonians flushed to HEFF files (see Sec. 6.1) remain non-Hermitian.

Syntax: **hermit**

Default: “hermitization” is disabled.

**mdprop** enable calculations of transition property matrix elements (not only dipole moments). Property operator matrix elements in the basis of molecular spinors are to be loaded from the DIRAC’s MDPROP unformatted file. To avoid huge outputs, use options **nroots** or **roots\_cutoff** to restrict the set of target roots (ot the **expt\_spectrum.py** utility to conveniently extract data for the specific transitions, see Sect. 6.4). Note that the currently available maximum truncation level is quadratic, which might be not enough for the systems with strong dynamic correlations (and thus large cluster amplitudes).

The details on the direct method of transition matrix element calculations are given in [4]. Within this approach property matrix element  $O_{if}$  for the pair of electronic states  $\psi_i$  and  $\psi_f$  can be calculated via the relation [20] (**scheme non-hermitian**):

$$O_{if} = \langle \tilde{\psi}_i^{\perp\perp} | (\Omega^\dagger \Omega)_{closed} \Omega^\dagger O \Omega | \tilde{\psi}_f \rangle \cdot N_i N_f^{-1}, \quad (1)$$

where  $\tilde{\psi}_i^{\perp\perp}$  stands for the left model vector and the normalization factors are defined as

$$N_i = \langle \psi_i | \psi_i \rangle^{1/2} = \langle \tilde{\psi}_i | \Omega^\dagger \Omega | \tilde{\psi}_i \rangle^{1/2} \quad (2)$$

(the same for  $N_f$ ). This definition of the effective property operator leads to the non-Hermitian property matrix,  $O_{if} \neq O_{fi}^*$ . Any hermitization procedure can be applied.

There is also an alternative definition (**scheme hermitian**):

$$O_{if} = \langle \tilde{\psi}_i | \Omega^\dagger O \Omega | \tilde{\psi}_f \rangle \cdot N_i^{-1} N_f^{-1} \quad (3)$$

which is inherently Hermitian [20]. Expressions  $\Omega^\dagger \Omega$  and  $\Omega^\dagger O \Omega$  are evaluated using the FS-CC Ansatz  $\Omega = \{e^T\}$  and have to be artificially truncated at some power of  $T$  (the **approx** keyword). It is natural to use the same level of truncation for both these expressions. Finally, the transformation properties with respect to the molecular point group operations of the specific property operator should be explicitly given (the **sym** keyword).

Syntax: `mdprop "<property-name>" [sym <irrep>] [approx <n> <m>] [scheme hermitian | non-hermitian]`

<b>sym</b>	symmetry of the property operator under consideration;
<b>approx</b>	truncation level for the numerator $\Omega^\dagger O \Omega$ and the metric operator $\Omega^\dagger \Omega$ ; 0 for full neglect of terms containing cluster amplitudes, 1 for linear approximation, 2 for quadratic approximation;
<b>scheme</b>	particular form of the effective operator to be used, <b>non-hermitian</b> for (1) or <b>hermitian</b> for (3).

Default: disabled.

Example: calculation of the whole set of possible dipole transition moments for a linear diatomic heteronuclear molecule (the  $C_{\infty v}$  point group). Terms which are quadratic in cluster amplitudes in both numerator and denominator are included (**approx 2 2**). The hermitian formula is used. The list of instructions will be as follows:

```
mdprop "XDIPLN" sym 1u+ approx 2 2 scheme hermitian
mdprop "XDIPLN" sym 1u- approx 2 2 scheme hermitian
mdprop "YDIPLN" sym 1u+ approx 2 2 scheme hermitian
mdprop "YDIPLN" sym 1u- approx 2 2 scheme hermitian
mdprop "ZDIPLN" sym 0u approx 2 2 scheme hermitian
```

*Matrix elements of some operators calculated by DIRAC can be purely imaginary even if the molecular point group allows one to use real arithmetics. For this reason we recommend to thoroughly check the diagnostics in the EXP-T output. If matrix elements of such an operator are to be calculated, we recommend to solve amplitude equations in real arithmetic, then switch on the complex one using the **arith complex** instruction and calculate property matrix elements of interest.*

*The code for properties is currently experimental; please, we kindly ask you to report all failures and obviously incorrect results.*

**mstdm** enable calculations of the model-space approximations to transition dipole moments (wave-functions are represented by model vectors) [21, 22, 12]). To avoid huge outputs, use options **nroots** or **roots\_cutoff** to restrict the set of target roots.

Note that left model vectors are used in bra:

$$d_{if,\eta} = \langle \tilde{\psi}_i^{\perp\perp} | d_\eta | \tilde{\psi}_f \rangle \quad \eta = x, y, z$$

and if the “hermitization” of the effective Hamiltonian matrix is disabled, the TDM matrix will be (normally slightly) non-Hermitian ( $|d_{if}| \neq |d_{fi}|$ ).

This approach typically overestimates transition moments by 30-50%, hence we recommend using it only for semiquantitative estimations, e. g. detection of the most intensive transitions and discerning between  $0^+$  and  $0^-$  states (such  $E1$ -transitions are strictly forbidden).

Syntax: **mstdm**

Default: disabled.

**txtprop** enable calculations of arbitrary properties. Property operator matrix elements is loaded from two formatted files. To avoid huge outputs, use options **nroots** and **roots\_cutoff** to restrict the set of target roots. Other options are the same as for the **mdprop** keyword.

Syntax: **txtprop** <string file\_re> <string file\_im> [sym <irrep>] [approx <n> <m>]  
[scheme hermitian | non-hermitian]

Default: disabled.

Example:

**mdprop** PropIntsRe.txt PropIntsIm.txt

*The code for properties is currently experimental; please, we kindly ask you to report all failures and obviously incorrect results.*

**natorb** calculation of “quasi-natural” spinors (NS) and transition spinors (NTS).

Note: density matrices  $d_{pq}^{IJ} = \langle \tilde{\psi}_I^{\perp\perp} | a_p^\dagger a_q | \tilde{\psi}_J \rangle$  are constructed with model vectors instead of true wavefunctions.

Syntax: **natorb** [<rep>:<state> | <rep1:state1>-<rep2:state2>] ...

Electronic states for which NS and NTS should be calculated are specified by the <rep>:<state> pair, where:

<rep> name of irreducible representation in square braces. See Sect. C for the list of irrep names used in EXP-T.

<state> sequential number of the state in the irrep (1, 2, ...).

Pair of electronic states separated by a hyphen shows that NTS between these states are to be calculated. You can ask EXP-T to calculate NS and NTS for arbitrary number of states (or pairs of states).

Default: calculation of NS and NTS is disabled.

Examples:

- NS for the ground and the first excited states of the RaCl molecule [23]:

**natorb** [1/2+] :1 [1/2+] :2

- NTS for the  $(1)0^+ - (2)0^+$  transition in the RbCs molecule:

**natorb** [0] :1-[0] :3

(note that in the latter example the [0] :2 state is excluded, since it is the  $(1)0^-$  state).

## *Iterative solution and convergence*

**conv** specifies the requested convergence threshold (in amplitudes):

$$\left| |t_K^{(n+1)}| - |t_K^{(n)}| \right| < \text{conv} \quad \forall K \quad \rightarrow \text{converged}$$

Syntax: `conv <real thresh>`

Default: `1e-9`.

**crop** enables the CROP extrapolation technique to accelerate convergence [24, 25]. It is recommended to use the least possible number of last steps used for extrapolation: `crop 3`.

Syntax: `crop [ ( off || triples || <integer dim> ) ]`

Disable CROP: `crop off`

Enable CROP for triples: `crop triples`

Default: CROP technique is disabled.

*It is highly recommended to enable CROP for triples if the CCSDT-n or CCSDT models are employed.*

**damping** enable damping in the given FS sector. Amplitudes obtained at the  $n$ -th step will be mixed with amplitudes from the  $(n - 1)$ -th step using the damping factor  $\alpha$ :

$$t_K^{(n)'} = \alpha t_K^{(n-1)} + (1 - \alpha) t_K^{(n)}$$

Damping can aid the convergence of equations in some non-pathological cases (when the lack of convergence is caused by amplitude oscillations rather than intruder states). Note that in other cases damping can significantly slow down convergence.

Syntax: `damping <H>h<P>p <integer last_step> <real factor>`

`<H>h<P>p` FS sector in which these damping parameters will be applied

`last_step` at which iteration damping will be disabled

`factor` damping factor  $\alpha$ . Can be negative.

Default: disabled in all sectors

Example: `damping 0h2p 100 0.5`

**diis** enables the DIIS extrapolation technique [26, 27].

Syntax: `diis [ ( off || triples || <integer dim> ) ]`

Disable DIIS: `diis off`

Enable DIIS for triples: `diis triples`

Default: `diis 10` (DIIS is enabled for singles and doubles, disabled for triples)

*It is highly recommended to enable DIIS for triples if the CCSDT-n or CCSDT models are employed.*

**div\_thresh** specifies the divergence threshold (in amplitudes). Solution of amplitude equation is diverged if for some  $t_K$  holds:

$$\left| |t_K^{(n+1)}| - |t_K^{(n)}| \right| > \text{div\_thresh} \quad \rightarrow \text{diverged}$$

May be useful if few initial steps of the iterative solution are divergent.

Syntax: `div_thresh <real thresh>`

Default: `1e+3`.

**flush** indicates that cluster amplitudes must be flushed to disk every  $N$  iterations. Can be useful for very time-consuming calculations with poor convergence. Allows one to change the convergence acceleration strategy.

Syntax: `flush <integer N> iter`

Default: no flush.

Example: `flush 5 iter`

**nroots** specifies the number of roots (electronic states) of interest in each irrep (in the target Fock space sector). Model vectors analysis will be performed only for the **nroots** lowest states.

Syntax: `nroots <pairs irrep:number-of-roots>`

Default: all roots are of interest.

Example: consider the electronic states of the RbCs molecule, corresponding to the first three dissociation limits (see, for example, [5, 28] and references therein). In the Hund's case  $a$  these electronic states are  $X^1\Sigma^+$ ,  $a^3\Sigma^+$ ,  $b^3\Pi$ ,  $A^1\Sigma^+$ ,  $c^3\Sigma^+$ ,  $B^1\Pi$ . In the Hund's case  $c$  these states are classified according the projection of the total electronic angular momentum and can be rearranged as follows:  $(1-3)0^+$ ,  $(1-3)0^-$ ,  $(1-4)1$ ,  $(1)2$  states. The names of irreps used in EXP-T are given in Appendix C (the point group of RbCs is  $\overline{C}_{\infty v}$ ). All output and analysis of model vectors will be restricted to these 11 states using the following command:

`nroots [0]:6 [1+]:4 [1-]:4 [2+]:1 [2-]:1`

(note that as in DIRAC  $0^+$  and  $0^-$  states belong to the same irrep).

**maxiter** maximum number of iterations allowed to solve the CC equations.

Syntax: `maxiter <integer max>`

Default: `maxiter 50`.

**reuse** indicates that sorted integrals and cluster amplitudes from the previous calculation should be reused. Cluster amplitudes will be used as an initial guess. If EXP-T fails to locate the files containing amplitudes, they will be recalculated.

Syntax: `reuse <list-of-arguments>`

Possible values of arguments:

`integrals` load one- and two-electron integrals (from a scratch directory);

`1-integrals` one-electron integrals only;

`2-integrals` two-electron integrals only;

`amplitudes` load amplitudes for all FS sectors occuring in the calculation;

`0h0p, 0h1p, 1h0p, 1h1p, 0h2p, 2h0p, 0h3p, 1h2p`

load amplitudes for the given sector only

Default: no reuse

Note: files with converged amplitudes are flushed to the scratch directory after each calculation (see also Appendix B). To prevent the deletion of files with amplitudes or integrals it is necessary to use the `--no-clean` command-line option (see Sect. 3.3).

Example: `reuse integrals 0h0p 0h1p`

**roots\_cutoff** specifies the upper energy bound for the electronic states to be analyzed and printed. Model vectors analysis and properties calculations will be performed only for the states with energy lower than **roots\_cutoff**. Allowed units of energy are eV, cm<sup>-1</sup> or Hartrees.

Syntax: **roots\_cutoff** <real max\_energy> ( ev || cm || au )

Default: all roots are of interest.

Example: **roots\_cutoff** 30000 cm

**shift** sets the denominator shift parameters in the  $n_h h n_p p$  Fock space sector.

**shift** <H>h<P>p <int n> <real shift\_T1> <real shift\_T2> [<real shift\_T3>]

**n** attenuation parameter (see eqs. (4) and (7));

**shift\_T1** shift value for the  $T_1^{n_h h n_p p}$  cluster operator (singles). Must be omitted in the  $2h0p$  and  $0h2p$  FS sectors. It is recommended to set **shift\_T1** = 0.0 in the  $1h1p$  sector, unless you really understand the consequences of using nonzero values. Note that **shift\_T1** value in this sector does not affect the resulting energies;

**shift\_T2** shift value for  $T_2^{n_h h n_p p}$  (doubles);

**shift\_T3** shift value for  $T_3^{n_h h n_p p}$  (triples). Must be used only for CC models including non-perturbative triples.

Default:  $n = 3$ , all shifts = 0.0

Examples:

**shift** 0h1p 3 -0.3 -0.6 -0.9

**shift** 0h1p 3 -0.6

**shift** 1h1p 4 0.0 -0.5

**shifttype** indicates which formula for energy denominator shifts should be used [5, 7, 29].

**shifttype** is the same for all FS sectors. If **shifttype** is not equal to **none**, you must specify the shift parameters for at least one FS sector (see keyword **shift**; except for  $0h0p$ ).

Syntax: **shifttype** ( none || real || realimag || imag || taylor )

Possible values:

**none** no shift

**real** real shift

$$D'_K = D_K + S \left( \frac{S}{D_K + S} \right)^n \quad (4)$$

**realimag** real simulation of imaginary shift [13]

$$D'_K = D_K + \frac{S^2}{D_K} \left( \frac{S^2}{D_K^2 + S^2} \right)^n \quad (5)$$

**imag** imaginary shift [13]

$$D'_K = D_K + iS \left( \frac{|S|}{|D_K + iS|} \right)^n \quad (6)$$

**taylor** extrapolated intermediate Hamiltonian-like shift [30]

$$D'_K = (D_K + S) \frac{\left(1 - \frac{S}{D_K + S}\right)}{1 - \left(\frac{S}{D_K + S}\right)^{n+1}} \quad (7)$$

Default: `shifttype none`

*Shift is never applied in the 0h0p sector!*

**skip** indicates which sectors will be skipped in the FS-CC calculation. Can be useful in very costly calculations (like CCSDT) in order to avoid recalculation of the first step in already converged sectors. To be used with the `reuse` option.

Syntax: `skip <list-of-sector-symbols>`

Default: no skip.

Example: `skip 0h0p 0h1p`

## Interfaces

**integrals** sets paths to files containing transformed molecular integrals.

Syntax: `integrals <string "1-el int-s"> <string "2-el int-s">`  
`[<string "properties int-s">]`

Arguments:

- one-electron integrals file;
- two-electron integrals file;
- properties transformed integrals file.

Default: `integrals MRCONEE MDCINT MDPROP`

Example: `integrals ../MRCONEE-CinFv ../MDCINT-CinFv /home/user/MDPROP`

**oneprop** imports one-electron property integrals from the MDPROP unformatted file. The one-electron operator  $\hat{O}_1$  is added to the Fock operator at the integral sorting stage:

$$\hat{f}' = \hat{f} + \lambda \hat{O}_1$$

where  $\lambda$  is some perturbation parameter. EXP-T does not assume Kramers symmetry, so both  $\mathcal{T}$ -odd and  $\mathcal{T}$ -even operators are allowed.

Syntax: `oneprop <real L_re> <real L_im> <quoted-string property-name>`

**L\_re, L\_im** real and imaginary parts of  $\lambda$ ;

**property-name** string identifier used to encode property matrix in the MDPROP file (can be also found in the DIRAC output file).

Default: disabled.

Example: add interaction with an external electric field:

`oneprop 1e-5 0.0 "ZDIPLN"`

**x2cmmf** since DIRAC's unformatted files do not contain any information about the relativistic Hamiltonian used, the `x2cmmf` flag **must** be used if the molecular-mean-field X2C Hamiltonian (X2Cmmf) was employed at the DIRAC stage.

Syntax: `x2cmmf`

## Memory management

**compress** enables compression of all data written to disk. The LZ4 algorithm [31] is employed (it provides the fastest decompression to date). Compression can slow down calculations slightly (depends on the particular harddrive), but the disk space used can be reduced dramatically (up to 3 times).

Syntax: `compress`

Default: disabled (except for `disk_usage=4`)

**disk\_usage** indicates which data should be stored on the disk. Note that very intensive disk usage will slow down calculations; however, disk usage is hardly avoidable in case of large tasks.

Syntax: `disk_usage <integer mode>`

Possible values of `<mode>`:

- 0 all data is stored in RAM;
- 1 tensors of rank  $\geq 6$  are stored on disk ( $T_3$  amplitudes etc);
- 2 tensors of rank  $\geq 6$  and  $\langle pp||pp \rangle$  (4 particles) two-electron integrals are stored on disk;
- 3 tensors of rank  $\geq 6$ ,  $\langle pp||pp \rangle$  and  $\langle *p||pp \rangle$  (3 particles) two-electron integrals are stored on disk;
- 4 the same as 3, + compression of all data. Is suitable for extremely large tasks only.

Default: 2 ( $\langle pp||pp \rangle$  and tensors of rank  $\geq 6$  are stored on disk).

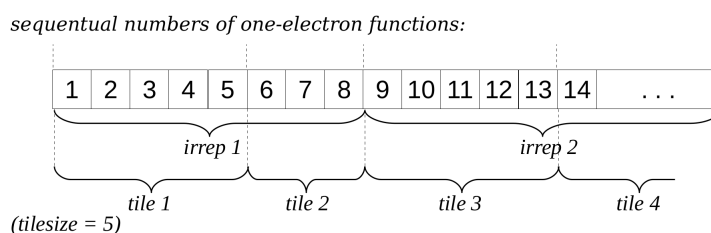
**memory** specifies the amount of memory that EXP-T can use for the job (just for *dynamically* allocated memory).

Syntax: `memory <real size> ( mb || gb )`

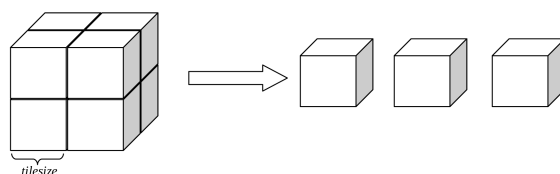
Min value: 10 Mb

Default: `memory 1024 mb` (1 Gb)

**tilesize** the whole set of one-electron functions (spinors or spin-orbitals) is divided into blocks: (1) by irrep; (2) then into sub-blocks with size not exceeding **tilesize** (actually the same as “tiles” in NWChem-TCE):



The  $N$ -dimensional arrays of integrals and amplitudes (tensors) also turn out to be divided into blocks containing  $\sim (\text{tilesize})^N$  elements:





`tilesize` must be large enough to place at least one  $N$ -dimensional array of size  $(\text{tilesize})^N$  in RAM. We recommend using as large `tilesize` as possible, otherwise memory management overheads can become enormous.

Syntax: `tilesize <integer size>`

Default: `tilesize 100`

### *Parallel execution*

**nthreads** number of OpenMP threads. Note that scaling with respect to number of threads is much better for large tasks ( $> 400$  spinors).

Syntax: `nthreads <integer n_omp_threads>`

Default: `nthreads 1` (sequential execution).

*At the moment parallelization is not used at the integral sorting stage, hence OpenMP can accelerate only the amplitude equations solution stage.*

**openmp** the same as **nthreads**.

**openmp\_algorithm** the approach to parallelization. The two parallelization algorithms are implemented in EXP-T:

**external** suits well for the problems with high granularity of tensors; it is recommended for all point groups except for  $C_1$ .

**internal** is recommended for the  $C_1$  symmetry only.

Syntax: `openmp_algorithm ( external | internal )`

Default: `external`

**cuda** enables parallel calculations on NVIDIA GPU (only a single GPU is supported at the moment). Requires `nthreads 1` (the OpenMP+CUDA hybrid model is not implemented yet).

Syntax: `cuda`

Default: CUDA disabled.

## 5 Running typical calculations

*The input and output files discussed in this section can be found in the `examples` directory of the EXP-T distro.*

### 5.1 Ground state energy with CCSD: the CO molecule

*For input/output files see `examples/CO_ccsd`.*

Consider the calculation of the CCSD correlation energy of the CO molecule in the cc-pVDZ [32] basis set.

DIRAC input files:

*(CO.mol)*

```
DIRAC
CO molecule, R = 2.132 bohrs
symmetry C1
C 2 0
      6. 1
C      0.0 0.0 0.0
LARGE BASIS cc-pVDZ
      8. 1
0      0.0 0.0 2.132
LARGE BASIS cc-pVDZ
FINISH
```

*(TRA.inp)*

```
**DIRAC
.TITLE
CO molecule
.WAVE FUNCTION
.4INDEX
**WAVE FUNCTION
.SCF
*SCF
.CLOSED
14
.ERGCNV
1E-12
**MOLTRA
.ACTIVE
all
*END OF INPUT
```

We run DIRAC with the following command:

```
pam --inp=TRA --mol=CO --get="MRCONEE MDCINT" --noarch
```

Note that the `--get` option is used so that `pam` exports the transformed molecular integrals (stored in the MRCONEE and MDCINT files) from DIRAC's scratch directory to the working directory. The `-noarch` option is used in order to prevent creation of a `tgz` archive.

In some cases, it can be convenient to rename the files containing the integrals (this is not mandatory):

```
mv MRCONEE MRCONEE-C1
mv MDCINT MDCINT-C1
```

Now the EXP-T input file `input-C1` is set up:

```
# CO molecule, CCSD/cc-pVDZ
# nonrelativistic, symmetry C1

# task title (of type "string")
title "CO/CCSD/cc-pVDZ"

# print level, default medium
print medium

# max number of iterations
maxiter 30

# convergence threshold (by cluster amplitudes)
conv 1e-9

# target Fock space sector
sector 0h0p

# CC model: ccsd, ccsdt-1, etc
model ccsd

# import integrals from
integrals MRCONEE-C1 MDCINT-C1
```

Running EXP-T:

```
expt.x input-C1
```

The string with the correlation energy can be found at the end of the output. Note that by default EXP-T flushes all output simply to `stdout`.

```
SCF reference energy = -112.820480227130
CCSD correlation energy = -0.298117912040
Total CCSD energy = -113.118598139170
```

## 5.2 Simple atomic FS-CCSD calculation: the Pb atom

*For input/output files see [examples/Pb\\_fs\\_ccsd](#).*

We now turn to simple atomic relativistic calculations employing the FS-CCSD approach. Since wave functions of most low-lying electronic states of one-electron atoms and atomic ions are effectively single-reference, it is not very interesting to apply the multireference methodology to such cases. In contrast, electronic states of the “two-electron” atoms can hardly be simulated within any other approaches except those based on the multireference wave functions. Consider for example the  $6s^26p^2$  low-lying states of the Pb atom. The reference state will be  $\text{Pb}^{2+} 6s^2$ , and one should select  $6p$ -spinors as the active ones (overall 6 spinors).

Pb atom is a purely relativistic system, and one should use four-component Hamiltonian or relativistic pseudopotential approach. The latter allows one to incorporate bulk of the Breit interaction and QED corrections. Here the semilocal valence version of the N.S. Mosyagin’s RECP for Pb is used (see [33] and references therein).

Input file for the FS-CCSD calculation will be as follows:

```
sector 0h2p
nactp 6
maxiter 500
memory 110 gb
conv 1e-7
disk_usage 0
nthreads 8
model ccscd
```

After the FS-CCSD calculation is finished, one can compare the calculated FS-CCSD excitation energies of Pb with their experimentally measured counterparts (7819, 10650, 21458 and 29467 cm<sup>-1</sup>, respectively [34]):

	Level	Re(eigenvalue)	. . .	Rel eigv, eV	Rel eigv, cm-1	deg	symmetry
		-----	. . .	-----	-----		
@	1	-0.8258538771	. . .	0.0000000000	0.000000	1	0g
@	2	-0.7916687782	. . .	0.9302239316	7502.761992	3	0g 1g+ 1g-
@	3	-0.7784232250	. . .	1.2906537953	10409.824894	5	0g 1g+ 1g- 2g+ 2g-
@	4	-0.7298818976	. . .	2.6115306047	21063.414836	5	0g 1g+ 1g- 2g+ 2g-
@	5	-0.6892150215	. . .	3.7181326781	29988.762480	1	0g

The remaining error can be significantly reduced by inclusion of triple excitations [10].

### 5.3 Electronic states of the HgH<sup>2+</sup> molecular ion. Energy denominator shifts technique

*For input/output files see [examples/HgH2+\\_shifts](#).*

In almost every problem involving the exploration of potential energy surfaces using the FS-CC method in a fairly wide range of internuclear distances, the intruder state problem arises. The presence of intruder states usually manifests itself as (but does not not simply arise from!) the appearance of small energy denominators in amplitude equations; the presence of small denominators makes the iterative procedure unstable. A straightforward solution of the intruder-state problem can be obtained by modifying (shifting) all energy denominators in the problematic Fock space sector(s) in such a way that the shifts are significant for ill-defined (nearly zero or positive) energy denominators and remain negligibly small for large negative denominators [5, 7]. Note, however, that this does not imply any modification of the right-hand side of the amplitude equations and, thus, introduces an additional (although controllable) approximation.

The denominator shift technique is implemented in EXP-T; different formulas are available (see Sect. 4, keyword **shifttype**). The example discussed below employs the simplest *real* shifts.

Consider the HgH<sup>2+</sup> molecular ion at  $R = 2.0$  bohr (we partially follow the paper of N. S. Mosyagin et al [35]). The FS-CC equations cannot be solved at all without using denominator shifts or intermediate Hamiltonian technique. Let the active space be comprised of the 8 lowest virtual spinors. The EXP-T input file will look like this:

```
# Test:
```

```

# (1) HgH2+ ion, FSCC scheme: HgH3+ -> HgH2+
# (2) hamiltionian: 2-comp gatchina ECP
# (3) symmetry Cinfv
# (4) sector 0h1p

title "Test HgH3+ -> HgH2+/gatchina ECP/Cinfv"
maxiter 200
conv 1e-9
active -10 -0.5
sector 0h1p

# import integrals from:
integrals MRCONEE-Cinfv MDCINT-Cinfv

# shifts of denominators:

# real shift:
shifttype real

# shift parameters:
# 1. <n> -- attenuation parameter (here: 3)
# 3. <S1> -- shift for all S1 amplitudes (here: -0.5)
# 3. <S2> -- shift for all S2 amplitudes (here: -1.0)
shift 0h1p 3 -0.5 -1.0

```

Approaches to the selection of shift parameters are discussed in [5, 7]. You can also perform IH-IMMS calculations or do Pade extrapolation of the series of effective Hamiltonian matrices to the zero shift limit in order to minimize distortions introduced by the shift [7] (see also Sect. 6.1).

## 5.4 Intermediate Hamiltonian for incomplete main model spaces: the C atom

*For input/output files see [examples/C\\_atom\\_ih-imms](#).*

Let us consider low-lying electronic states of the C atom. Using the NIST ASD database <https://www.nist.gov/pml/atomic-spectra-database> we find that for the states below 80000 cm<sup>-1</sup> the following configurations dominate in wave functions:

- $2s^22p^2$ ;
- $2s^12p^3$ ;
- $2s^22p^13s^1$ ;
- $2s^22p^13p^1$ ;
- $2s^22p^13d^1$ ;
- $2s^22p^14s^1$ .

Within the Fock space coupled cluster formalism, electronic states dominated by the  $2s^12p^3$  configuration (e. g. the  $^5S_2^o$  state, 33735 cm<sup>-1</sup>) can be accessed only in  $1h3p$  or  $0h4p$  sectors. Implementation of corresponding CC models is not available to date, thus we will not consider these states in the further discussion. In contrast, other states of the carbon atom can be easily obtained in the  $0h2p$  Fock space

sector provided that the  $2s^2$  state of the  $C^{2+}$  ion is considered as the Fermi vacuum. For the sake of simplicity we will not also consider electronic states involving shells with principal quantum number  $n = 4$  (the generalization of the IH-IMMS procedure to such states is straightforward).

At this point we have several useful observations:

- active space should comprise at least  $2p$ ,  $3s$ ,  $3p$ ,  $3d$  spinors of the  $C^{2+}$  ion;
- only the  $2p$  shell can be doubly occupied in the target electronic states;
- all target electronic states involve configurations with at least one  $2p$ -electron;
- we can expect that electronic states dominated by the  $3s^2$ ,  $3s^1 3p^1$ , etc configurations will be very high in energy (and even lie well above the  $IP = 90820 \text{ cm}^{-1}$ ). These states arise inevitably in the  $0h2p$  sector since the “classical” FS-CC is formulated for quasicomplete model spaces. Moreover, these *intruder states* will destroy convergence of amplitude equations;
- the linear span of these “malicious” determinants can be considered as the *intermediate space*;
- *main model space* should include only determinants belonging to the  $2p^2$ ,  $2p^1 3s^1$ ,  $2p^1 3p^1$ ,  $2p^1 3d^1$  configurations. These determinants will be dominating in the model vectors representing target electronic states of carbon.

We start actual calculation with the molecular integral transformation in DIRAC:  
(*C.mol*)

```
C atom
doubly augmented triple-zeta basis set (d-aug-cc-pVTZ)
symmetry Dinfh
C 1
      6.      1
C 0.0000000000 0.0000000000 0.0000000000
LARGE EXPLICIT 4 2 2 1 1
# s functions
F 10 2
      8236.00000000 0.00053100 -0.00011300
      1235.00000000 0.00410800 -0.00087800
      280.80000000 0.02108700 -0.00454000
      79.27000000 0.08185300 -0.01813300
      25.59000000 0.23481700 -0.05576000
      8.99700000 0.43440100 -0.12689500
      3.31900000 0.34612900 -0.17035200
      0.90590000 0.03937800 0.14038200
      0.36430000 -0.00898300 0.59868400
      0.12850000 0.00238500 0.39538900
F 4 0
      0.90590000
      0.12850000
      0.04402000
      0.01510000
# p functions
F 5 1
      18.71000000 0.01403100
      4.13300000 0.08686600
```

```

        1.20000000    0.29021600
        0.38270000    0.50100800
        0.12090000    0.34340600
F   4   0
        0.38270000
        0.12090000
        0.03569000
        0.01050000
# d functions
F   4   0
        1.09700000
        0.31800000
        0.10000000
        0.03140000
# f functions
F   3   0
        0.76100000
        0.26800000
        0.09440000
FINISH
      (TRA.inp)
**DIRAC
.TITLE
Carbon atom
.4INDEX
.WAVE FUNCTION
**HAMILTONIAN
.X2Cmmf
.GAUNT
**WAVE FUNCTION
.SCF
*SCF
.CLOSED
4 0
.ERGCNV
1E-12
**MOLTRA
.SCHEME
4
.ACTIVE
all
*END OF INPUT

```

*Note that the .X2Cmmf keyword is used, thus it also must be used in the EXP-T input file.*

Command line:

```
pam --inp=TRA --mol=C --noarch --get="MRCONEE MDCINT MDPROP"
```

Let us now look at the DIRAC output. We find that one-electron energies of our active spinors are (in a.u.):

$$\varepsilon_{2p} \sim -0.86$$

$$\varepsilon_{3s} \sim -0.36$$

$$\varepsilon_{3p} \sim -0.28$$

$$\varepsilon_{3d} \sim -0.23$$

We split these spinors into two subsets. Spinors from the first subset can be doubly occupied in the main model space determinants, and spinors from the second subset can be only singly occupied. In some cases it can be useful to define the third subset of spinors which must be unoccupied in all main determinants. This procedure resembles that used to define active space in the RASSCF method. For the C atom these subsets are:

1.  $2p$ ;
2.  $3s, 3p, 3d$ .

In terms of these two subspaces of active spinors the main model space determinants can be defined using the following directives inside the `ih_imms` block in the EXP-T input file:

- `main_occ 2 0`: determinants in which both electrons occupy spinors from the first subspace, the  $2p^2$  configuration;
- `main_occ 1 1`: one electron occupy spinor from the first subspace ( $2p$ ), the other one occupy spinor from the second subspace ( $3s, 3p$  or  $3d$ ). These determinants correspond to the  $2p^1 3s^1$ ,  $2p^1 3p^1$  and  $2p^1 3d^1$  configurations.

We will rely on the automatic determination of the `frontier_energy` parameter (by default, the uppermost energy of main model space determinants is used). Finally, the EXP-T input file will be as follows:

```
# relativistic CC model
sector 0h2p
model ccscd
nactp 24
x2cmmf

# intermediate Hamiltonian parameters.
# spinor subspaces are defined via energy ranges (in a.u.)
ih_imms
  sectors 0h2p
  subspace energy -1.0 -0.5 # 2p spinors
  subspace energy -0.5 -0.2 # 3s, 3p, 3d spinors
  main_occ 2 0 # 2p^2 determinants
  main_occ 1 1 # 2p3s, 2p3p, 2p3d determinants
end

# memory
memory 4 gb
disk_usage 0

# convergence
maxiter 300
diis 300
conv 1e-9
```



```
# print compositions of model vectors in terms of
# effective occupation numbers of active spinors
print "eff config"
```

Let us take a look at the table with calculated energy levels in the 0h2p sector in the EXP-T output file:

Level	Re(eigenvalue)	...Rel eigv, cm-1	% main	deg	symmetry
-----					
@ 1	-1.2955562077	... 0.000000	100.0	1	0g
@ 2	-1.2954943219	... 13.582372	100.0	3	0g 1g+ 1g-
@ 3	-1.2953712703	... 40.589069	100.0	5	0g 1g+ 1g- 2g+ 2g-
@ 4	-1.2503086362	... 9930.694080	99.9	5	0g 1g+ 1g- 2g+ 2g-
@ 5	-1.1923569864	... 22649.611052	99.8	1	0g
@ 6	-1.0208724411	... 60286.118415	99.9	1	0u
@ 7	-1.0207910577	... 60303.980008	99.9	3	0u 1u+ 1u-
@ 8	-1.0206248742	... 60340.453071	99.9	5	0u 1u+ 1u- 2u+ 2u-
@ 9	-1.0089659280	... 62899.295993	99.9	3	0u 1u+ 1u-
@ 10	-0.9902128248	... 67015.126416	100.0	3	0g 1g+ 1g-
@ 11	-0.9824896577	... 68710.165670	100.0	3	0g 1g+ 1g-
@ 12	-0.9824017917	... 68729.450018	100.0	5	0g 1g+ 1g- 2g+ 2g-
@ 13	-0.9822669729	... 68759.039338	100.0	7	0g 1g+ 1g- 2g+ 2g- 3g+ 3g-
@ 14	-0.9751409822	... 70323.013514	100.0	3	0g 1g+ 1g-
@ 15	-0.9723223910	... 70941.622775	100.0	1	0g
@ 16	-0.9722734205	... 70952.370551	100.0	3	0g 1g+ 1g-
@ 17	-0.9721863073	... 70971.489684	100.0	5	0g 1g+ 1g- 2g+ 2g-
@ 18	-0.9616074654	... 73293.277111	99.8	5	0g 1g+ 1g- 2g+ 2g-
@ 19	-0.9497229655	... 75901.623363	99.9	1	0g
@ 20	-0.9322863070	... 79728.527553	100.0	5	0u 1u+ 1u- 2u+ 2u-
@ 21	-0.9307044048	... 80075.714943	100.0	5	0u 1u+ 1u- 2u+ 2u-
@ 22	-0.9306318565	... 80091.637473	100.0	7	0u 1u+ 1u- 2u+ 2u- 3u+ 3u-
@ 23	-0.9305012392	... 80120.304651	100.0	9	0u 1u+ 1u- 2u+ 2u- 3u+ 3u- ...
@ 24	-0.9303011549	... 80164.218067	100.0	3	0u 1u+ 1u-
@ 25	-0.9302612163	... 80172.983578	100.0	5	0u 1u+ 1u- 2u+ 2u-
@ 26	-0.9302131715	... 80183.528205	100.0	7	0u 1u+ 1u- 2u+ 2u- 3u+ 3u-
@ 27	-0.9264080659	... 81018.652356	100.0	7	0u 1u+ 1u- 2u+ 2u- 3u+ 3u-
@ 28	-0.9244722663	... 81443.511260	100.0	5	0u 1u+ 1u- 2u+ 2u-
@ 29	-0.9243950805	... 81460.451580	100.0	3	0u 1u+ 1u-
@ 30	-0.9243547369	... 81469.305985	100.0	1	0u
@ 31	-0.9218925156	... 82009.701090	99.9	3	0u 1u+ 1u-
@ 32	-0.5545617414	... 162629.487352	9.6	1	0g
@ 33	-0.5088229529	... 172667.991098	0.0	1	0u
@ 34	-0.5088105565	... 172670.711776	0.0	3	0u 1u+ 1u-
@ 35	-0.5087857581	... 172676.154402	0.0	5	0u 1u+ 1u- 2u+ 2u-
...					
Ionization potential 0h2p -> 0h1p = ... = 10.9819 eV = 88575.16 cm <sup>-1</sup>					
Ionization potential 0h1p -> 0h0p = ... = 24.2720 eV = 195766.56 cm <sup>-1</sup>					

The column named “% main” contains total weight of main model space determinants in model vectors describing the given electronic states. It can be seen that these weights are very close to 100% for all target (or main) electronic states. Intermediate states (with weighs of main model space determinants not exceeding several percents) are also obtained as a by-product. However, they can hardly be considered as physical ones (compare their energies with the  $IP_1 \sim 90000 \text{ cm}^{-1}$ ). The greater the weight of main

model space determinants, the less the dependence on the parameters of the applied denominator shifting scheme.

It is worth noting that in some cases convergence of amplitude equations can be achieved only by the introduction of additional active spinors, which are unoccupied in all main model space determinants. These spinors serve as buffer ones. In calculations accounting for triples such an extension of active space can result in an increase of computational cost. So it is recommended to thoroughly choose the upper bound of the active space to make it as small as possible. However, this is not a problem for calculations employing the CCSD model only. Introduction of additional buffer states also greatly improves stability of energy levels with respect to the shifting parameters (see Figures 3 and 4 in [8] for the case of electronic states of the  $\text{Lu}^+$  ion).

## 5.5 Finite-field transition dipole moments calculations: the Rb atom

*For input/output files see `examples/Rb_atom_TDMs_finite_field`.*

See [22, 36, 3] for detailed discussions on the finite field (FF) technique for transition dipole moments. The algorithm for any FF calculation is as follows:

- solve the HF problem for the non-perturbed Hamiltonian (no external fields);
- transform the molecular integrals to the basis of “non-perturbed” one-electron functions;
- perform two FS-CC calculations with these integrals at external fields strengths  $-F$  and  $+F$ ;
- estimate TDMs are estimated using the finite-difference-type formula:

$$\mathbf{d}_{\eta,if}^{FF} = (E_i - E_f) \lim_{\substack{F_\eta \rightarrow 0 \\ F_{\eta'}=0, \eta' \neq \eta}} \frac{\langle \tilde{\psi}_i^{\perp\perp}(-F_\eta) | \tilde{\psi}_f(+F_\eta) \rangle}{2F_\eta} \quad (\eta = x, y, z), \quad (8)$$

where  $\tilde{\psi}_i$  and  $\tilde{\psi}_f$  are model vectors corresponding to initial and final electronic states, respectively.

Consider the FF calculation of TDMs for the  $^2S_{1/2} \leftrightarrow ^2P_{1/2}^o$  and  $^2S_{1/2} \leftrightarrow ^2P_{3/2}^o$  transitions in the Rb atom. The basis set and effective core potential employed were taken from [36]; basis set was reduced to  $[7s7p5d3f2g]$ . The simplest active space required to describe  $^2S_{1/2}$ ,  $^2P_{1/2}^o$  and  $^2P_{3/2}^o$  states of Rb comprised 5s- and 5p-spinors (overall 8 spinors, or 4 Kramers pairs).

Firstly, we perform the Hartree-Fock calculation and subsequent transformation of integrals. Note that transformed integrals over one-electron property operators (in this case, the dipole moment operator) are stored in the MDPROP unformatted file which should be copied from DIRAC scratch to the working directory:

```
pam --noarch --inp=TRA.inp --mol=Rb.mol --get="MRCONEE MDCINT MDPROP"
```

Other integrals are saved to the MRCONEE (one-electron Fock) and MDCINT (two-electron Coulomb) unformatted files. Note that the .PRPTRA option as well as the \*\*PROPERTIES/.DIPOLE specification is required in the TRA.inp input file:

```
**MOLTRA
.PRPTRA
.SCHEME
4
.ACTIVE
energy -100.0 20.0 0.5
**PROPERTIES
.DIPOLE
```

These lines are used to ask DIRAC to calculate and transform dipole moment integrals (these integrals are used later to construct the perturbation due to the external field). Also note that the external uniform electric field lowers spherical symmetry of the atom to  $C_{\infty v}$ .

Now we are ready to run FSCC calculations in EXP-T. At this step we use the `oneprop` directive to add an external field  $\mathbf{F}$  contribution to the Fock operator:

$$f'_{pq} = f_{pq} + (d_x)_{pq}F_x + (d_y)_{pq}F_y + (d_z)_{pq}F_z$$

Here we use only the  $d_z$  component, stored in the MDPROP file in the ZDIPLN record. The operator which is added to the Fock matrix must be fully symmetric. The first EXP-T input file (for field strength  $-F$ ):

```
# title for the task (of type "string")
title "Rb atom -- relativistic EA-CCSD calculation"

# max number of iterations
maxiter 50

# convergence threshold (by cluster amplitudes)
conv 1e-9

# target Fock space sector
sector 0h1p

# active space specification: 8 lowest virtual spinors (5s,5p1/2,5p3/2)
nactp 8

# add the external field contribution to the Fock matrix:
# Fock = Fock + d_z * F_z
# (F_z = 1e-5)
oneprop -1e-5 0.0 "ZDIPLN"
```

For the other field strength  $+F$  it is convenient to reuse two-electron integrals, which are already sorted (the `reuse` option). One-electron integrals depend on the finite perturbation parameter and must be recomputed. Cluster amplitudes converged at  $-F$  can also serve as a good initial guess for the calculation at  $+F$ . This will lead to significant computational savings. Use the `--no-clean` option to prevent the deletion of files containing sorted two-electron integrals and converged amplitudes.

The second EXP-T input file (for field strength  $+F$ ):

```
title "Rb atom -- relativistic EA-CCSD calculation"
maxiter 50
conv 1e-9
sector 0h1p
nactp 8

reuse 2-integrals amplitudes
oneprop +1e-5 0.0 "ZDIPLN"
```

Run EXP-T and save formatted files HEFF with effective Hamiltonian matrices to the working directory:

```
expt.x --no-clean input_F- | tee ccscd_F-.out
mv scratch/HEFF HEFF1
expt.x --no-clean input_F+ | tee ccscd_F+.out
mv scratch/HEFF HEFF2
```

The electronic spectrum is given at the end of the EXP-T output file. Corresponding lines begin with the @ symbol:

	Level	Re(eigenvalue)	. . .	Rel eigv, cm-1	deg	symmetry
@	1	-0.1531234146	. . .	0.000000	2	1/2+ 1/2-
@	2	-0.0959179975	. . .	12555.137832	2	1/2+ 1/2-
@	3	-0.0948635671	. . .	12786.558570	2	1/2+ 1/2-
@	4	-0.0948635506	. . .	12786.562182	2	3/2+ 3/2-

(compare with experimental values  $12578.950 \text{ cm}^{-1}$  and  $12816.545 \text{ cm}^{-1}$  [34]; note that the  $^2P_{3/2}^o$  state is split in the external electric field).

Finally, we turn to the calculation of transition moments. The input file for the `heffman.x` utility is as follows (see Sec. 6.1 for details and explanation):

```
file: HEFF1
file: HEFF2
sector: 0h1p
rep: 1
step: 0.00002
print: 1
```

Run `heffman.x`:

```
heffman.x < ff.inp | tee ff.out
```

Transition moments and Einstein coefficients:

transition	energy, cm <sup>-1</sup>	. . .	d  <sup>2</sup>	d	osc str	A, 10 <sup>6</sup> s <sup>-1</sup>
. . .						
1 -> 2	12555.138	. . .	2.627905	1.62108158	0.100220	10.537579
1 -> 3	12786.559	. . .	5.173064	2.27443710	0.200921	21.911672
2 -> 3	231.421	. . .	0.000000	0.00001167	0.000000	0.000000

Note: this is only the  $|d_z|$  component of the full transition moment  $d$ . It should be mentioned that the small, but non-zero value of  $|d|$  in the last line is an artifact of the FF approach.

Taking into account the degeneracy of the  $^2P_{3/2}^o$  state and the spherical symmetry of the Rb atom, the full transition moments  $|d|$  and full Einstein coefficients can be calculated:

$$A(^2S_{1/2} \leftarrow ^2P_{1/2}^o) = 31.6 \text{ s}^{-1}$$

$$A(^2S_{1/2} \leftarrow ^2P_{3/2}^o) = 32.9 \text{ s}^{-1}$$

(compare with experimental values  $34.0 \text{ s}^{-1}$  and  $37.0 \text{ s}^{-1}$  [34]).

Results can be improved significantly by extending the basis set and active space [36].

## 5.6 Direct approach to transition dipole moment calculations: the Rb atom

*For input/output files see `examples/Rb_atom_TDMs_direct`.*

The direct approach to transition moment calculations consists in the substitution of the CC wave functions  $|\psi_i\rangle = \{e^T\} |\tilde{\psi}_i\rangle$  and  $|\psi_f\rangle = \{e^T\} |\tilde{\psi}_f\rangle$  into the expression for the matrix element  $O_{if} = \langle\psi_i|O|\psi_f\rangle$ . Resulting infinite summations are truncated at some power of  $T$ . Detailed description of the theoretical

background is given in [4]. Actually the same approach was previously developed for atomic applications, see the papers [37, 38, 39] (and references therein).

Let us apply this direct technique to calculate transition dipole moments in Rb. Since property matrix elements are evaluated analytically, there is no need to reduce the symmetry from  $D_{\infty h}$  to  $C_{\infty v}$ . We again begin with the DIRAC step to obtain unformatted files with transformed molecular integrals:

```
pam --inp=TRA --mol=Rb --noarch --get="MRCONEE MDCINT MDPROP"
```

The MDPROP file contains three entries XDIPLN, YDIPLN and ZDIPLN representing matrices of the  $d_x$ ,  $d_y$  and  $d_z$  components of the dipole moment operator. For some reasons the XDIPLN and ZDIPLN matrix elements are purely imaginary (this was found in the series of preliminary numerical experiments), appealing to complex arithmetics in CC calculation. Such a situation is quite typical.

Thus we recommend to perform CC calculation of properties in two steps. At the first step we run the usual FS-CC calculation with the real numbers employed. EXP-T input file looks like:

```
title "Rb atom -- relativistic EA-CCSD calculation"
maxiter 50
conv 1e-9
sector 0h1p
nactp 8
disk_usage 0
```

At the second step we calculate transition moments. We should turn on complex arithmetics and restart the calculation from the pre-sorted integrals and converged amplitudes (they will be automatically expanded to the complex arithmetics):

```
title "Rb atom -- relativistic EA-CCSD calculation"
maxiter 50
conv 1e-9
sector 0h1p
nactp 8
disk_usage 0
```

```
reuse 2-integrals amplitudes
arith complex
print "model vectors"
```

```
mdprop "XDIPLN" sym 1u+ approx 2 2 scheme hermitian
mdprop "XDIPLN" sym 1u- approx 2 2 scheme hermitian
mdprop "YDIPLN" sym 1u+ approx 2 2 scheme hermitian
mdprop "YDIPLN" sym 1u- approx 2 2 scheme hermitian
mdprop "ZDIPLN" sym 0u approx 2 2 scheme hermitian
```

Note that the instruction `print "model vectors"` was added. It prints additional information about electronic energy levels and is mandatory for further successful processing of the output file with the `expt_spectrum.py` script (see Sect. 6.4).

Running EXP-T:

```
expt.x --no-clean ccsd.inp > ccsd.out
expt.x --no-clean tdm.inp > tdm.out
```

The second run of EXP-T typically produces huge output files since all possible pairs of transition matrix elements are calculated. The required TDM values can be found in it manually or extracted using the `expt_spectrum.py` script:

```
expt_spectrum.py ccscd.out -irep 1/2g+
```

where the `-irep` option defines the irrep to which the initial states belong. The output will be as follows:

```
initial irreps:  ['1/2g+']
initial states:  all
final irreps   :  all
final states   :  all

transitions  1/2g+  ->  1/2u+

      e_i,cm^-1  e_f,cm^-1  . . .  |d|,a.u.  osc.str.
1 ->  1      0.0000 12555.1431 . . .  1.757863  0.117846
1 ->  2      0.0000 12786.5663 . . .  2.480855  0.239046
      . . .
transitions  1/2g+  ->  1/2u-
      . . .
      e_i,cm^-1  e_f,cm^-1  . . .  |d|,a.u.  osc.str.
1 ->  1      0.0000 12555.1431 . . .  2.485994  0.235693
1 ->  2      0.0000 12786.5663 . . .  1.754230  0.119523
      . . .
transitions  1/2g+  ->  3/2u+
      . . .
      e_i,cm^-1  e_f,cm^-1  . . .  |d|,a.u.  osc.str.
1 ->  1      0.0000 12786.5663 . . .  3.038415  0.358569
```

One can see that the direct technique in the quadratic approximation (approx 2 2) overestimates transition moments by  $\sim 9\%$  (compared to the finite-field approach). It can be useful to recalculate transition moments in the linear approximation (approx 1 0); for the particular case of the Rb atom it gives nearly the same answers. This is not a surprising result since cluster amplitudes are not large ( $< 0.07$ ), ensuring even the linear approximation to work fine.

## 5.7 «High-spin» CCSD for open shell systems

*For input/output files see [examples/02\\_highspin](#).*

The example considered in this subsection is borrowed from the DIRAC program manual [17]. Let us calculate the energy of the ground (triplet) state of the  $O_2$  molecule.

The DIRAC input file contains directives for the HF calculation and subsequent integrals transformation:

```
(O2.mol)
```

```
test of open-shell CCSD calculation
molecular oxygen at eq distance taken from NIST
automatic symmetry detection: DIRAC will identify the Dinfh group
C   1           A
      8.      2
```

```

0      0.0      0.0      0.60376
0      0.0      0.0     -0.60376
LARGE BASIS cc-pVDZ
FINISH

```

(*TRA.inp*)

```

!
! calculation of the triplet ground state of molecular oxygen
! (Dirac-Coulomb Hamiltonian)
**DIRAC
.TITLE
molecular oxygen -- ground state
.WAVE F
.4INDEX
**WAVE FUNCTIONS
.SCF
*SCF
.CLOSED SHELL
6 8
.OPEN SHELL
1
2/4,0
*END OF

```

DIRAC writes spinor occupation numbers to the `MRCONEE` unformatted file, but only spinors belonging to closed shell (the `.CLOSED_SHELL` keyword) are labeled as occupied. This is why EXP-T will calculate the energy for the  $O_2^{2+}$  cation without manually specified occupation numbers.

EXP-T provides two ways to set the occupation numbers of spinors:

- by setting the number of occupied spinors in each irrep (the `occ_irreps` keyword). For the example under consideration:

```

occ_irreps [1/2g+]:3 [1/2g-]:2 [3/2g+]:0 [3/2g-]:1
occ_irreps [1/2u+]:2 [1/2u-]:2 [3/2u+]:1 [3/2u-]:1

```

Note that the 1s-orbitals of oxygen atoms are frozen here, and the corresponding electrons should not be accounted for in the `occ_irreps` instructions. For the example discussed:

- 3 electrons occupy the lowest spinors belonging to the 1/2g+ irrep;
- 1/2g-, 1/2u+, 1/2u-: 2 electrons in each irrep;
- 3/2g-, 3/2u+, 3/2u-: 1 electron in each irrep.

- you can also specify the occupation number for *each* spinor explicitly:

```

occ 1 1 1 1 0 0 0 0 0 0 0 0 0 0 1 1 0 0 0 0 0 0 0 0 0 0 0 0 1 1 1 0 0 0 0 0 0 0 0 0 ...

```

To identify spinors which should be populated in the electronic state under consideration, we again recommend starting the calculation with the default occupation numbers, then interrupting the task, finding information about spinors and restarting the calculation with the correct occupation numbers.

*We recommend to use the `dirac_mointegral_export` program from DIRAC to process the `MRCONEE` unformatted file and get such a string of occupation numbers.*

Note that, in fact, non-canonical orbitals are used, therefore the Fock matrix is not diagonal and the vacuum determinant energy  $\langle \Phi_0 | H | \Phi_0 \rangle$  is not equal to the SCF energy value obtained before:

```
Total SCF energy = -149.686661451842
...
sorting one-electron integrals ...
Fock matrix reconstruction ...
SCF energy (energy of reference determinant) = -149.718144633810 a.u.
SCF energy (energy of reference determinant) was updated:
  old energy = -149.686661451842 a.u.
  new energy = -149.718144633810 a.u.
...
      SCF reference energy = -149.718144633810
      CCSD correlation energy = -0.366958682652
      Total CCSD energy = -150.085103316462
```



## 6 Utility programs

### 6.1 heffman.x – manipulations with effective Hamiltonian matrices

The `heffman.x` program (written by A. Zaitsevskii) is designed to perform manipulations with FS-RCC effective Hamiltonians matrices. Implemented features are:

- the finite-field technique for transition dipole moments calculations [22, 36, 3];
- extraction of spin-orbit interactions from full-relativistic models by projection [5];
- Pade extrapolation of series of effective Hamiltonians [7].

`heffman.x` reads matrices of effective Hamiltonians from formatted files supported by both EXP-T and the latest versions of DIRAC.

- to compute finite-field transition moments [36, 3] two files with effective Hamiltonians must be provided, calculated at field 1 and field 2;
- to separate spin-orbit interactions by projection, two files with effective Hamiltonians must be provided, the first for spin-orbit (nearly) switched off and the second for spin-orbit switched on.

*In this case you cannot freeze spinors at the FS-CC step!*

- to perform Pade extrapolation of the series of effective Hamiltonians, you have to put a sequence of effective Hamiltonians to a single file using the `cat` command:

```
cat heff_n_eq_1 heff_n_eq_2 heff_n_eq_3 > some_file_name
```

Recall that each Hamiltonian is calculated at its own attenuation parameter  $n$ . You can also perform extrapolation before TDM or SO calculation, just use such “composite” files with effective Hamiltonians.

To run `heffman.x` program, input file containing the list of instructions must be redirected to `stdin`:

```
heffman.x < input_file
```

`heffman.x` input files are very similar to EXP-T input files, but keywords are separated from their arguments with the `:` symbol, and the symbol `#` at the beginning of a comment must be placed in the first position of the line.

List of instructions:

**file:** file with the first effective Hamiltonian or with a sequence of heff’s to be extrapolated, e. g.

- heff for the first field value;
- heff for the spin-orbit interaction (nearly) switched off;
- simply heff you want to get the eigenstates;
- sequence of heff’s you want to Pade-extrapolate.

Syntax: `file: <string path-to-first-heff>`

If you are doing finite-field transition moment calculations or SO separation, you have to supply the second file (see the next item).

**file:** heff for another field value, or heff for the spin-orbit switched on, respectively. If there is no second file, the effective Hamiltonian eigenvectors and eigenvalues are written to the formatted file HEFFEVF.  
 Syntax: `file: <string path-to-second-heff>`

**sector:** the Fock space sector you are interested in (heff files for higher sectors contain several heff matrices).  
 Syntax: `sector: <H>h<P>p`  
 Example: 0h1p, 1h0p, 2h0p, 0h2p, 1h1p.

**rep:** irreducible representation you are interested in. As a rule, `rep: 1` stands for the fully symmetrical rep.  
 Syntax: `rep: <integer n>`  
*Enumeration of irreps begins from 1!*

**main:** for the FF TDM calculations or Pade extrapolation: simply the number of lowest states or the range of states of given sector and symmetry you want to see in the output file. For the SO extraction by the projected approximant construction [7] this keyword defines the subspace of states used for projection.  
 Syntax: `main: (<integer number> | <integer number1>-<integer number2>).`  
 Default: all states.  
 Example: `main: 10` (or, equivalently, `main: 1-10`)

**[L/M]** *(optional)* to perform Pade extrapolation, you have to indicate which Pade approximant [L/M] should be constructed ([0/1], [1/1], [0/2] etc). You should have L+M+2 effective Hamiltonian matrices to build the [L/M] approximant. You can cut off all states above subspace done by the `main` keyword (see above); to do this, add the `cut` keyword.  
 Syntax: `[L/M] [cut]`  
 Default: Padé extrapolation disabled  
 Example: `[0/1] cut`

**step:** *(only for FF calculations.)* Difference of field strenghts (a.u.) in two finite-field calculations. The presence of this line activates the FF TDM calculation mode (do not use this keyword in other types of calculations).  
 Syntax: `step: <real value>`

**scale:** *(only for SO calculations.)* Fraction of effective spin-orbit retained in “scalar” calculations to get good relativistic symmetries (typically of order  $10^{-4}$ ). Omit this line if you do not want to diabatize anything.  
 Syntax: `scale: <real value>`

**ground:** ground state energy (a.u.). Useful only when you have to compute energies with respect to some state (normally ground) which belongs to another rep or sector.  
 Syntax: `ground: <real energy>`  
 Default: `ground: 0.0`

**print:** print level. **print:** 0 or **print:** 1 are normally ok; enlarging this number, you can get any amount of superfluous information listed.  
 Syntax: **print:** <integer level>  
 Default: **print:** 1

**Bloch** activates the computation of finite-field transition dipoles with Bloch effective Hamiltonian eigenvectors (note: TDM matrices will be non-Hermitian, this has no physical meaning). Otherwise, FF computations are performed with des Cloizeaux effective Hamiltonian eigenvectors (“hermitization”).  
 Syntax: **Bloch**  
 Default: “hermitization” is enabled in finite-field calculations

When using any of the techniques implemented in the `heffman.x` program, please, cite the corresponding paper.

## 6.2 `expt_transform_natorb.x` – transformation of quasi-natural spinors to the AO basis

Having model vectors  $|\tilde{\psi}_i\rangle$  we can construct approximate density  $d_{pq} = \langle \tilde{\psi}_i | a_p^\dagger a_q | \tilde{\psi}_i \rangle$  and transition density matrices  $d_{pq} = \langle \tilde{\psi}_i | a_p^\dagger a_q | \tilde{\psi}_j \rangle$  and then calculate “quasi-natural” (transition) molecular spinors (NS and NTS, respectively). These operations can be performed by the EXP-T itself (see Sec. 4, keyword `natorb`). EXP-T stores NS and NTS expanded *in the basis of molecular spinors* in formatted files named `NATORB*.dat`. To use visualization tools one have to transform NS or NTS to the *AO basis*. This transformation can be performed by the `expt_transform_natorb.x` utility.

`expt_transform_natorb.x` requires two command-line arguments:

- path to the DIRAC output file containing molecular spinors expanded in the basis of atomic orbitals;
- path to the `NATORB*.dat` formatted file produced by EXP-T and stored in its scratch directory (contains natural spinors expanded in the basis of molecular spinors).

To ask DIRAC to print molecular spinors (vectors) to the output, enable the `.ANALYZE` module in the `**DIRAC` section and then add the following text to the `**ANALYZE` section of the DIRAC `.inp` input file [40]:

```
**ANALYZE
.PRIVEC
*PRIVEC
.AOLAB
.VECPRI
all
```

(`.AOLAB` = “print vectors in the AO basis”). Note that for point groups with inversion one must add the second string specifying the range of molecular spinors (e. g. `all`).

Running `expt_transform_natorb.x` (for example):

```
expt_transform_natorb.x dirac.out NATORB_0h1p_1:1.dat > nts.out
```

The transformed spinors are flushed to `stdout` again in the DIRAC four-column format and can be redirected to file.

### 6.3 expt2pam.x – input file format converter

EXP-T does not provide subroutines for solution of Hartree-Fock equations and integral transformation, it completely relies on molecular integrals calculated with the help of any other quantum chemistry software. Thus EXP-T input file do not contain any information on molecular geometry, basis set and pseudopotentials. However, to simplify interaction with the third-party software, the special file format was developed. It is designed to be quite flexible and free of any format restrictions typical for software written in Fortran.

The EXP-T-style input files containing information on molecular geometry, basis sets and pseudopotentials are recognized by the `expt2pam.x` program, which can produce input files for the following software:

- DIRAC [1, 2]: option `-dirac`;
- CFOUR [41]: option `-cfour`;
- OneProp [6]: option `-oneprop`.

The input file format closely resembles that of NWChem [42, 43, 44, 45], but is substantially simplified. The most important points on the format to be emphasized are:

- only Cartesian coordinates for molecular geometry definition are available to the moment;
- primitive Gaussian functions can be defined without the superfluous contraction coefficient 1.0;
- primitive Gaussian functions representing the uncontracted part of the basis set with the given angular momentum  $L$  can be placed into the same  $L$ -block.

Below the example of such an input file demonstrating the main features of the `expt2pam` format is presented (the  $\text{UO}_2$  molecule [46]):

```
#
# Uranium dioxide molecule UO2
#
geometry units angstrom
  U  0.0  0.0  0.000
  O  0.0  0.0  1.775
  O  0.0  0.0 -1.775
end

#
# Contracted basis set adapted for the 28-in-core GRPP by N.S. Mosyagin
#
basis
U S
11931.71300000
6539.04200000
3678.23270000
2139.54940000
1288.45330000
792.07718000
484.69932000
298.00127000
186.73959000
120.33238000
```

75.85031400  
49.22312100  
30.97937000  
19.33898600  
11.90917900  
7.28108690  
4.52381560  
2.69147870  
1.62933420  
1.02810670  
0.60588439  
0.35564698  
0.20180019  
0.12481356  
0.06383616

U P

8256.41640000  
4196.77840000  
2191.89420000  
1174.82830000  
644.61478000  
361.41388000  
206.27034000  
119.33670000  
70.14308600  
41.70407000  
24.70288000  
14.49639800  
8.57587000  
4.98086080  
2.84040830  
1.59903720  
0.86476597  
0.45724205  
0.23893352  
0.11879300  
0.05700662

U D

6012.79360000  
2754.36670000  
1351.96790000  
699.79805000  
377.01141000  
209.73941000  
119.30191000  
69.11171400  
40.43241500  
23.65423900  
13.80639900  
8.06231670

```

4.66375400
2.63565040
1.45796000
0.77481216
0.37248472
0.17195534
0.07613361
U F
1163.36020000
573.50499000
285.71163000
136.47329000
69.43427500
36.84465700
19.84804900
10.72168500
5.70450120
2.92433440
1.43960400
0.67385930
0.29434970
0.11323985
U G
28.78919130    0.00068974   -0.00118120   -0.00737416    0.00494647   -0.10867784
14.01320380   -0.00898795   -0.05421964    0.17284128   -0.36594951   -0.33163329
 6.82095857    0.07975524    0.18134441   -0.50920321    1.20716202    1.79274020
 3.32011698    0.29993353    0.65729862   -0.50617914   -0.67702022   -2.65141994
 1.61607443    0.39302861    0.04007231    1.01049051   -0.71780643    2.66362756
 0.78662787    0.34151054   -0.44799971    0.05077223    1.59628888   -2.01035588
 0.38289289    0.18576214   -0.38383279   -0.74551549   -1.12509753    0.90492997
U H
14.01320380   -0.02449353   -0.07337288   -0.15906456   -0.23132505
 6.82095857    0.10594999    0.30442614    0.71623431    1.22980099
 3.32011698    0.35765256    0.65468802    0.09614021   -1.24473080
 1.61607443    0.43019757   -0.18764249   -0.95514471    0.32540556
 0.78662787    0.31957043   -0.48353526    0.41946211    0.73545263
 0.38289289    0.10197395   -0.22548628    0.48672026   -0.90679010
U I
 6.82095857    0.12524957   -0.37984959    0.81416792
 3.32011698    0.42961205   -0.61109425   -0.35518331
 1.61607443    0.42313291    0.38916709   -0.73501069
 0.78662787    0.31396902    0.50454838    0.88347742
end

#
# Relativistic pseudopotential (RPP) for Uranium by N.S. Mosyagin
# 28e in core, QED+Breit are included
#
ecp

```

U nelec 28

U UL

1	573.3050904771354	-11.40084159918683
1	192.8309334143903	-7.097553073552547
1	59.69944003435170	-28.01857233638748
1	41.19441327874497	42.95299466064716
1	27.48466038227223	-39.29896548592660
1	17.41575927233871	21.07523831226354
1	10.74156012298913	-8.338244516015038
1	6.516110723607048	3.069168416643151
1	4.072460983953957	-1.269035430883378
1	2.593752889495458	0.4038040550003643
1	1.642108539873937	-0.7510043731679161E-001
1	0.5908313234915240	0.3890633153407208E-002

U S

0	197.0298350128211	6.000000000000000
1	129.5661840079536	-355.1867566615911
1	93.02818620674168	1191.419958549814
1	66.13198912807648	-1657.083906766264
1	45.36994786350133	1304.226236566319
1	31.03973237770222	-448.9389445476668
1	21.15323065428634	86.95891078559328
1	8.842323178530615	-7.379538028367257
1	2.503929576228269	3.473180786461057
2	2.925942781684598	-5.455412335112918

U P

0	8.311409755029183	5.000000000000000
1	126.5274319867533	-10.06000092823524
1	85.18677663478607	70.55297376279486
1	51.21216731114048	-221.8073735731159
1	29.49108937084788	312.1302683559188
1	17.84600190857478	-299.1627976468299
1	5.463491362893393	229.1321036359295
2	8.266178701884957	-440.5446582608856
2	5.564984596440512	-230.2801015020814
2	3.621496981299310	0.6144684865466843

U D

0	63.75445017844640	3.000000000000000
1	35.83829800943973	-244.0643648227415
1	25.77961295248244	369.6289272300128
1	16.62718251626653	-66.05286509307552
2	21.10083097720674	-511.0304327796694
2	13.00689068383810	209.7715531529684
2	7.652250767129301	-56.31696437943174
2	4.429977591227489	19.86068552036704
2	2.777850799855992	-8.087414881056247
2	1.804331049757116	2.539779591468687
2	1.174834421468355	-0.5000680379316691
2	0.7571835654831253	0.4510869608679968E-001

end

```

#
# spin-orbit part of RPP for Uranium
#
so
U P
  1 126.5274319867533 -60.8272897577457000
  1 85.18677663478607 144.881442506022000
  1 51.21216731114048 -174.959781119600000
  1 29.49108937084788 113.392635098503000
  1 17.84600190857478 -60.8426035265438000
  1 5.463491362893393 45.8248263173737000
  2 8.266178701884957 -82.3448048559949000
  2 5.564984596440512 -47.9408659655601000
  2 3.621496981299310 0.4919304400803720
U D
  1 35.83829800943973 -0.4757330698863370
  1 25.77961295248244 -8.8286299074417900
  1 16.62718251626653 9.6090737588470800
  2 21.10083097720674 14.829424758465000
  2 13.00689068383810 -30.085848351789200
  2 7.652250767129301 10.782019233677400
  2 4.429977591227489 -3.9646231214668700
  2 2.777850799855992 1.4116480556389400
  2 1.804331049757116 -0.3371713502943750
  2 1.174834421468355 0.0452391741906467
  2 0.7571835654831253 -0.0020991859739297
U F
  1 573.3050904771354 1.9478068936173300
  1 192.8309334143903 0.3189229591513530
  1 59.69944003435170 1.1230953284521100
  1 41.19441327874497 -2.2059715944841200
  1 27.48466038227223 2.4430555431733500
  1 17.41575927233871 -1.7928190693741500
  1 10.74156012298913 1.0519241531739200
  1 6.516110723607048 -0.5026634876599670
  1 4.072460983953957 0.2165908956875290
  1 2.593752889495458 -0.0639500309090571
  1 1.642108539873937 0.0107075321136888
  1 0.5908313234915240 0.0000807064226547
end

#
# basis for oxygen: aug-cc-pVQZ-DK
#
basis
O S
  61420.00000000 0.00019890 -0.00004520

```



	9199.00000000	0.00088840	-0.00020260
	2091.00000000	0.00394250	-0.00089480
	590.90000000	0.01560720	-0.00360580
	192.30000000	0.05294610	-0.01230330
	69.32000000	0.14643820	-0.03646840
	26.97000000	0.30541480	-0.08316710
	11.10000000	0.39799790	-0.15217400
	4.68200000	0.21643540	-0.11462710
	1.42800000	0.01753570	0.29002590
	0.55470000	-0.00249230	0.58584370
	0.20670000	0.00095070	0.27673420
O S			
	1.42800000		
	0.55470000		
	0.20670000		
	0.06959000		
O P			
	63.42000000	0.00611070	
	14.66000000	0.04189570	
	4.45900000	0.16123290	
	1.53100000	0.35667520	
	0.53020000	0.44818370	
	0.17500000	0.24505420	
O P			
	1.53100000		
	0.53020000		
	0.17500000		
	0.05348000		
O D			
	3.77500000		
	1.30000000		
	0.44400000		
	0.15400000		
O F			
	2.66600000		
	0.85900000		
	0.32400000		
O G			
	1.84600000		
	0.71400000		
end			
#			
# Empty-core semilocal RPP for oxygen by N.S. Mosyagin			
#			
eCP			
O nelec 0			
O UL			
1	2.443097724280e+02	1.369170316080e-01	

```

1      8.520362677383e+01      -2.852592197455e-01
2      1.054731223008e+02       2.684494987739e+00
2      1.825657247757e+01      -9.433884948610e-03
2      4.806589859822e+00      -1.366233123930e-03
2      1.753580551235e+00       4.456314085999e-04
2      6.566864682586e-01      -2.781240176237e-04
2      4.686645649504e-01       3.558106708362e-04
0 S
1      1.376748432210e+02       5.591554374814e-02
1      1.378552088359e+01       3.868632083368e-03
2      6.768869843542e-01       5.419543370664e-04
2      4.618614187585e-01      -3.882304906071e-04
end

so
0 P
1      2.443097724280e+02      -9.027082481378e-02
1      8.520362677383e+01       2.802454585393e-01
2      1.054731223008e+02      -2.610156015857e+00
2      1.825657247757e+01       1.266811741578e-02
2      4.806589859822e+00       2.570019532778e-03
2      1.753580551235e+00       2.973424726019e-04
2      6.566864682586e-01       6.007087622745e-05
2      4.686645649504e-01      -5.673502079255e-05
end

```

## 6.4 `expt_spectrum.py` – a program for extraction of transition moments from EXP-T output files

EXP-T calculations of transition matrix elements can produce huge output files. To simplify their analysis and extraction of subsets of matrix elements needed for a particular problem, the `expt_spectrum.py` script is provided. It is written in Python 3 and requires the pre-installed NumPy library.

Options of the `expt_spectrum.py` script are as follows:

```

$ expt_spectrum.py --help
usage: expt_spectrum.py [-h] [-u UPPER] [-irep INITIAL_IRREP] [-frep FINAL_IRREP]
                        [-i INITIAL_STATE INITIAL_STATE] [-f FINAL_STATE FINAL_STATE]
                        [-H] [-s] [-ev] filename

```

parses exp-t output files and collects information about electronic transitions and their dipole moments

positional arguments:

filename

optional arguments:

```

-h, --help          show this help message and exit
-u UPPER            upper energy limit for the electronic states considered
                    (cm-1 or ev)
-irep INITIAL_IRREP irrep of initial electronic states

```

```

-frep FINAL_IRREP      irrep of final electronic states
-i INITIAL_STATE INITIAL_STATE
                        initial electronic state
-f FINAL_STATE FINAL_STATE
                        final electronic state
-H                      force hermiticity of transition moments
-s                      print detailed information on electronic spectrum
-ev                     use electron-volts units for energy

```

Names of irreducible representations are common for the EXP-T package and are listed in Appendix C.

For example, let us consider allowed  $E1$ -transitions in the AcF molecule. Its electronic states were thoroughly studied in [19]. Suppose that calculated transition moments are stored in the EXP-T output file named `tdms.out`. The following command should be used to show *all* possible allowed transitions from the ground state ( $\Omega = 0^+$ ):

```
expt_spectrum.py tdms.out -i 0 1
```

Note that DIRAC does not discern  $0^+$  and  $0^-$  states, they both are denoted as 0. The ground state is the first (1) in the irrep with name 0.

To calculate radiation lifetime of an excited state and estimate branching ratios during its decay, one should obtain information on transition dipole moments between this excited state and all states lying below it. For the particular case of the AcF molecule, the most strong transition from the  $X0^+$  ground state is the transition to the (8)1 state. Thus this excited state seems to be the most accessible in experiment. To extract all information about transitions from (8)1 to the low-lying states, one can use the following command:

```
python expt_spectrum.py tdms.out -i 1+ 8 -u 26200
```

Here the `-u` option is used to restrict the range of final states to those lying below (8)1 ( $\approx 26170 \text{ cm}^{-1}$ ).

The `expt_spectrum.py` routine can be easily combined with Unix `grep` and `awk` utilities to easily extract transition dipole moment functions or even surfaces from a large set of EXP-T output files.

## 6.5 expt\_diatomic.x – rotational-vibrational levels and properties of diatomic molecules

If one has a potential energy curve  $U(R)$  for a diatomic molecule, one can solve the radial Schrödinger equation and obtain rovibrational levels and wavefunctions as well as any other properties (molecular constants, transition moments, Franck-Condon factors). The radial Schrödinger equation is written as:

$$\left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \frac{J(J+1)}{2\mu R^2} + U(R) \right] \psi_{vJ}(R) = E_{vJ} \psi_{vJ}(R), \quad (9)$$

where

- $\mu = \frac{M_1 M_2}{M_1 + M_2}$  – reduced mass,
- $v$  – vibrational quantum number,
- $J$  – rotational quantum number.

Normally this second-order differential equation is solved numerically using some mesh of radial points (see, for example, [47, 48, 49]). Within the current implementation, the  $U(R)$  function is interpolated using the cubic natural spline. The matrix version of either the Numerov method [50] or the 2nd order finite-difference method [47] is used to perform integration. Only bound states can be treated to the moment.

### 6.5.1 Input file syntax

The syntax of input files for the solver is quite similar to that of the coupled-cluster program. Single line comments start with the '#' symbol. The following directives are allowed:

**masses** masses of isotopes  $M_1$  and  $M_2$  (in amu).  
Syntax: `masses <float M1> <float M2>`

**charge** net charge of the molecule  $q$ . For charged molecules the “charge-modified reduced mass” formula [51, 49] is used:

$$\mu = \frac{M_1 M_2}{M_1 + M_2 - m_e q}, \quad (10)$$

where  $m_e$  stands for the electron mass. Can be useful for light molecular ions.

Syntax: `charge <integer q>`

**viblevels** range  $[v_{min}, v_{max}]$  of vibrational levels of interest.

Syntax: `viblevels <integer vmin> <integer vmax>`

Default: `viblevels 0 0`

**rotlevels** range  $[J_{min}, J_{max}]$  of rotational levels of interest.

Syntax: `rotlevels <integer Jmin> <integer Jmax>`

Default: `rotlevels 0 0`

**grid\_size** number of radial mesh points.

Syntax: `grid_size <integer npoints>`

Default: `grid_size 300`

**solver** integration algorithm:

`solver numerov` Numerov method [50, 49] (default)

`solver fd2` 2nd order finite-difference method [47]

**mapping meshkov08** `<float ra in Angstroms> <float beta>`

mapping formula for the radial variable (disabled by default). Reduced variable mapping first proposed by V. V. Meshkov and co-authors [47]:

$$y(r) = \frac{r^\beta - r_a^\beta}{r^\beta + r_a^\beta} \quad y \in [-1, 1] \quad (11)$$

*Mapping is available only for the finite-difference solver (`solver fd2`).*

**write\_psi** flush wavefunctions  $\psi_{Jv}(R)$  to the formatted text files (disabled by default).

**potential** point-wise potential energy curves and/or property matrix element. The first ( $r$ ) and the second ( $U_1(r)$ ) columns are mandatory. The third (property) and the fourth ( $U_2(r)$ ) columns are optional. If two potentials are specified, transition matrix elements will be calculated. To calculate Franck-Condon factors, use  $M(r) = 1$  in the third column.

Syntax:

```

potential <units of distance> <units of energy>
  <float r> <float U1(r)> [<float M(r)> [<float U2(r)>] ]
  . . .
end

```

Allowed units of distance are: `angstrom`, `atomic`, `bohr`, `au`.

Allowed units of energy are: `cm-1`, `cm`, `atomic`, `hartree`.

### 6.5.2 Example: Franck-Condon factors for the $\text{AcOH}^+$ molecular ion

To estimate the suitability of the molecule for the direct laser cooling one should calculate vibrational branching ratios and Franck-Condon factors for the working electronic transition. Recently the  $\text{AcOH}^+$  molecular ion was proposed as a candidate for direct laser cooling [52].

This molecule is linear in both the ground  $(1)1/2$  and the first excited  $(1)3/2$  electronic states. If we neglect the anharmonic couplings between stretching and bending modes, the total FCF between the  $(v'_1, v'_2, v'_3)$  and the  $(v''_1, v''_2, v''_3)$  vibrational states can be factorized:

$$\text{FCF} = |\langle v'_1 v'_3 | v''_1 v''_3 \rangle|^2 \times |\langle v'_2 | v''_2 \rangle|^2 \quad (12)$$

The latter factor is the one-dimensional bending mode FCF and it is expected to be very close to unity since the corresponding sections of potential energy surfaces are perfectly parallel to each other. The overlap integral over the  $v_3$  stretch mode is expected to be nearly equal to unity and, which is more important, this factor will be the same for the  $(v'_1, v'_2, 0)$  and  $(v''_1, v''_2, 0)$  vibrational states analyzed here since this stretching mode is not excited in the states under consideration. Thus the total FCF can be approximated with the squared one-dimensional  $\langle v'_1 | v''_1 \rangle$  overlap integral. To calculate this integral one should solve the radial Schrödinger equation, considering the OH group as a pseudoatom.

The input file for the `expt_diatomic.x` program:

```

#
# calculation of Frank-Condon factors for the (1)1/2-(1)3/2 transition in AcOH+
# potential curves were calculated by the relativistic FS-CCSD(Oh1p) method,
#
# for more details, see:
# A. Oleynichenko, L. V. Skripnikov, A. V. Zaitsevskii, V. V. Flambaum
# Laser-coolable AcOH+ ion for CP-violation searches (2022)
# arXiv:2112.02307 [physics.atom-ph]
#
#           Ac           OH
masses 227.028000 17.003000
rotlevels 0 0
viblevels 0 5

# r      potential1(r)  property(r)=1.0  potential2(r)
# units:  dist    energy
potential atomic atomic
0.340150702E+01 -0.451045595E+03  1.0 -0.451004746E+03
0.349599333E+01 -0.451064998E+03  1.0 -0.451025470E+03
0.359047964E+01 -0.451079018E+03  1.0 -0.451040834E+03
0.368496594E+01 -0.451088543E+03  1.0 -0.451051696E+03
0.377945225E+01 -0.451094322E+03  1.0 -0.451058791E+03
0.387393856E+01 -0.451096994E+03  1.0 -0.451062746E+03

```

```

0.396842486E+01  -0.451097103E+03  1.0  -0.451064095E+03
0.406291117E+01  -0.451095111E+03  1.0  -0.451063297E+03
0.415739747E+01  -0.451091413E+03  1.0  -0.451060740E+03
0.425188378E+01  -0.451086341E+03  1.0  -0.451056758E+03
0.434637009E+01  -0.451080177E+03  1.0  -0.451051631E+03
0.444085639E+01  -0.451073161E+03  1.0  -0.451045598E+03
0.453534270E+01  -0.451065491E+03  1.0  -0.451038858E+03
end

```

Run the job:

```
expt_diatomic.x AcOH+_FCF.inp | tee AcOH+_FCF.out
```

At the end of the output file one can find the table with transition moments (and their squares). We select only the FCFs with the wavenumber of the upper state  $v'' = 0$ :

	J'	J''	v'	v''	. . .	delta e,cm <sup>-1</sup>	prop	prop ^2
\$	0	0	0	0	. . .	7279.8734	-0.942947	0.889149
\$	0	0	1	0	. . .	6627.6841	0.325405	0.105888
\$	0	0	2	0	. . .	5979.2731	0.069678	0.004855
\$	0	0	3	0	. . .	5334.3122	0.010337	0.000107
\$	0	0	4	0	. . .	4692.7001	0.001070	0.000001
\$	0	0	5	0	. . .	4054.6587	-0.000079	0.000000

The sum of first three FCFs (see the last column) is equal to 0.9999, thus allowing one to conclude that the closed optical cycle can exist for the AcOH<sup>+</sup> molecular cation [52].

## Appendix A    Alphabetical index of keywords

active 15  
analyt\_prop 17  
arith 12  
compress 24  
conv 20  
crop 20  
cuda 25  
damping 20  
degen\_thresh 12  
density 17  
diis 20  
disk\_usage 24  
div\_thresh 20  
flush 21  
hermit 17  
ih\_imms 15  
ih\_imms : frontier\_energy 17  
ih\_imms : main\_occ 16  
ih\_imms : npower 16  
ih\_imms : scale 17  
ih\_imms : sectors 16  
ih\_imms : shift\_type 16  
ih\_imms : subspace 16  
integrals 23  
maxiter 21  
mdprop 17  
memory 24  
model 13  
mstdm 19  
nacth 14  
nactp 14  
natorb 19  
nroots 21  
nthreads 25  
occ 14  
occ\_irreps 14  
oneprop 23  
openmp 25  
openmp\_algorithm ??  
print 12  
reuse 21  
roots\_cutoff 22  
sector 13  
shift 22  
shifttype 22  
skip 23  
spinor\_labels 13  
tilesize 24

title 12  
txtprop 19  
x2cmmf 23



## Appendix B Temporary files

During the calculation, EXP-T operates with temporary files stored in the *scratch* directory. We recommend to remove these temporary files after every calculation (except for those planned to be used in the future, like the HEFF files or files with cluster amplitudes). All types of temporary files generated by EXP-T are listed and described below.

- HINT** one-electron integrals – core Hamiltonian matrix + one-particle part of perturbation (if presented). Recommended for removal after calculation.
- VINT-\*\*\*-\*\*\*** two-electron integrals. These files are generated during the integral sorting stage. Recommended for removal after calculation.  
*Approximate number of files:  $\sim N_b^4$  ( $N_b$  – number of blocks into which the whole set of spinors is divided by symmetry and the `tilesize` parameter)*
- \*.sb** single symmetry block of molecular integrals/cluster amplitudes. It is just a part of a diagram. During the calculation each file is mapped to some structure in RAM. Recommended for removal after calculation.  
*Approximate number of files:  $\sim 10 \times N_b^4$  for CCSD,  $\sim N_b^6$  for CCSDT-*n* and CCSDT models – **can be very large!***
- \*.dg** file containing diagram. Diagram files containing cluster amplitudes (`t1c.dg`, `t2c.dg` etc) can be used in subsequent calculations when constructing the initial approximation to amplitudes (see Sec. 4, keyword `reuse`).
- HEFF** formatted file containing effective Hamiltonian matrices. These files can be read by the `heffman.x` utility program used to perform Padé extrapolation of series of effective Hamiltonians [7], finite-field transition moments calculations [36, 3], spin-orbit coupling calculations [5].
- \*DIPLN** formatted files with dipole moment integrals (just its electronic part) in the basis of molecular spinors.
- MVCOEF\*\*** binary files containing model vectors expanded in the basis of model determinants. These files are used to organize data flow inside EXP-T in the most convenient and logical manner; model vectors are used for calculation of model-space approximations of TDMs and “quasi-natural” spinors, etc.
- NATORB\*.dat** formatted text files containing “quasi-natural” spinors expanded in the basis of molecular spinors. These expansions can be transformed to the AO basis with the `mknatorb.x` utility program (see Sec. 6.2).

## Appendix C Symmetry and irreducible representations

This section lists the names of irreducible representations (irreps) used in EXP-T.

- For nonrelativistic groups, irrep is determined by the spatial symmetry (Mulliken notation is used) and the  $M_s$  value (for  $M_s \geq 2$  only symbol 2 is used);
- For relativistic double groups we use Mulliken-type notation (completely inherited from DIRAC);
- For  $U(1) = \overline{C_{\infty v}}$  and  $U(1) \times C_i = \overline{D_{\infty h}}$  irreps are determined by  $\Omega$  values.

$C_1$

A\_a  
A\_b  
A\_-3/2  
A\_+3/2  
A\_0  
A\_4  
A\_+1  
A\_-1

$C_2$

A\_a      B\_a  
A\_b      B\_b  
A\_-3/2   B\_-3/2  
A\_+3/2   B\_+3/2  
A\_0      B\_0  
A\_2      B\_2  
A\_+1      B\_+1  
A\_-1      B\_-1

$C_s$

A'\_a      A''\_a  
A'\_b      A''\_b  
A'\_-3/2   A''\_-3/2  
A'\_+3/2   A''\_+3/2  
A'\_0      A''\_0  
A'\_2      A''\_2  
A'\_+1      A''\_+1  
A'\_-1      A''\_-1

$C_i$

Ag_a	Au_a
Ag_b	Au_b
Ag_-3/2	Au_-3/2
Ag_+3/2	Au_+3/2
Ag_0	Au_0
Ag_2	Au_2
Ag_+1	Au_+1
Ag_-1	Au_-1

$C_{2v}$

A1_a	B2_a	B1_a	A2_a
A1_b	B2_b	B1_b	A2_b
A1_-3/2	B2_-3/2	B1_-3/2	A2_-3/2
A1_+3/2	B2_+3/2	B1_+3/2	A2_+3/2
A1_0	B2_0	B1_0	A2_0
A1_2	B2_2	B1_2	A2_2
A1_+1	B2_+1	B1_+1	A2_+1
A1_-1	B2_-1	B1_-1	A2_-1

$C_{2h}$

Ag_a	Bg_a	Bu_a	Au_a
Ag_b	Bg_b	Bu_b	Au_b
Ag_-3/2	Bg_-3/2	Bu_-3/2	Au_-3/2
Ag_+3/2	Bg_+3/2	Bu_+3/2	Au_+3/2
Ag_0	Bg_0	Bu_0	Au_0
Ag_2	Bg_2	Bu_2	Au_2
Ag_+1	Bg_+1	Bu_+1	Au_+1
Ag_-1	Bg_-1	Bu_-1	Au_-1

$D_2$

A_a	B3_a	B1_a	B2_a
A_b	B3_b	B1_b	B2_b
A_-3/2	B3_-3/2	B1_-3/2	B2_-3/2
A_+3/2	B3_+3/2	B1_+3/2	B2_+3/2
A_0	B3_0	B1_0	B2_0
A_2	B3_2	B1_2	B2_2
A_+1	B3_+1	B1_+1	B2_+1
A_-1	B3_-1	B1_-1	B2_-1

$D_{2h}$

Ag_a	B1u_a	B2u_a	B3g_a	B3u_a	B2g_a	B1g_a	Au_a
Ag_b	B1u_b	B2u_b	B3g_b	B3u_b	B2g_b	B1g_b	Au_b
Ag_-3/2	B1u_-3/2	B2u_-3/2	B3g_-3/2	B3u_-3/2	B2g_-3/2	B1g_-3/2	Au_-3/2
Ag_+3/2	B1u_+3/2	B2u_+3/2	B3g_+3/2	B3u_+3/2	B2g_+3/2	B1g_+3/2	Au_+3/2
Ag_0	B1u_0	B2u_0	B3g_0	B3u_0	B2g_0	B1g_0	Au_0
Ag_2	B1u_2	B2u_2	B3g_2	B3u_2	B2g_2	B1g_2	Au_2
Ag_+1	B1u_+1	B2u_+1	B3g_+1	B3u_+1	B2g_+1	B1g_+1	Au_+1
Ag_-1	B1u_-1	B2u_-1	B3g_-1	B3u_-1	B2g_-1	B1g_-1	Au_-1

$\overline{C_1}$

A  
a

$\overline{C_2}$

1E 2E  
a b

$\overline{C_s}$

1E 2E  
a b

$\overline{C_i}$

AG AU  
ag au

$\overline{C_{2v}}$

1E 2E  
a b

$\overline{D_2}$

1E 2E  
a b

$\overline{D_{2h}}$

1Eg 2Eg 1Eu 2Eu  
ag bg au bu

$\overline{C_{\infty v}}$

1/2+	1/2-	3/2+	3/2-	5/2+	5/2-	7/2+	7/2-
9/2+	9/2-	11/2+	11/2-	13/2+	13/2-	15/2+	15/2-
17/2+	17/2-	19/2+	19/2-	21/2+	21/2-	23/2+	23/2-
25/2+	25/2-	27/2+	27/2-	29/2+	29/2-	31/2+	31/2-
0	1+	1-	2+	2-	3+	3-	4+
4-	5+	5-	6+	6-	7+	7-	8+
8-	9+	9-	10+	10-	11+	11-	12+
12-	13+	13-	14+	14-	15+	15-	16+

$\overline{D_{\infty h}}$

1/2g+	1/2g-	3/2g+	3/2g-	5/2g+	5/2g-	7/2g+	7/2g-
9/2g+	9/2g-	11/2g+	11/2g-	13/2g+	13/2g-	15/2g+	15/2g-
1/2u+	1/2u-	3/2u+	3/2u-	5/2u+	5/2u-	7/2u+	7/2u-
9/2u+	9/2u-	11/2u+	11/2u-	13/2u+	13/2u-	15/2u+	15/2u-
0g	1g+	1g-	2g+	2g-	3g+	3g-	4g+
4g-	5g+	5g-	6g+	6g-	7g+	7g-	8g+
0u	1u+	1u-	2u+	2u-	3u+	3u-	4u+
4u-	5u+	5u-	6u+	6u-	7u+	7u-	8u+

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