

DALTON2013 – LSDALTON Program Manual

V. Bakken, R. Bast, S. Coriani, P. Ettenhuber,
T. Helgaker, S. Høst, I.-M. Høyvik, B. Jansík,
P. Jørgensen, J. Kauczor, T. Kjærgaard,
A. Krapp, K. Kristensen, P. Merlot, C. Nygaard,
J. Olsen, S. Reine, V. Rybkin, P. Sałek,
A. Teale, E. Tellgren, A. Thorvaldsen,
L. Thøgersen, M. Watson, and M. Ziolkowski

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Preface

This is the manual for the LSDALTON quantum chemistry program — Release DALTON2013 — for computing Hartree-Fock and DFT wave functions, energies, and molecular properties. For correlated models, MP2 geometry optimizations and CCSD energies (not linear-scaling) are available. Most parts of LSDALTON employ *linear scaling* and massively parallel implementations, which makes it suitable for calculations on large molecular systems, in particular when the calculations are carried out on large super computer architectures.

If results obtained with this code are published the following paper should be cited:

K. Aidas, C. Angeli, K. L. Bak, V. Bakken, R. Bast, L. Boman, O. Christiansen, R. Cimigli, S. Coriani, P. Dahle, E. K. Dalskov, U. Ekström, T. Enevoldsen, J. J. Eriksen, P. Etenhuber, B. Fernández, L. Ferrighi, H. Fliegl, L. Frediani, K. Hald, A. Halkier, C. Hättig, H. Heiberg, T. Helgaker, A. C. Hennum, H. Hettema, E. Hjertenæs, S. Høst, I.-M. Høyvik, M. F. Iozzi, B. Jansik, H. J. Aa. Jensen, D. Jonsson, P. Jørgensen, J. Kauczor, S. Kirpekar, T. Kjærgaard, W. Klopper, S. Knecht, R. Kobayashi, H. Koch, J. Kongsted, A. Krapp, K. Kristensen, A. Ligabue, O. B. Lutnæs, J. I. Melo, K. V. Mikkelsen, R. H. Myhre, C. Neiss, C. B. Nielsen, P. Norman, J. Olsen, J. M. H. Olsen, A. Osted, M. J. Packer, F. Pawłowski, T. B. Pedersen, P. F. Provasi, S. Reine, Z. Rinkevicius, T. A. Ruden, K. Ruud, V. Rybkin, P. Salek, C. C. M. Samson, A. Sánchez de Merás, T. Saue, S. P. A. Sauer, B. Schimelpfennig, K. Snegov, A. H. Steindal, K. O. Sylvester-Hvid, P. R. Taylor, A. M. Teale, E. I. Tellgren, D. P. Tew, A. J. Thorvaldsen, L. Thøgersen, O. Vahtras, M. A. Watson, D. J. D. Wilson, M. Ziolkowski, and H. Ågren, "*The Dalton quantum chemistry program system*", **WIREs Comput. Mol. Sci.** (doi: 10.1002/wcms.1172)

We emphasize the conditions under which the program is distributed. It is furnished for your own use, and you may not redistribute it further, neither in whole nor in part. Even though LSDALTON is completely separate from the original DALTON program, the program packages are distributed together in the DALTON2013 suite. Thus, anyone interested in obtaining LSDALTON should check out the DALTON homepage at <http://daltonprogram.org>. Visit <http://daltonprogram.org/installation/2013/> for comprehensive installation in-

structions, and visit the Forum <http://daltonprogram.org/forum> for tutorials on how to run LSDALTON and other useful information. The Forum is also open for general discussions, and is the place to look/ask for assistance if you do not find the answers you are looking for in this manual.

Finally note that the program represents experimental code that is under constant development. No guarantees of any kind are provided, and the authors accept no responsibility for the performance of the code or for the correctness of the results.

Part I

LSDALTON User's Guide

Chapter 1

Getting started with LSDALTON

In this chapter we give an introduction to the two input files needed for doing a calculation with the LSDALTON program (MOLECULE.INP and LSDALTON.INP), as well as the shell script file that is supplied with the program for moving relevant files to the scratch-directory and back to the home directory after a calculation has completed. A couple of examples of input files are also provided. Finally, the different output files generated by the program are discussed.

Note! The DALTON and LSDALTON programs use different input keywords! MOLECULE.INP files used for LSDALTON can also be used for DALTON – but NOT vice versa! The DALTON.INP input file of DALTON is different from the LSDALTON.INP input file of LSDALTON. Thus, DALTON keywords CANNOT be assumed to work in LSDALTON or vice versa.

Before going into detail with the MOLECULE.INP and LSDALTON.INP files in chapters 1.1 and 1.2, we provide a simple input example for the impatient reader. The example below will yield the HF energy for water and the two lowest lying excitation energies and their associated transition strengths:

MOLECULE.INP:

```
BASIS
cc-pVDZ Aux=Ahlrichs-Coulomb-Fit
water R(OH) = 0.95Aa , <HOH = 109 deg.
Distance in Angstroms
Atomtypes=2 Angstrom
Charge=8.0 Atoms=1
0      0.00000  0.00000  0.00000
Charge=1.0 Atoms=2
```

```
H      0.55168   0.77340   0.00000
H      0.55168  -0.77340   0.00000
```

LSDALTON.INP:

```
**WAVE FUNCTIONS
.HF
**RESPONS
.NEXCIT
2
*END OF INPUT
```

To run this simple example, you may (i) create a new directory, (ii) copy the two files above into this directory, and (iii) run the calculation from your newly created directory using the `lsdalton.x` executable located in your build directory (as mentioned above, installation details are given at <http://daltonprogram.org/installation/2013/>).

The converged HF energy can be found in the output file `LSDALTON.OUT` by grepping for "Final HF energy":

```
Final HF energy:                -76.026476337669
```

while the two excitation energies and associated transition strengths are given at the end of `LSDALTON.OUT`:

```
*****
*                               ONE-PHOTON ABSORPTION RESULTS (in a.u.)                               *
*****
Excitation      Transition Dipole Moments      Oscillator
Energies        x          y          z          Strengths
=====
0.33897330      -0.94893963E-15  -0.30390933E-15  0.36349099  0.29858056E-01
0.42634048      0.57831041      -0.15070410E-14  -0.14539976E-14  0.95057706E-01
```

Note that if you run this test your results may vary slightly from the above due to numerical inaccuracies.

1.1 The MOLECULE input file

Basically, the `MOLECULE` file contains the following information:

- The Cartesian coordinates and nuclear charges of all atoms
- The basis set(s) to be used

Please note the following:

- Supplying the molecular geometry in the form of a Z-matrix is not supported by LSDALTON since this format is ill suited for large scale calculations.
- Molecular symmetry is not exploited by LSDALTON (since the target systems of the program are large biomolecules, which hardly ever contains any symmetry).
- The LSDALTON program does not support the use of effective core potentials.

There are two different types of molecule files, using either BASIS or ATOMBASIS. ATOMBASIS is relevant only if different basis sets on individual atoms are required. In the first two subsections, we describe these two types of MOLECULE files using simple examples. The basis can be selected from the provided basis-set library or can be specified by the user (as described under section 1.1.3).

1.1.1 BASIS

Here we describe our example water molecule input file line by line using the BASIS MOLECULE format:

```
1 BASIS
2 cc-pVDZ Aux=Ahlrichs-Coulomb-Fit
3 water R(OH) = 0.95Aa , <HOH = 109 deg.
4 Distance in Angstroms
5 Atomtypes=2 Angstrom
6 Charge=8.0 Atoms=1
7 0 0.00000 0.00000 0.00000
8 Charge=1.0 Atoms=2
9 H 0.55168 0.77340 0.00000
10 H 0.55168 -0.77340 0.00000
```

- Line 1: The word "BASIS", indicating that the same basis set should be used for all atoms.
- Line 2: The name of the basis set, in this case cc-pVDZ. Optional: The name of the auxiliary basis set, in this case Ahlrichs-Coulomb-Fit (only referenced if density-fitting is requested in LSDALTON.INP)

- Lines 3-4: Comments (may be left blank)
- Line 5: **Atomtypes=** Number of different atoms - in the case of H₂O, there are two different atom types, H and O. **Angstrom** If this keyword is omitted, the program will assume that coordinates are given in atomic units (1bohr=0.5291772083Å). Other options in this line are: **Charge=** Molecular charge - assumed to be zero if omitted. **Nosymmetry** This have no effect as no pointgroup symmetry have been implemented.
- Lines 6 and 8: A line of this type has to come before the Cartesian coordinates of each atom type, indicating a) **Charge=** the nuclear charge of the atom type, and b) **Atoms=** the number of atoms of this type.
- Lines 7, 9-10: Cartesian coordinates of the atoms (in Angstrom, since this was specified in line 5). An atom name (1-4 characters long) must be placed at the beginning of these lines.

1.1.2 ATOMBASIS

Our example water molecule may also be specified as an ATOMBASIS MOLECULE file :

```

1  ATOMBASIS
2  water R(OH) = 0.95Aa , <HOH = 109 deg.
3  Distance in Aangstroms
4  Atomtypes=2 Angstrom
5  Charge=8.0 Atoms=1 Basis=cc-pVDZ Aux=Ahlrichs-Coulomb-Fit
6  0      0.00000  0.00000  0.00000
7  Charge=1.0 Atoms=2 Basis=cc-pVDZ Aux=Ahlrichs-Coulomb-Fit
8  H      0.55168  0.77340  0.00000
9  H      0.55168 -0.77340  0.00000

```

As seen from the example, there is little difference between the two formats. Line 2 in the BASIS file has been removed, and instead the basis sets (and optionally, the auxiliary basis sets) are now given for each atom. In this example they are the same, as it would probably not make much sense to use different basis sets for the atoms in water. This can make sense, though, for larger molecules. An example could be a biomolecule containing an active site with one or more transition metal atoms. It may be useful to describe such an active site with a more sophisticated basis set than the surroundings.

1.1.3 User defined basis sets

The user may supply his or her own basis set in two ways. Both ways require that the MOLECULE.INP file is argumented with a basis as in the following two examples

```
1 BASIS
2 USERDEFINED
3 water R(OH) = 0.95Aa , <HOH = 109 deg.
4 Distance in Angstroms
5 Atomtypes=2 Angstrom
6 Charge=8.0 Atoms=1
7 O 0.00000 0.00000 0.00000
8 Charge=1.0 Atoms=2
9 H 0.55168 0.77340 0.00000
10 H 0.55168 -0.77340 0.00000
11
12 USERDEFINED BASIS
13 a 1
14 $ HYDROGEN (4s,1p) -> [2s,1p]
15 $ HYDROGEN segmented contracted
16 $ S-TYPE FUNCTIONS
17 4 2 0
18 18.7311370 0.03349460 0.00000000
19 2.8253937 0.23472695 0.00000000
20 0.6401217 0.81375733 0.00000000
21 0.1612778 0.00000000 1.00000000
22 $ P-TYPE FUNCTIONS
23 1 1 0
24 1.1000000 1.00000000
25 a 8
26 $ OXYGEN (10s,4p) -> [3s,2p]
27 $ S-TYPE FUNCTIONS
28 10 3 0
29 5484.6717000 0.00183110 0.00000000 0.00000000
30 825.2349500 0.01395010 0.00000000 0.00000000
31 188.0469600 0.06844510 0.00000000 0.00000000
32 52.9645000 0.23271430 0.00000000 0.00000000
33 16.8975700 0.47019300 0.00000000 0.00000000
34 5.7996353 0.35852090 0.00000000 0.00000000
35 15.5396160 0.00000000 -0.11077750 0.00000000
36 3.5999336 0.00000000 -0.14802630 0.00000000
37 1.0137618 0.00000000 1.13076700 0.00000000
38 0.2700058 0.00000000 0.00000000 1.00000000
```

```

39  $ P-TYPE FUNCTIONS
40      4      2      0
41      15.5396160  0.07087430  0.00000000
42      3.5999336  0.33975280  0.00000000
43      1.0137618  0.72715860  0.00000000
44      0.2700058  0.00000000  1.00000000
45  $ D-TYPE FUNCTIONS
46      1      1      0
47      0.8000000  1.00000000

```

Line 13 to 24 contain the Basis set information for the Hydrogen atom. Line 13 denote the nuclear charge. Line 14 through 16 are comments. Line 17 states that there are 4 primitive functions and 2 contracted functions. Lines 18 to 21 contain information about the primitive functions. The first number is the exponent and the next 2 numbers are the coefficients for the 2 contracted functions. Line 22-24 contain info about p orbitals on hydrogen, while Line 25-47 contain similar information about oxygen.

Alternative the userdefined basis may be used in connection with the ATOMBASIS

```

ATOMBASIS
water R(OH) = 0.95Aa , <HOH = 109 deg.
Distance in Aangstroms
Atomtypes=2 Angstrom
Charge=8.0 Atoms=1 Basis=cc-pVDZ
O      0.00000  0.00000  0.00000
Charge=1.0 Atoms=2 Basis=USERDEFINED
H      0.55168  0.77340  0.00000
H      0.55168 -0.77340  0.00000

```

```

USERDEFINED BASIS
a 1
$ HYDROGEN      (4s) -> [2s]
$ HYDROGEN      (1p)
$ S-TYPE FUNCTIONS
      4      2      0
      18.7311370  0.03349460  0.00000000
      2.8253937  0.23472695  0.00000000
      0.6401217  0.81375733  0.00000000
      0.1612778  0.00000000  1.00000000
$ P-TYPE FUNCTIONS

```

```
1    1    0
1.1000000  1.00000000
```

Finally the basis set files from the Basis Set exchange (EMSL) <https://bse.pnl.gov/bse/portal> may be downloaded and put into the basis set directory (the directory called "basis" located at the root of the Dalton library) and used directly. The name specified by the input should match the name of the file in the basis set directory (see testcase LSDALTON/test/linsca/linsca.emsl for an example).

1.2 The LSDALTON.INP file

In this section, we show two typical examples of a LSDALTON.INP file, one for small molecules and one for large molecules. Many other examples of input files for requesting e.g. specific molecular properties may be found at <http://daltonprogram.org>, and a complete reference manual of all keywords is found in Chapter 3.

In general, the LSDALTON.INP is divided in different sections under the headlines (see Section 3 for details):

- ****GENERAL** contains general settings (optional)
- ****INTEGRAL** contains settings for the calculation of integrals (optional)
- ****WAVE FUNCTION** contains information about the wave function (e.g. HF/DFT) and settings for the optimization of the wave function (mandatory)
- ****OPTIMIZE** contains settings for geometry optimization (optional)
- ****DYNAMI** contains settings for Born-Oppenheimer molecular dynamics (optional)
- ****LOCALIZE ORBITALS** contains settings for orbital localization procedure (optional)
- ****RESPONS** contains information about requested molecular properties for HF and DFT (optional)
- ****DEC** or ****CC** contains info about MP2 and coupled-cluster calculations (optional)
- ****PLT** contains information about construction of *.plt files which may be used to visualize densities and orbitals using e.g. the Chimera program [1] (optional).
- ****PLTGRID** contains information about grid used for construction of *.plt files (optional).

Each of these sections may contain subsections, indicated by a single asterisk. The LSDALTON.INP file should always end with `*END OF INPUT`.

A typical example of LSDALTON.INP for a **small molecule** could look like:

```
**WAVE FUNCTIONS
.HF
*DENSOPT
.RH
.DIIS
.CONVTHR
1.0D-6
**RESPONS
.NEXCIT
5
*END OF INPUT
```

Here, we have requested a Hartree-Fock optimization under `**WAVE FUNCTION`. The subsection `*DENSOPT` contains setting for how the density should be optimized. The `.RH` (i.e. Roothaan-Hall) and `.DIIS` keywords request a standard diagonalization combined with the DIIS scheme for convergence acceleration. With the keyword `.CONVTHR` (i.e. convergence threshold) it is requested that iterations are terminated when the Frobenius norm of the SCF gradient, divided by the square root of the number of occupied orbitals, is smaller than 10^{-6} . Finally, we have under `**RESPONS` requested the calculation of the five lowest excitation energies with `.NEXCIT` (i.e. number of excitation energies).

A typical example of LSDALTON.INP for a **large molecule** could look like:

```
**INTEGRAL
.DENSFIT
**WAVE FUNCTIONS
.DFT
BP86
*DENSOPT
.START
TRILEVEL
.ARH
.CONVDYN
STANDARD
*END OF INPUT
```

Under `**INTEGRAL`, we have requested the use of density-fitting to speed up the calculation (the use of J-engine is default). Under `**WAVE FUNCTIONS`, we have requested a

DFT calculation using the BP86 exchange-correlation functional.

Since this is a calculation on a large molecule, we request the trilevel starting guess (atomic, valence, and then full optimization) and the Augmented Rothaan-Hall (ARH) method for density optimization. Note that ARH is default, so this keyword is actually unnecessary. ARH is more robust than the standard diagonalization/DIIS scheme. Furthermore, the ARH scaling with system size is asymptotically linear provided sparse-matrix algebra is employed. You may use sparse-matrix algebra by putting `.CSR` (i.e. Compressed-Sparse Row) under `*DENSOPT` (NB: requires linking to the MKL library). We have used a dynamic SCF convergence threshold (`.COVNDYN`, see 3.4.2). This is suitable for calculations on large molecules, since the standard SCF convergence threshold is based on the Frobenius norm of the SCF gradient, which is not size-extensive. The use of the STANDARD dynamic threshold corresponds to 10^{-5} times the square root of the number of electrons in the system.

Chapter 2

Interfacing to LSDALTON

In this chapter we give an introduction to the normalization, basis set and ordering of atomic orbitals used in the LSDALTON program.

This is provided in case you want to interface to the LSDALTON program or want to read one of the files written by the LSDALTON program, for instance the local orbitals. Certain functionality can also be incorporated into other programs by linking to the LSDALTON-library bundle, as outlined in section 2.5.

2.1 The Grand Canonical Basis

Unlike all other Quantum Chemistry Programs the LSDALTON program, uses the so called grand canonical basis [2, 3] as the internal default basis. The results therefore cannot directly be compared to other programs unless the

`.NOGCBASIS`

keyword is specified. This keyword deactivates the use of the grand canonical basis and uses the input basis instead. An exception is Dunning’s correlation consistent basis sets (cc-pVDZ, cc-pVTZ, ..., aug-cc-pVDZ, etc.) for which the `.NOGCBASIS` keyword is used by default.

2.2 Basisset and Ordering

In LSDALTON the default basis set are real-valued spherical harmonic Gaussian type orbitals (GTOs)

$$G_{ilm}(\mathbf{r}; a_i; \mathbf{A}) = S_{lm}(x_A; y_A; z_A) \exp(-a_i r_A^2) \quad (2.1)$$

where $S_{lm}(x_A; y_A; z_A)$ is a real solid harmonic introduced in section 6.4.2 of Ref. [4] (see Table 6.3). Concerning the ordering of basis functions, it is one atomtype after the other

as given in the input, and for each atomtype, it is one atom after another as given in input. For each atom increasing with angular momentum l , within one angular momentum l , the ordering is first the components (e.g. p_x, p_y, p_z), and then the contracted functions.

So for an atom consisting of 3 s functions 2 p functions and 1 d function, the ordering is $\{1s; 2s; 3s; 1p_x; 1p_y; 1p_z; 2p_x; 2p_y; 2p_z; 1d_{xy}; 1d_{yz}; 1d_{z^2-r^2}; 1d_{xz}; 1d_{x^2-y^2}\}$ In LSDALTON the ordering of the basis functions are $m = \{-l, \dots, 0, \dots, l\}$ for a given angular momentum l . Although for computational efficiency the p orbitals are treated as a special case with $p = \{p_x, p_y, p_z\}$ which corresponds to $m = \{1, -1, 0\}$.

2.3 Normalization

For an unnormalized primitive spherical harmonic GTO, the overlap is given by

$$\langle \chi_{ilm}^{\text{GTO}} | \chi_{ilm}^{\text{GTO}} \rangle = (N_i^{\text{P}})^2 \left(\frac{\pi}{2a_i} \right)^{3/2} \frac{1}{(4a_i)^l} \quad (2.2)$$

(where the last term corresponds to $1/(2p)^l$ according to for example Eq. 9.3.8 of Ref. [4]. This gives the primitive normalization factor N^{P}

$$N_i^{\text{P}} = \frac{(4a_i)^{l/2+3/4}}{\pi^{3/4}} \quad (2.3)$$

Naturally the default in LSDALTON is not primitive GTOs but contracted GTOs written as linear combinations of primitive spherical-harmonic GTOs of different exponents

$$G_{\mu lm}(\mathbf{r}; a; \mathbf{A}) = \sum_i G_{ilm}(\mathbf{r}; a_i; \mathbf{A}) d_{i\mu}^{\text{norm}} \quad (2.4)$$

in LSDALTON we determine $d_{i\mu}^{\text{norm}}$ as

$$d_{i\mu}^{\text{norm}} = N_i^{\text{P}} N_i^{\text{C}} d_{i\mu}^{\text{basis}} \quad (2.5)$$

As explained, N_i^{P} is the normalization of the primitive GTOs, $d_{i\mu}^{\text{basis}}$ are the unmodified contraction coefficients read from the basis set file. N_i^{C} is the normalization of the contracted functions and is determined using the overlap between two normalized primitive GTOs of the same angular momentum, but different exponents

$$\langle \chi_{a_i lm}^{\text{GTO}} | \chi_{a_j lm}^{\text{GTO}} \rangle = \left(\frac{\sqrt{4a_i a_j}}{a_i + a_j} \right)^{\frac{3}{2}+l} \quad (2.6)$$

so that the contraction coefficients for the contracted function N_i^{C} are found by first finding the overlap

$$\mathcal{S}_{\mu} = \sum_{ij} d_{i\mu}^{\text{basis}} d_{j\mu}^{\text{basis}} \langle \chi_{ilm}^{\text{GTO}} | \chi_{jlm}^{\text{GTO}} \rangle = \sum_{ij} d_{i\mu}^{\text{basis}} d_{j\mu}^{\text{basis}} \left(\frac{\sqrt{4a_i a_j}}{a_i + a_j} \right)^{\frac{3}{2}+l} \quad (2.7)$$

where $d_{i\mu}^{\text{basis}}$ are the unmodified coefficients and then construct the coefficients

$$d_{i\mu}^{\text{norm}} = N_i^{\text{p}} N_{i\mu}^{\text{c}} d_{i\mu}^{\text{basis}} = N_i^{\text{p}} \frac{d_{i\mu}^{\text{basis}}}{\sqrt{\mathcal{S}_\mu}} = \frac{d_{i\mu}^{\text{basis}}}{\sqrt{\mathcal{S}_\mu}} \left(4a_i\right)^{\frac{l}{2} + \frac{3}{4}} \left(\frac{1}{\pi}\right)^{\frac{3}{4}} \quad (2.8)$$

2.4 Matrix File Format

During an LSDALTON calculation a number of files may be generated. This list of files include

dens.restart - The density matrix
 fock.restart - The fock matrix
 overlapmatrix - The overlap matrix
 cmo_orbitals.u - The canonical Molecular orbitals
 lcm_orbitals.u - The local Molecular orbitals

the files are all written using the Fortran 90 code

```
1 OPEN(UNIT=IUNIT, FILE='dens.restart', STATUS='UNKNOWN', FORM='UNFORMATTED', IOSTAT
   =IOS)
2 WRITE(iunit) A%Nrow, A%Ncol
3 WRITE(iunit) (A%elms(I), I=1, A%nrow*A%ncol)
4 CLOSE(UNIT=IUNIT, STATUS='KEEP')
```

Where A is a derived type containing the number of rows (A%nrow), the number of columns (A%ncol), and the elements stored in a vector array (A%elms).

The dens.restart is different as it contains an additional logical

```
1 OPEN(UNIT=IUNIT, FILE='dens.restart', STATUS='UNKNOWN', FORM='UNFORMATTED', IOSTAT
   =IOS)
2 WRITE(iunit) A%Nrow, A%Ncol
3 WRITE(iunit) (A%elms(I), I=1, A%nrow*A%ncol)
4 WRITE(iunit) GCBASIS
5 CLOSE(UNIT=IUNIT, STATUS='KEEP')
```

IMPORTANT: When interfacing to other programs, the logical GCBASIS should always be false, i.e. by specifying the keyword

.NOGCBASIS

in the LSDALTON.INP. If the logical GCBASIS is true the dens.restart is given in terms of the grand canonical basis rather than the input basis.

2.5 The LSDALTON library bundle

The LSDALTON library bundle `liblsdalton.a` allows for porting LSDALTON code functionality to other programs. Currently this functionality is limited to the evaluation of certain standard AO integrals and integral components: the overlap matrix, the one-electron integral matrix (combining kinetic energy and nuclear-electron attraction contributions), the Coulomb, exchange and exchange-correlation matrices and the four-center two-electron repulsion integrals. Also, the first derivatives of these integral components with respect to the nuclear displacements are available, see the file `LSDALTON/lsdaltonsrc/LSlib_tester.F90` for details.

After building LSDALTON under a build directory (consult the installation guide <http://daltonprogram.org/installation/2013/> for assistance), the LSDALTON library `liblsdalton.a` can be found under `build\lib`. You can now link your program to the LSDALTON library. The use is perhaps best illustrated by a simple example. The file `lslib_test.F90`

```
PROGRAM testlslib
implicit none
integer :: nbast,natoms,nelectrons,lupri,luerr
integer :: i,j
double precision, allocatable :: Smat(:,,:)

call lsinit_all()

lupri = 6 !logical unit number of standard output
luerr = 0 !logical unit number of standard error
CALL LSlib_get_dimensions(nbast,natoms,nelectrons,lupri,luerr)
allocate(Smat(nbast,nbast))
CALL LSlib_get_overlap(Smat,nbast,lupri,luerr)

deallocate(Smat)
call lsfree_all()

END PROGRAM testlslib
```

calculates the AO overlap matrix (`Smat`). To compile `lslib_test.F90` you have to link to the external libraries required by LSDALTON, typically `lapack` and `blas`. For an example `intel/mkl` build

```
./setup --fc=ifort --cc=icc --cxx=icpc --mkl=parallel --omp
```

you can build the executable `lslib_test.x` from `lslib_test.F90` according to

```
ifort -mkl=parallel -openmp -parallel -O3 lslib_test.F90 -o lslib_test.x
/dalton-path/build/lib/liblsdalton.a
```

Exactly how to compile and link your code to `liblsdalton.a` for other types of build varies, and it can then be instructive to see how LSDALTON is built. To see how `lsdalton.x` is compiled and linked, you can type

```
make VERBOSE=1 lsdalton.x
```

in the `build` directory. The actual build of `lsdalton.x` can be found towards the end of the standard output.

The execution of `lslib_test.x` requires the presence of valid MOLECULE and LSDALTON input files in the directory where you execute your program, for example the MOLECULE.INP

```
BASIS
STO-3G
```

```
Atomtypes=2
Charge=8.0 Atoms=1
O    0.00000 0.00000 0.00000
Charge=1.0 Atoms=2
H    0.00000 0.50000 0.00000
H    0.00000 0.00000 0.50000
```

and the LSDALTON.INP

```
**GENERAL
.NOGCBASIS
**WAVE FUNCTION
.DFT
BLYP
*END OF INPUT
```

Part II

LSDALTON Reference Manual

Chapter 3

List of LSDALTON keywords

In this chapter, we describe all keywords for the different sections of the LSDALTON.INP file. In general, LSDALTON.INP is divided into the following sections under the headlines:

- ****GENERAL** contains general settings (optional)
- ****INTEGRAL** contains settings for the calculation of integrals (optional)
- ****WAVE FUNCTION** contains information about the wave function (e.g. HF/DFT) and settings for the optimization of the wave function (mandatory)
- ****OPTIMIZE** contains settings for geometry optimization (optional)
- ****DYNAMI** contains settings for Born-Oppenheimer molecular dynamics (optional)
- ****LOCALIZE ORBITALS** contains settings for orbital localization procedure (optional)
- ****RESPONS** contains information about requested molecular properties for HF and DFT (optional)
- ****DEC** or ****CC** contains info about MP2 and coupled-cluster calculations (optional)
- ****PLT** contains information about construction of *.plt files which may be used to visualize densities and orbitals using e.g. the Chimera program [1] (optional).
- ****PLTGRID** contains information about grid used for construction of *.plt files (optional).

Each of these sections may contain subsections, indicated by a single asterisk. LSDALTON.INP should always end with ***END OF INPUT**.

3.1 **GENERAL

This input module defines the way the integrals should be calculated.

`.SCALAPACK` Use SCALAPACK matrices.

NB: Requires linking to the scalapack lib (provided by MKL) and the use of the `-scalapack` keyword during installation.

`.SCALAPACKBLOCKSIZE` the blocksize used in SCALAPACK matrices

`.CSR` Use Compressed-Sparse Row matrices. NB: Requires linking to MKL library and the use of the `-csr` keyword during installation!

`.TIME` Activate the printout of timings.

`.NOGCBASIS` Deactivate the use of the Grand Canonical basis [2, 3]

`.FORCEGCBASIS` The Grand Canonical basis [2, 3] is deactivated when the program detects the use of a Dunning basis set like (cc-pVXZ) but the calculation will force the use of the Grand Canonical basis using this keyword.

3.2 **INTEGRAL basic keywords

This input module defines the way the integrals should be calculated.

`.ADMM` Use the Auxiliary Density Matrix Method (ADMM) [5] to approximate the exact-exchange contribution. When using this keyword, an auxiliary basis set has to be specified in the MOLECULE file such as:

```
1    BASIS
2    6-31+G* Aux=df-def2 CABS=STO-2G JK=3-21G
...

```

where the "JK" basis is used as ADMM auxiliary basis set. You also have to provide a valid "CABS" basis from the library (which is needed for technical reasons, but will not actually be used in the calculation). *Note of caution: we do not recommend to use ADMM in combination with geometry optimization.*

`.AOPRINT`

<Print level>

Print the Atomic Orbital information. The higher the print level, the more information will be printed. Default value is 0.

.BASPRINT

<Print level>

Print the basis set information. The higher the print level, the more information will be printed. Using a print level of 6 will print the input exponents and contraction coefficients read from file as well as the normalized basis used in LSDALTON.

- .DENSFIT** Use density-fitting for the Coulomb contribution (no exact exchange density-fitting method have been introduced). When using this keyword, an auxiliary basis set has to be specified in the MOLECULE file. For the Poples basis sets we recommend df-def2 and for Dunning's basis sets use the corresponding cc-pVXZdenfit basis sets, with $X = T, Q, 5$.

.LINSCAPRINT

<Print level>

Print level in the integral code. The higher the print level, the more information will be printed. This keyword corresponds to

.AOPRINT

<Print level>

.BASPRINT

<Print level>

.MOLPRINT

<Print level>

See the individual keywords for more details. Default value is 0.

.MOLPRINT

<Print level>

Print information about the molecule. The higher the print level, the more information will be printed. Default value is 0.

- .NOJENGINE** Turn off J-engine algorithm (which is default) for the calculation of the Coulomb matrix (see Refs. [6] and [7]). Compute instead Coulomb-like contributions from the explicitly calculated integrals.

- .NOLINK** Turn off the LinK algorithm (which is default) for the calculation of the exchange matrix (see Ref. [8]).

- .NO SCREEN** Deactivate the use of all screening methods.

- .NOFAMILY** Deactivate the exploitation of family type basis set, basis set sharing exponents for different angular momentums.

`.PARI` Use the Pair-Atomic Resolution-of-the-Identity approximation [9] for the Coulomb and exact Exchange contribution. When using this keyword, an auxiliary basis set has to be specified in the MOLECULE file.

We do not recommend to use this method for any production runs, and have included it in case other method developers would like to explore it (see the reference for details).

`.RUNMM` Use the (Fast) Multipole Method.

`.THRESH`

<Threshold>

An overall screening threshold for integral evaluation. The default value is 10^{-8}

The various integral-evaluation thresholds (below) are set according to this Threshold.

- The Cauchy-Schwarz screening threshold is set equal to Threshold (can be set separately by `.THR_CS`)
 - The Screening threshold used for Coulomb is $\text{Threshold} \cdot 10^{-2}$ (Default: 10^{-10})
 - The Screening threshold used for Exchange is $\text{Threshold} \cdot 10^{-0}$ (Default: 10^{-8})
 - The Screening threshold used for One-electron operators is $\text{Threshold} \cdot 10^{-7}$ (Default: 10^{-15})
- The Primitive Cauchy-Schwarz screening threshold is set equal to $\text{Threshold} \cdot 10^{-1}$ (can be set separately by `.THR_PS`)
- The Overlap-distribution distance-screening threshold is set equal to $\text{Threshold} \cdot 10^{-1}$. When calculating overlap integrals, this threshold is used for setting up AO extents. Overlap distributions (ODs) for which the distance between the two AOs are larger than the sum of the extents are screened away.
- The Overlap-distribution extent-screening threshold is set equal to $\text{Threshold} \cdot 10^{-1}$. When calculating overlap integrals, this threshold is used for setting up OD extents. Overlap integrals between two ODs separated by more than the sum of the extents are screened away.
- The FMM threshold is used to distinguish the Coulomb repulsion into classical and non-classical interactions, based on the non-classical extent of the continuous charge distribution (orbitals or orbital products). By default this threshold is set equal to $\text{Threshold} \cdot 10^{-1}$ (can be set separately by `.SCREEN` under `*FMM`)

3.3 ****INTEGRAL** advanced keywords

This input module defines the way the integrals should be calculated. This section contains some advanced keywords which is mostly useful for debugging or comparisons with other codes.

`.NO CS` Deactivate the use of Cauchy-Schwarz screening. Note that this does not deactivate the Primitive Cauchy-Schwarz screening.

`.NO PS` Deactivate the use of primitive Cauchy-Schwarz screening.

`.THR_CS`

<CS_Threshold>

Cauchy-Schwarz screening threshold. The default value is 10^{-8} . Note that

- The Screening threshold used for Coulomb is $\text{CS_Threshold} \cdot 10^{-2}$ (Default: 10^{-10})
- The Screening threshold used for Exchange is $\text{CS_Threshold} \cdot 10^{-0}$ (Default: 10^{-8})
- The Screening threshold used for One-electron operators is $\text{CS_Threshold} \cdot 10^{-7}$ (Default: 10^{-15})

`.THR_PS`

<PS_Threshold>

Primitive Cauchy-Schwarz screening threshold. The default value is 10^{-9}

`.CART-E` Use cartesian E-coefficients instead of hermite E-coefficients for the McMurchie-Davidson integral-evaluation scheme [10] used in LSDALTON. The use of Cartesian E-coefficients is default in most integral programs. We however use hermite E-coefficients according to ref. [11].

`.FTUVMAXPRIM`

<Maxprim>

Sets the maximum number of primitives used in the FTUV batches in the J-engine algorithm.

`.LOW RJ000 ACCURACY` Use a decreased accuracy for the calculation of the Boys function.

`.MAXPASSES`

<maxpass>

Change the maximum number of collected overlap distributions (default is 40).

`.NO PASS` Deactivate the use of Passes, the collection of overlap distributions which is used as default in order to increase efficiency.

- .NOSEGMENT Deactivate the use of segments. The use of segments is used to reduced the number of primitive functions in the calculation of integrals. The basis is considered to be a general contracted basis where all primitives contribute to all contracted functions.
- .NSETUV Use non-spherical E-coefficients.
- .OVERLAP-DF-J Use the Overlap density fitting algorithm for the calculation of the Coulomb matrix.
- .UNCONT Treat the basis functions (given by input) as fully uncontracted basis functions (i.e. ignore any contraction coefficients given in the basis and treat instead all the primitives as separate basis functions).

3.3.1 *FMM

This input block is used to specify settings for the (continuous) fast multipole moment (FMM) treatment of classical Coulomb interactions.

For gradients OpenMP parallelization is turned off. The reason for this is that a continuous counter used to identify moments for orbital products has to be the same in both moments and derivative moments. For the same reason screening [only during writing (see printmm routines)!!] is turned off both for the serial and parallel cases. As a consequence of the screening been turned off the moments have to be recalculated for the gradient and can not be reused from the preceding energy evaluation. The gradient implementation has been tested both for regular and density fitting Coulomb interactions. It works for the combined N-e + e-e + N-N interactions (default), and for the e-e interaction only (invoked by .NOONE). It has however not been tested for speed and efficiency.

.LMAX

<Lmax>

The maximum multipole-moment expansion order of a given orbital product. Default Value is 8.

.TLMAX

<TLmax>

The maximum order used for translated multipole-moments. Default Value is 20.

.SCREEN

<Threshold>

The FMM threshold is used to distinguish the Coulomb repulsion into classical and non-classical interactions, based on the non-classical extent of the contineous charge distribution (orbitals or orbital products). By default this threshold is set equal to

$\cdot 10^{-9}$ Defines the threshold used to determine if a contribution can be calculated classically or non-classically.

.NOONE Do not use FMM for the nuclear-electron attraction.

.NOMMBU Do not use io-buffers for interfacing multipole-moments to the FMM driver.

3.4 **WAVE FUNCTION

.HF Hartree-Fock calculation.

.DFT

<FUNCTIONAL>

DFT calculation.

The exchange—correlation functionals in LSDALTON can be divided into two groups: generic and combined functionals. A number of generic functionals are included within LSDALTON. The combined functionals are linear combinations of generic ones.

It should be noted that the input is not case sensitive, although the notation employed in this manual makes use of case to emphasise exchange or correlation functional properties and to reflect the original literature sources.

3.4.0.1 Exchange Functionals

Slater Dirac-Slater exchange functional [12, 13, 14].

Becke 1988 Becke exchange GGA correction [15]. Note that the full Becke88 exchange functional is given as Slater + Becke.

OPTX Handy’s 2001 exchange functional correction [16]. The full OPTX exchange functional is given by $1.05151 \cdot \text{Slater} - 1.43169 \cdot \text{OPTX}$.

PBEx Perdew, Burke and Ernzerhof 1996 exchange functional [17].

PW86x Perdew and Wang 1986 exchange functional (the PWGGA-I functional)[18].

3.4.0.2 Correlation Functionals

VWN3 correlation functional of Vosko, Wilk and Nusair, 1980 (equation III) [19]. This is the form used in the Gaussian program.

VWN5 correlation functional of Vosko, Wilk and Nusair, 1980 (equation V – the recommended one). The VWN keyword is a synonym for VWN5 [19].

LYP correlation functional by Lee, Yang and Parr, 1988 [20, 21].

P86c non-local part of the correlation functional of the Perdew 1986 correlation functional [22]. PZ81 (1981 Perdew local) is usually used for the local part of the functional, with a total correlation functional of P86c + PZ81.

PBEc Perdew, Burke and Ernzerhof 1996 correlation functional, defined as PW91c local and PBEc non-local correlation [17].

PW91c 1991 correlation functional of Perdew and Wang (the pwGGA-II functional) [23]. This functional includes both the PW91c non-local and PW91c local (ie PW92c) contributions. The non-local PW91c contribution may be determined as PW91c - PW92c.

PZ81 local correlation functional of Perdew and Zunger, 1981 [24].

3.4.0.3 Standalone Functionals

LB94 asymptotically correct functional of Leeuwen and Baerends 1994 [25]. This functional improves description of the asymptotic density on the expense of core and inner valence.

3.4.0.4 Combined functionals

GGAKey is a universal keyword allowing users to manually construct arbitrary linear combinations of exchange and correlation functionals from the list above. Even fractional Hartree–Fock exchange can be specified. This keyword is to be followed by a string of functionals with associated weights. The syntax is NAME=WEIGHT As an example, B3LYP may be constructed as:

```
.DFT
GGAKey HF=0.2 Slater=0.8 Becke=0.72 LYP=0.81 VWN=0.19
```

The following GGA and hybrid functional aliases are defined within LSDALTON and provide further examples of the GGAKey keyword.

SVWN5 is a sum of Slater functional and VWN (or VWN5) correlation functional. It is equivalent to

```
GGAKey Slater=1 VWN5=1
```

SVWN3 is a sum of the Slater exchange functional and VWN3 correlation functional. It is equivalent to the Gaussian program LSDA functional and can alternatively be selected by following set of keywords

```
GGAKey Slater=1 VWN3=1
```

LDA A synonym for SVWN5.

BLYP is a sum of Slater functional, Becke88 correction and LYP correlation functional.

It is equivalent to

```
GGAKey Slater=1 Becke=1 LYP=1
```

B3LYP 3-parameter hybrid functional [26] equivalent to:

```
GGAKey HF=0.2 Slater=0.8 Becke=0.72 LYP=0.81 VWN=0.19
```

B3LYP-G hybrid functional with VWN3 form used for correlation—this is the form used by the Gaussian quantum chemistry program. Keyword B3LYPGauss is a synonym for B3LYPg. This functional can be explicitly set up by

```
GGAKey HF=0.2 Slater=0.8 Becke=0.72 LYP=0.81 VWN3=0.19
```

BP86 Becke88 exchange functional and Perdew86 correlation functional (with Perdew81 local correlation). The explicit form is:

```
GGAKey Slater=1 Becke=1 PZ81=1 P86c=1
```

B3P86 variant of B3LYP with VWN used for local correlation and P86 for the nonlocal part.

```
GGAKey HF=0.2 Slater=0.8 Becke=0.72 P86c=0.81 VWN=1
```

B3P86-G variant of B3LYP with VWN3 used for local correlation and P86 for the non-local part. This is the form used by the Gaussian quantum chemistry program.

```
GGAKey HF=0.2 Slater=0.8 Becke=0.72 P86c=0.81 VWN3=1
```

BPW91 Becke88 exchange functional and PW91 correlation functional. The explicit form is:

```
GGAKey Slater=1 Becke=1 PW91c=1
```

CAMB3LYP Coulomb Attenuated Method Functional of Yanai, Tew and Handy [27].

This functional accepts additional arguments `alpha`, `beta` and `mu` to modify the fraction of HF exchange for short-range interactions, additional fraction of HF exchange for long-range interaction and the interaction switching factor μ . This input can be specified as follows:

```
.DFT
CAMB3LYP alpha=0.190 beta=0.460 mu=0.330
```

KT1 Slater-VWN5 functional with the KT GGA exchange correction [28, 29].

```
GGAKey Slater=1 VWN=1 KT=-0.006
```

KT2 differs from KT1 only in that the weights of the Slater and VWN5 functionals are from an empirical fit (not equal to 1.0) [28, 29].

```
GGAKey Slater=1.07173 VWN=0.576727 KT=-0.006
```

KT3 a hybrid functional of Slater, OPTX and KT exchange with the LYP correlation functional [30]. The explicit form is

```
GGAKey Slater=1.092 KT=-0.004 LYP=0.864409 OPTX=-0.925452
```

OLYP is the sum of the OPTX exchange functional with the LYP correlation functional [16, 20, 21].

```
GGAKey Slater=1.05151 OPTX=-1.43169 LYP=1
```

PBE0 a hybrid functional of Perdew, Burke and Ernzerhof with 0.25 weight of exact exchange, 0.75 of PBE_x exchange functional and the PBE_c correlation functional [31]. Alternative aliases are PBE1PBE or PBE0PBE.

```
GGAKey HF=0.25 PBEx=0.75 PBEc=1
```

PBE same as above but with exchange estimated exclusively by PBE_x functional [17]. Alias of PBE1PBE. This is the form used by CADPAC and NWChem quantum chemistry programs.

```
GGAKey PBEx=1 PBEc=1
```

Note that the Molpro quantum chemistry program uses the PW91c non-local correlation functional instead of PBE_c, which is equivalent to the following:

```
GGAKey PBEx=1 PW91c=1 .
```

Note that combinations of local and non-local correlation functionals can also be generated with the GGAKey keyword. For example, GGAKey P86c=1 PZ81=1 combines the PZ81 local and P86c non-local correlation functional, whereas GGAKey VWN=1 P86c=1 combines the VWN local and P86 non-local correlation functionals.

Linear combinations of all exchange and correlation functionals listed above are possible with the GGAKey keyword.

3.4.0.5 XCFUN functionals

Recently some support have been added for using the functionals from the XCFUN lib **fixme: insert proper reference**. Full support is expected in the next release, but unfortunately time constraints did not allow for full support in this release.

Currently only LDA and GGA type functionals are currently supported and only upto and including linear response. The XCFUN functionals are activated using the .XCFUN keyword under the ****INTEGRALS** section (see Section 3.2)

```
**INTEGRALS  
.XCFUN
```

Linear combinations XCFUN functionals are possible with the GGAKey keyword.

3.4.1 *DFT INPUT

Controls the XC-integration grid. The grid is generated as follows: For each atom a radial grid is created (different radial grids available, see below), which is multiplied with an angular grid (Lebedev-grids). The angular grids are by default pruned for radial points close to the nucleus, following Murray, Handy and Laming. [32] Grid weights for the grid points are calculated following different schemes (see below). Grid points with weights below 10^{-20} are disregarded. Please note that the grid construction routines in the LSDALTON program changed compared to the DALTON program which may result in small deviations in the number of grid points etc.

.ANGINT

<ANGINT>

Determines the quality of the angular Lebedev grid – the angular integration of spherical harmonics will be exact up to the specified order. Default value is 31. Maximum value is 64. Note that the value of ANGINT is changed by the following keywords: COARSE, NORMAL, FINE, ULTRAFINE. The GRIDX keywords also imply specific ANGINT values.

.COARSE Shortcut keyword for radial integration accuracy 10^{-11} and angular expansion order equal to 35.

.DFTELS

<DFTELS>

safety threshold – stop if the charge integration error becomes larger then this threshold.

.DFTTHR

<DFTHRO, DFTHRL, DFTHRI, RHOTHR>

DFTHRO is not used

DFTHRL is not used

DFTHRI threshold for screening product of gaussian atomic orbitals

RHOTHR threshold for screening of the electron density

.DISPER Activates the addition of the empirical dispersion correction following S. Grimme. [33, 34] The S6 factors and van der Waals radii of Ref. [34] are used. Implemented for the functionals BP86, BLYP, PBE, B3LYP for energies and gradients. Does not work when functionals are defined with the `combine` command.

.FINE Shortcut keyword for radial integration accuracy 10^{-13} and angular expansion order equal to 42.

.GRID TYPE

<GC2 LMG TURBO BECKE BECKEORIG SSF BLOCK BLOCKSSF>

GC2, LMG, TURBO define radial quadrature schemes, only one can be set. BECKE, BECKEORIG, SSF, BLOCK, BLOCKSSF define the grid partitioning schemes, only one can be set.

GC2 Gauss-Chebyshev quadrature of second kind.

LMG As proposed by Lindh, Malmqvist and Gagliardi (default). [35]

TURBO Treutler-Ahlrichs M4-T2 scheme. [36] Implies also that the angular integration quality becomes Z-dependant (see also ANGINT) and that pruning is used (see also NOPRUN).

BECKE Becke partitioning scheme with atomic size correction. [37]

BECKEORIG Becke partitioning scheme without atomic size correction (default). [37]

SSF Stratmann-Scuseria-Frisch partitioning scheme. [38]

BLOCK Becke partitioning scheme with atomic size correction [37] combined with a blockwise handling of grid points [39]. Useful for large molecules.

BLOCKSSF Stratmann-Scuseria-Frisch partitioning scheme [38] combined with a blockwise handling of grid points [39]. Useful for large molecules.

.GRID1 Shortcut for radial integration accuracy $1.0 * 10^{-5}$, angular expansion order equal to 17, radial quadrature TURBO, grid partitioning scheme BLOCK.

.GRID2 Shortcut for radial integration accuracy $2.15447 * 10^{-7}$, angular expansion order equal to 23, radial quadrature TURBO, grid partitioning scheme BLOCK.

.GRID3 Shortcut for radial integration accuracy $4.64159 * 10^{-9}$, angular expansion order equal to 29, radial quadrature TURBO, grid partitioning scheme BLOCK.

.GRID4 Shortcut for radial integration accuracy $5.01187 * 10^{-14}$, angular expansion order equal to 35, radial quadrature TURBO, grid partitioning scheme BLOCK.

.GRID5 Shortcut for radial integration accuracy $2.15443 * 10^{-17}$, angular expansion order equal to 47, radial quadrature TURBO, grid partitioning scheme BLOCK.

.HARDNESS

<HARDNESS>

sets the hardness of the partitioning function in the Becke weighting scheme. Only positive integer values allowed. The higher the hardness the more stepfunction like the partitioning functions. Default value is 3 as proposed by Becke. [37]

- .NOPRUN Suppresses the default pruning of the atomic angular integration grids for radial points close to the nucleus.
- .NORMAL Shortcut keyword for radial integration accuracy 10^{-13} and angular expansion order equal to 35.
- .RADINT
 - <RADINT>
 - Determines the quality of the radial integration grid. Default radial integration accuracy is 10^{-11} . Note that the value of RADINT is changed by the following keywords: NORMAL, FINE, ULTRAFINE. The GRIDX keywords also imply specific RADINT values.
- .ULTRAF Shortcut keyword for radial integration accuracy 10^{-15} and angular expansion order equal to 64.
- .LB94 Uses the van Leeuwen-Baerends asymptotic correction. This correction can be combined with all GGA type functionals
- .CS00 Using the Casida-Salahub asymptotic correction[\[40\]](#)

$$V'_{XC}(\mathbf{r}) = \max(V_{XC} + \Delta, V_{XC} + V_{LB94,correction}), \quad (3.1)$$

with a Zhan-Nichols-Dixon shift [\[41, 42\]](#)

$$\Delta = NZD_1 \cdot \epsilon_{HOMO} - NZD_2 \quad (3.2)$$

Where $NZD_1 = 0.2332$ and $NZD_2 = 0.315$. Note that NWCHEM have introduced the same correction but uses a $NZD_2 = 0.0116$. The parameters have been optimized with respect to a B3LYP functional so these parameters can be changed using the following keywords. Note that this keyword only works with GGA type functionals. The CS00 keyword only work with a method which calculates the HOMO energy.

- .CS00 NZD1
 - <NZD1>
 - Changes the parameter NZD_1 (default $NZD_1 = 0.2332$) see .CS00
- .CS00 NZD1
 - <NZD2>
 - Changes the parameter NZD_2 (default $NZD_2 = 0.315$) see .CS00
- .CS00
 - <Delta>
 - Using the Casida-Salahub correction with a shift of Delta see .CS00

3.4.2 *DENSOPT

This section contains the different options for obtaining the SCF wave function and energy. The default is augmented Roothaan–Hall density optimization in combination with a conjugate residual optimal trialvectors (CROP) scheme for solving the (level-shifted) Newton equations ((see ref. [43])) and using an atom-in-a-molecule starting guess.

- .2ND_ALL Use second order optimization in all SCF iterations.
- .2ND_LOC Use second order optimization in local SCF iterations.
- .ARH Use Augmented Roothaan-Hall scheme for density optimization (default) [44, 45] where the CROP solver ([43]) is used for solving the (level-shifted) Newton equation.
- .ARH FULL Use Augmented Roothaan-Hall for density optimization - no truncation of the reduced space, keep all micro vectors for the CROP algorithm.
- .ARH DAVID Use Augmented Roothaan-Hall for density optimization where the (level-shifted) Newton equations are solved using a reduced space solver based Davidson’s algorithm [46]. This setting may be used if default settings converges to a saddle point.
- .ARH(LS) DAVID The same procedure as described for .ARH DAVID augmented with a line search to accelerate convergence for very large molecular systems, but is less efficient than .ARH DAVID for smaller molecular systems.
- .STABILITY Check stability of the optimized wave function by calculation of the lowest Hessian eigenvalue.
- .STAB MAXIT
<Max. number of stability iterations>
Max. number of iterations in calculation of lowest Hessian eigenvalue (default is 40).
- .CHOLESKY Do Cholesky decomposition of overlap matrix (for density optimization in orthogonal AO basis) - default is Löwdin decomposition by diagonalization.
- .CONFAC
<Contraction factor>
For update of trust-radius (used in ARH and second order optimization). If trust-radius should be contracted, contract it by this factor (default is 0.7).
- .CONTRAC
<Contraction criterion>
For update of trust-radius (used in ARH and second order optimization). Contract trust-radius if trust-radius ratio is smaller than this criterion (default is 0.25).

.CONVDYN**<Option>**

Dynamic SCF convergence threshold. This is suitable for calculations on large molecules, since the standard SCF convergence threshold is based on the Frobenius norm of the SCF gradient, which is not size-extensive. Options are SLOPPY, STANDARD, TIGHT, VTIGHT corresponding to 10^{-4} , 10^{-5} , 10^{-6} , 10^{-7} times the square root of the number of electrons in the system.

.CONVTHR**<Threshold>**

SCF convergence threshold - Frobenius norm of SCF gradient (default is 1.0d-4). Note that this convergence criterion is not size-extensive. For large molecules, it is recommended to use .CONVDYN instead.

.DIIS Pulay's DIIS scheme is used to speed up SCF convergence [47, 48].

.DISK Store densities and Fock/KS matrices from previous iterations on disk instead of in core when constructing the new Fock/KS matrix (*memory-saving option*).

.DISKSOLVER Store trial and sigma vectors on disk instead of in core when solving linear equations (*memory-saving option*). Only referenced using ARH , Direct Density optimization or second order optimization.

.EDIIS The energy-DIIS scheme is used to speed up SCF convergence [49].

.EXPAND**<Expansion criterion>**

For update of trust-radius (used in ARH and second order optimization). Expand trust-radius if trust-radius ratio is larger than this criterion (default is 0.75).

.EXPFAC**<Expansion factor>**

For update of trust-radius (used in ARH and second order optimization). If trust-radius should be expanded, expand it by this factor (default is 1.2).

.FIXSHIFT**<Shift>**

Use a fixed level shift in all SCF iterations.

.HESVEC**<Number of Hessian eigenvalues>**

Number of lowest Hessian eigenvalues to be calculated with keyword .STABILITY (default is 1).

- .LCV** Compute the Least-Change Valence orbitals after valence density optimization step. All subsequent calculations are computed using Least-Change Valence orbitals augmented with atomic virtual orbitals of the Atomic density as basis set. Keyword only effective with TRILEVEL starting guess.
- .LCM** Compute the Least-Change Molecular orbitals after the Full molecular density calculation. All subsequent calculations are computed using these orbitals as basis set. **.LCV** is automatically included. Keyword only meaningful with TRILEVEL starting guess.
- .LEVELSH**
<N> <shift1> <shift2> ...<shiftN>
Use custom level shifts in the first *N* SCF iterations.
- .LOW ACCURACY START** Use low accuracy settings in the first couple of iterations until the appropriate gradient threshold have been reached.
- .MAXELM**
<Trust radius (max. element)>
Absolute max. element of step allowed (default is 0.35). Used in ARH and second order optimization.
- .MAXIT**
<Max. number of iterations>
Max. number of SCF iterations (default is 100).
- .MAXSTEP**
<Trust radius (Frobenius norm)>
Absolute max. Frobenius norm of step allowed (default is 0.6). Used in ARH and second order optimization.
- .MICTHRS**
<Threshold for micro iterations>
The micro iterations of the CROP algorithm are converged to gradient norm times this factor (default is 1.0d-2). Only referenced if ARH, Direct Density optimization or second order optimization.
- .MICROVECS**
<Max. number of microvectors>
Max. number of microvectors to be kept in the CROP scheme (default is 2). Only referenced if ARH, Direct Density optimization or second order optimization.

.MINDAMP

<Minimum damping>

Never allow level shift to be smaller than this.

.NOAV Turn off Fock matrix averaging in SCF iterations (this is default since the default optimization scheme is ARH, which contains implicit averaging).

.NVEC

<Max. no of vectors for averaging>

Maximum number of previous Fock and density matrices to be stored and used for ARH and DIIS (default is 10 for HF and 7 for DFT).

.NOPREC Turn off preconditioning of linear equations (ARH, TrFD, and second order optimization).

.NOSHIFT Do no level shifting.

.RESTART The code automatically saves the density matrix in each SCF iteration in a file called `dens.restart`. This option restart the calculation from this density matrix. If the program cannot find the `dens.restart` file the keyword have no effect.

.RH Use standard Roothaan-Hall scheme (diagonalization) for density optimization.

.SOEO Use second order ensemble optimization. Remember to specify active space and starting occupations. Use only in combination with **.NOGCBASIS**. Requires **.HF** or **.DFT** as wave function. After an ensemble optimization, the orbitals are written to file `cmo.out` and the AO density matrix is written to `dao.out`, which may be used to plot molecular orbitals and charge density plots.

.SOEOSPACE

<core> <act>

Specification of the orbitals in the active space. <core> being the number of core orbitals (occupations not optimized), and <act> the number of active orbitals, where the orbital occupations are optimized.

.SOE00CC

<fully occupied>

<fractionally occupied>

<n1> <n2> ...

Specification of the distribution of electron pairs in the starting orbitals in a second order ensemble optimization. <fully occupied> is the number of fully occupied orbitals and <fractionally occupied> is the number of fractionally occupied orbitals. <n1>, <n2> etc. are the fractional occupations of the fractionally occupied

spin-orbitals in the starting guess. The given occupations must lie between zero and one. If they are either zero or one, this orbital occupation is not optimized. Equal distribution may result in wrong results due to symmetry. The sum of the fully occupied orbitals and the given orbital occupations `<n1>`, `<n2>` etc., must equal the total number of electron pairs in the system. (NOTE that it is possible to specify an active space of zero orbitals, but still include fractional occupations. The optimization will thus optimize the shapes of the orbitals, without optimizing the orbital occupations.)

- `.SOEOSAVE` Saves the AO Fock matrix (and the AO density matrix) to the file `soeosave.out`. Used for restart.

- `.SOEORST` Restart second order ensemble optimization from orbitals stored in `soeosave.out` (so remember to copy this file to the working directory). The molecular geometry need not be the same as in the calculation where the stored orbitals were created. The active space and starting occupations still need to be specified using `.SOEOSPACE` and `.SOE00CC`.

- `.SOEOGC` Grand-canonical ensemble optimization. Removes the restriction on the total number of electrons from the second order ensemble optimization. The sum of the starting occupations still must be correct.

- `.SOEOMATHR`
`<macro threshold>`
Specifies the convergence threshold for the macro iterations in second order ensemble optimization.

- `.SOEOMITHR`
`<micro threshold>`
Specifies the convergence threshold for the micro iterations in second order ensemble optimization.

- `.SOEOTRUST`
`<trust-radius>`
Specifies the starting trust-radius in the ensemble optimization. Trust-radius will still be updated throughout the optimization.

- `.SOEODIPOLE` Use the ensemble density matrix to determine electric dipole moment and static electric polarizability.

- `.START`
`<Option>`
Starting guess for SCF optimization. Options are:

- **H1DIAG** Obtain initial guess by diagonalizing one-electron Hamiltonian
- **ATOMS** Obtain initial guess by atoms-in-molecules approach (default)
- **TRILEVEL** Optimization in three steps. 1. Atomic densities, 2. Valence molecular density, 3. Full molecular density [2, 3].

Note that Huckel guess is not supported by LSDALTON.

.VanLenthe Use Van Lenthe's scheme for level shifting and averaging [50].

3.4.3 \$INFO

For the different parts of the wave function optimization, it is possible to get very detailed information. This section describes these keywords. They must be put under ***DENSOPT** in a section beginning with **\$INFO** and ending with **\$END INFO**. Note that these keywords do NOT start with a dot!

INFO_CROP Detailed info from Conjugated Residual OPTimal vectors scheme (Direct Density Optimization, ARH and second order optimization).

INFO_DIIS Detailed info from Direct Inversion in the Iterative Subspace algorithm.

INFO_LEVELSHIFT Detailed info from determination of dynamic level shift (Direct Density Optimization, ARH and second order optimization).

INFO_LINEQ Detailed info from solution of linear equations and trust-radius update (Direct Density Optimization, ARH and second order optimization).

INFO_RH Detailed info from Roothaan-Hall algorithm (diagonalization).

INFO_RH_DETAIL Even more detailed info from Roothaan-Hall algorithm (diagonalization).

INFO_STABILITY Detailed info from calculation of lowest Hessian eigenvalue (stability analysis) and HOMO-LUMO gap.

INFO_STABILITY_REDSPACE Reduced space info from calculation of lowest Hessian eigenvalue (stability analysis) and HOMO-LUMO gap.

3.5 **OPTIMIZE

This input module describes the keywords needed to optimize a molecular geometry. In the current release no second-order algorithms are available since the molecular Hessian is not implemented, but a number of quasi-Newton trust-radius level-shifted techniques

for finding equilibrium geometries are available (`.BFGS`, `.PSB`, `.DFP`). The methods differ in the way approximate Hessians are built and updated: `.INIMOD`, `.INIRED` and `.INITEV` provide different approximations for the initial Hessian, while `.MODHES` recomputes the approximated Hessian at every geometry.

The geometry optimization generates a sequence of geometry steps. The coordinates of each accepted step are stored in the files `MOLECULE.XXX`, where `XXX` is the geometry step number, and the final converged geometry in `MOLECULE.OUT`.

Geometric structure can be optimized in redundant internal (`.REDINT`) or Cartesian (`.CARTES`) coordinates with two sets of convergence criteria (two for the gradient and two for the step). Convergence is obtained when the following four quantities are respectively smaller than the four convergence criteria ϵ , 5ϵ , 3ϵ and 15ϵ [51]:

- the root-mean-square of the gradient,
- the maximum absolute value of the gradient,
- the root-mean square of the step vector,
- and the maximum absolute element (in internal or Cartesian coordinates) of the step vector.

The default setting specifies the minimization in internal coordinates [52], with a model Hessian [53] updated with BFGS formula. The atoms-in-molecule approach is used to set up the initial density-matrix at each new geometry step. However, it is possible to take as starting guess McWeeny-purified converged density-matrix at the previous geometry. This is achieved by setting the `.RESTART` option under the `*DENSOPT` subsection. The default value of ϵ is 10^{-5} (Other predefined values for the convergence criteria can be set using the keywords `.VLOOSE`, `.LOOSE`, `.TIGHT` and `.VTIGHT`). Alternatively the convergence criteria of Baker [54] can be set using `.BAKER`.

Example of test cases for geometry optimization calculations

The test cases are located in `LSDALTON/test/geomopt`. These test cases illustrate the main features of the geometry optimization:

- *geomopt/cartes_bfgs_min*: performs a DFT/LDA geometry optimization in Cartesian coordinates, with BFGS update of an initial Hessian equal to a unit matrix and Baker convergence criteria.
- *geomopt/redint_bfgs*: performs a DFT/BLYP geometry optimization in redundant internal coordinates with a model Hessian updated with BFGS formula and Baker convergence criteria.

- *geomopt/Excited_state_opt*: performs a DFT/B3LYP geometry optimization of an excited state in redundant internal coordinates and Baker convergence criteria.
 - *geomopt/cartes_psb_min*: performs a DFT/BLYP geometry optimization in Cartesian coordinates with a diagonal initial Hessian updated by PSB formula, McWeenie's purification used for constructing the initial guess and Baker convergence criteria.
 - *geomopt/geomopt_constrain*: shows a constrained geometry optimization of ethane, keeping the C-C bond distance fixed (Internal coordinate #1 as determined from the use of `.FINDRE`).
 - *geomopt/cartes_trilevel_newconv*: performs a geometry optimization in Cartesian coordinates with `.TRILEVEL` starting guess and a default convergence criteria, a diagonal initial Hessian updated by a loose DFP formula.
- `.BAKER` Activates the convergence criteria of Baker [54]. The minimum is then said to be found when the largest element of the gradient vector (in Cartesian or redundant internal coordinates) falls below $3 \cdot 10^{-4}$ and either the energy change from the last iteration is less than 10^{-6} or the largest element of the predicted step vector is less than $3 \cdot 10^{-4}$.
- `.BFGS` Specifies the use of a first-order method with the Broyden-Fletcher-Goldfarb-Shanno (BFGS) update formula for optimization. This is the preferred first-order method for minimizations, as this update is able to maintain a positive definite Hessian.
- `.CARTES` Specifies that Cartesian coordinates should be used in the optimization.
- `.CONSTR`
- ```
<Number of constrained redundant internal coordinates>
<Indices of each constrained redundant internal coordinate, one per line>
```
- Specifies a constrained geometry optimization. You will need to give the total number of redundant internal coordinates to constrain and their indices as defined using the `.FINDRE` keyword. For example fixing redundant internal coordinates 4 and 9 would read like:
- ```
...
**OPTIMIZE
.CONSTR
2
4
9
```

- ...
- **END OF INPUT**
- .DFP** Specifies that a first-order method with the Davidon-Fletcher-Powell (DFP) update formula should be used for optimization.
- .FINDRE** Using this keyword no geometry optimization is carried out, but only the redundant internal coordinates are found.
- .INIMOD** Use a simple model Hessian [53] diagonal in redundant internal coordinates as the initial Hessian. All diagonal elements are determined based on an extremely simplified molecular mechanics model, yet this model provides Hessians that are good starting points for most systems, thus avoiding any calculation of the exact Hessian. This is the default for optimizations in redundant internal coordinates. Currently this is not an option for optimization in Cartesian coordinates.
- .INIRED** Specifies that the initial Hessian should be diagonal in redundant internal coordinates. The different diagonal elements are set equal to 0.5 for bonds, 0.2 for angles and 0.1 for dihedral angles, unless **.INITEV** has been specified. If the optimization is run in Cartesian coordinates, the diagonal internal Hessian is transformed to Cartesians.
- .INITEV**
<Read EVLINI, the eigenvalues>
The default initial Hessian for first-order minimizations is the identity matrix when Cartesian coordinates are used, and a diagonal matrix when redundant internal coordinates are used. If **.INITEV** is used, all the diagonal elements (and therefore the eigenvalues) are set equal to the value EVLINI.
- .LOOSE** Default convergence criterion ϵ set to $1.0 \cdot 10^{-4}$.
- .MAX IT** Maximum number of iterations in geometry optimization scheme (default set to 100).
- .MODHES** Determine a new model Hessian (see **.INIMOD**) at every geometry without doing any updating. The model is thus used in much the same manner as an exact Hessian, though it is obviously only a relatively crude approximation to the analytical Hessian.
- .PRINT**
<Print level>
Print level for the output. The higher the print level, the more information is printed to the output file.

- .REDINT Specifies that redundant internal coordinates should be used in the optimization. This is the default.
- .PSB Specifies that a first-order method with the Powell-Symmetric-Broyden (PSB) update formula should be used for optimization.
- .TIGHT Default convergence criterion ϵ set to $1.0 \cdot 10^{-6}$.
- .VLOOSE Default convergence criterion ϵ set to $1.0 \cdot 10^{-3}$.
- .VTIGHT Default convergence criterion ϵ set to $1.0 \cdot 10^{-7}$.

3.6 **DYNAMI

This input module is devoted to molecular dynamics simulations. LSDALTON provides some tools for performing direct Born-Oppenheimer molecular dynamics, i.e. trajectories are integrated with forces calculated on the fly. Trajectory integration is available for SCF-type wavefunctions (with dispersion correction for DFT) and for DEC wavefunctions. Properties could be calculated along the trajectories and should be specified in the **RESPONSE section. LSDALTON simulates microcanonical(NVE) ensembles. Currently no sampling is available and the starting coordinates and velocities must be provided as input. Trajectories are integrated with gradient-based velocity-Verlet method [55].

LSDALTON provides several options for the choice of starting guess for SCF-type electronic theory methods. By default, the guess is generated anew each time step according to the corresponding input. Alternatively, one can restart from the density optimized at the previous time-step. This is achieved by setting the .RESTART option under the *DENSOPT subsection. This reduces the number of SCF iterations per time-step and accelerates the integration. Two more efficient algorithms for starting guess propagation are implemented in LSDALTON Fock matrix dynamics [56] and time-reversible propagator [57].

Example test cases for **DYNAMI calculations:

These test cases illustrate the main features of direct dynamics. The test cases are located in LSDALTON/test/ddynam:

- *ddynam/H2O_fmd*: free water molecule with Fock matrix dynamics;
- *ddynam/HCN_ddyn*: HCN dissociation with restart density;
- *ddynam/HF_vib*: a vibrating HF molecule with time-reversible propagator.

.PRINT

<Print level>

Print level for the output. The higher the print level, the more information is printed to the output file.

.TIMESTEP

Defines integration time step in femtoseconds which should be given in the next line (real). The default is 0.5 fs.

.MAX ITER

Defines maximum number of time steps. Must be given in the next line (integer). The default is 100.

.MASSWE

States that the integration is carried out in mass-weighted coordinates. The default is FALSE.

.MWVEL

States that the input velocities are mass-weighted. The default is FALSE.

.VELOCI

Begins the input of the velocities. In the next line the number of atoms should be given (integer), then the velocities grouped atom-wise: three(x,y,z) in a line (real). The default is for all velocities to be zero.

.FOCKMD

Fock matrix dynamics. Below number of points for extrapolation N and polynomial order M must be specified. Note that $M > N$ (both integer). Works only with .RESTART option under the *DENSOPT subsection

.TIMREV

Time-reversible density propagation. Below the number of points for extrapolation N (integer) must be specified. The only thoroughly tested option is $N = 2$.

3.7 **LOCALIZE ORBITALS

This section describes keywords needed to perform localization of Hartree–Fock orbitals. The optimization of the chosen localization function will be performed using a trust-region algorithm [58], and can be performed for the occupied space and/or the virtual orbital space. For the occupied space the core and valence spaces will be localized separately.

After running a Hartree-Fock calculation followed by an orbital localization two files with molecular orbital coefficients will be present; *cmo_orbitals.u* and *lcm_orbitals.u*.

cmo_orbitals.u contains coefficients for the canonical molecular orbitals (CMO) and *lcm_orbitals.u* contains coefficients for the localized molecular orbitals (LMO). The coefficient matrix row index refers to the atomic orbital basis index, while the column index refers to the molecular orbital basis. The format of the files are as described in the Matrix File Format part of Section 2.

For the most efficient orbital localization for large molecular systems [59], the .ARH, .START/TRILEVEL and .LCM options are recommended for use as described in Section 3.4.2, and .PSM with powers 2 2 are recommended for the **LOCALIZE ORBITALS section.

.PSM

<m m>

Use powers m of the second moment (PSM) localization function [60]. A power 0 specifies that no localization should be carried out (e.g., 0 1 to only localize the virtual space). m=1 is equivalent with the Boys localization function. For improved locality m \geq 2 is recommended.

.PFM

<m m>

Use powers m of the fourth moment (PFM) localization function [61]. A power 0 specifies that no localization should be carried out (e.g., 0 1 to only localize the virtual space). Using power 1 yields orbitals with good locality, but a power 2 is recommended if locality of the orbitals is essential. Powers higher than 3 are not recommended. The PFM localization function should be chosen if basis sets augmented with diffuse functions are used.

.PipekMezey

Use Pipek-Mezey localization function using an implementation based on Löwdin population analysis rather than the traditional Mulliken population analysis (see Ref. [62]). Both occupied and virtual orbitals will be localized. Please note, the Pipek-Mezey localization function suffers from system and basis set dependencies. For systems with complicated bonding structures or when using basis sets augmented with diffuse functions the PSM or PFM options should be used if good locality is essential.

.OccPipekMezey

Pipek-Mezey localization of only the occupied space.

.VirtPipekMezey

Pipek-Mezey localization of only the virtual space.

.PipekM(MULL)

Use Pipek-Mezey localization function using the Mulliken population analysis. A

power 0 specifies that no localization should be carried out. Otherwise the same considerations as for the `.PipekMezey` option.

`.OccPipekM(MULL)`

Pipek-Mezey localization (using Mulliken population analysis) of occupied space.

`.VirtPipekM(MULL)`

Pipek-Mezey localization (using Mulliken population analysis) of virtual space.

`.No Level2 Localization`

Should only be used in combination with the `.START/TRILEVEL` and `.LCM` options for the `*DENSOPT` section. The keyword is used to skip orbital localization after the second level in the three level procedure. Not recommended for general use, but can be used to save computational time if only the virtual space is to be localized.

`.Only Loc`

Provided the file with the molecular orbital coefficients (e.g., *cmo_orbitals.u* or *lcm_orbitals.u*) using this keyword the Hartree-Fock calculation will be skipped, and the orbitals will be read in and localized. Important: rename or copy the orbital coefficient file to *orbitals_in.u*, only this file will be read. After the localization procedure the molecular orbital coefficients corresponding to the localized basis is written to *orbitals_out.u*. Thus, for this keyword to be used, *orbitals_in.u* must exist and a localization function must be chosen.

`.Orbital Locality`

This keyword will make sure second and fourth moment orbital spreads are printed for all orbitals, not just the least local ones.

`.MACRO IT`

`|option|`, Set maximum number of macro iterations for orbital localization procedure. Default is 200.

`.LOOSE MICRO THRESH`

Looser threshold for solving level-shifted Newton equations in davidson solver in orbital localization procedure. Should only be used if a calculation fails and the error message tells you to use this keyword.

`.Orbital Plot`

`<orbital specification>`

Generates `.plt` file for either the least local or the most local orbitals. To generate `.plt` files for the least local orbitals use orbital specification `LEASTL`, whereas to generate `.plt` files for the most local orbitals use specification `MOSTL`. If both least

local and most local are wanted, make two `.Orbital Plot` sections with each of the specifications. The `.plt` files may be plotted using for example the UCSF Chimera program package [1]. Note: for plotting other orbitals, use the `**PLT` option described in section 3.10. Also note that the grid dimensions may be modified as described in Section 3.11.

3.8 ****RESPONS**

This section describes the keywords needed for obtaining molecular properties for HF and DFT based on the atomic orbital based response formulation [63]. The response section begins with `**RESPONS`. General response information related to more than one property (e.g. how many excitation energies) is put directly under `**RESPONS`. After this, each individual response property (e.g. the polarizability tensor) is labeled by an asterisk, and the specific (optional) information related to that property (e.g. which optical frequencies) follows below. All input values are given in atomic units. The general structure is thus:

```
**RESPONS

.General response information

*Label for property 1

.Specific (optional) information for property 1

*Label for property 2

.Specific (optional) information for property 2
```

Each of the properties below have a test case. The test cases may be found in the **LS-DALTON/test/LSresponse** directory. To run a test case, go to the `test/` directory and type:

```
./TEST <test case>
```

The test case files contains simple examples of input files.

Below, the list of general response input keywords follows.

`.NEXCIT`

`<Number of excitation energies>`

Determines the number of excitation energies to be calculated. If this keyword is set, the excitation energies and the corresponding one-photon dipole absorption strengths for the lowest NEXCIT excited states (i.e. excited states 1 to NEXCIT) are always calculated. **Important:** If properties involving excited states are to be requested

(e.g. two-photon absorption or the excited state gradient), this keyword must be listed *before* any of these properties.

Test case: LSresponse/LSresponse_HF_opa

3.8.1 *SOLVER

General information related to the way response equations are solved to obtain a given property. By default, standard and eigenvalue response equations are solved using the algorithm with paired trial vectors [64], whereas damped (complex) response equations are solved using the algorithm with symmetrized trial vectors [65].

This choice can be modified using the `.SYM_SOLVER` and `.PAIR_SOLVER` keywords, see below.

`.SYM_SOLVER`

The solver with symmetrized trial vectors is used for solving standard response equations.

Test case: LSresponse/LSresponse_HF_alpha_astv

`.PAIR_SOLVER`

The solver with paired trial vectors is used for solving damped (complex) response equations.

Test case: LSresponse/LSresponse_DFT_alpha_aptv

`.CONVTHR`

<Convergence threshold>

Convergence threshold to which response equations are solved. Default value is set to 10^{-4} .

`.MAXIT`

<Maximum number of iterations>

Maximum number of iterations in the iterative procedure. Default value is set to 100.

`.MAXRED`

<Maximum size of the reduced space>

Maximum size of the reduced space. Default value set equal to 200.

`.AOPREC`

AO preconditioning is used (MO preconditioning by default). AO preconditioning may only be used within the algorithm with paired trial vectors.

`.NOPREC`

No preconditioning is used.

.CONVDYN**<Option>**

Dynamic convergence threshold suitable for large calculations. Options are TIGHT, STANDARD, and SLOPPY.

.RESTEXC**<Number Of excitation Vectors on file>**

This is a restart option, that allows the user to restart the calculation.

Assume for instance that you have already done one calculation where you requested 6 excitation energies but realize that you need 10. You can provide the file `rsp_eigenvecs` and use

.RESTEXC

6

option to restart the calculation from the previous. This option can also be used to bypass the excitation vector step if the previous calculation failed for some property evaluation which needed the excitation vectors.

.DTHR**<Threshold>**

Threshold for when excited states are to be considered degenerate

Now follows a list of input keywords for the specific properties available in LSDALTON.

3.8.2 *ALPHA

Calculation of the (possibly complex) electric dipole polarizability tensor α_{AB} and its isotropic average. The polarizability equals minus the linear response function $\langle\langle\mu_A;\mu_B\rangle\rangle_{\omega_B}$, where ω_B is in general allowed to be complex – that is, $\omega_B = \omega_B^R + i\omega_B^I$. Unspecified frequencies are set to zero by default, i.e. if no frequencies are specified, the static polarizability is calculated.

Test case: LSresponse/LSresponse_HF_alpha

.BFREQ**<Number of real frequencies for B operator>****<Freq1, freq2, ... , freqN>**

Real frequencies ω_B^R in the corresponding linear response function. The first line after `.BFREQ` contains the number of frequencies and the second line contains all frequency values (on one single line).

.IMBFREQ**<Number of imaginary frequencies for B operator>**

<Freq1, freq2, ... , freqN>

Imaginary frequencies ω_B^I in the corresponding linear response function. The imaginary part of the complex polarizability describes a broadened one-photon absorption spectrum. If .IMBFREQ is not specified, only the real polarizability is calculated. Input as for .BFREQ.

For example, the following input is used to calculate complex polarizability tensors for the frequencies $\omega_B = 0.1 + 0.05i$ and $\omega_B = 0.2$ (in a.u.):

**RESPONS

*ALPHA

.BFREQ

2

0.1 0.2

.IMBFREQ

2

0.05 0.0

3.8.3 *BETA

Calculation of the (possibly complex) first electric dipole hyperpolarizability tensor β_{ABC} and the corresponding averages β_{\parallel} and β_{\perp} . The first hyperpolarizability tensor equals minus the quadratic response function $\langle\langle\mu_A; \mu_B, \mu_C\rangle\rangle_{\omega_B, \omega_C}$, where the frequencies are in general allowed to be complex – i.e. $\omega_B = \omega_B^R + i\omega_B^I$ and $\omega_C = \omega_C^R + i\omega_C^I$. The input is analogous to the *ALPHA input. Unspecified frequencies are set to zero by default, i.e. if no frequencies are specified, the static first hyperpolarizability is calculated.

Test case: LSresponse/LSresponse_HF_beta

.BFREQ <Number of real frequencies for B operator><Freq1, freq2, ... , freqN>Real
frequencies ω_B^R in the corresponding quadratic response function. Input as for .BFREQ
under *ALPHA.

.IMBFREQ

<Number of imaginary frequencies for B operator>

<Freq1, freq2, ... , freqN>

Imaginary frequencies ω_B^I in the corresponding quadratic response function. Input as
for .IMBFREQ under *ALPHA.

.CFREQ

<Number of real frequencies for C operator>

<Freq1, freq2, ... , freqN>

Real frequencies ω_C^R in the corresponding quadratic response function. Input as for .BFREQ under *ALPHA.

.IMCFREQ

<Number of imaginary frequencies for C operator>

<Freq1, freq2, ... , freqN>

Imaginary frequencies ω_C^I in the corresponding quadratic response function. Input as for .IMBFREQ under *ALPHA.

3.8.4 *DAMPED_TPA

Damped two-photon absorption [66] where both individual photons have the same energy (= half the excitation energy).

Test case: LSresponse/LSresponse_HF_dtpa

.OPFREQ

<Number of one-photon frequencies>

<Freq1, freq2, ... , freqN>

The frequencies in the input are one-photon frequencies (=half the excitation energy in case of resonance).

.GAMMA

<Damping parameter>

The damping parameter γ is used in *all* response equations, i.e. $i\gamma$ is effectively added to all frequencies occurring in the response equations. Default value: 0.005 a.u.

3.8.5 *QUASIMCD

Calculation of the \mathcal{A} and \mathcal{B} terms of magnetic circular dichroism (MCD), based on the method of Ref. [67], but reformulated using the formalism of Ref. [63]. The calculation of Damped MCD spectra according to Ref. [68] is also possible with this keyword.

Note that one or more of the 3 keywords { .DAMPEDXCOOR , .MCDEXCIT, .DAMPEDRANGE } must be specified

If .MCDEXCIT is specified, the default is to proceed in the following way:

1. Determine the excited states requested under .MCDEXCIT
2. Determine \mathcal{B} terms for all allowed transitions. Both London atomic orbitals LAO (also called Gauge including atomic orbitals GIAO) and non-LAOs are used to determine

the \mathcal{B} terms. LAOs are superior to standard AOs, but the difference can give an indication of how close the result is to the basis set limit.

3. Simulate the MCD spectrum based on the calculated \mathcal{B} terms (sticks) by associating a Lorentzian lineshape function (with lineshape parameter of 0.005 a.u.) to each \mathcal{B} term (See Ref. [67]). The simulated spectrum is written to a file MCDspectraAU.dat (in atomic units). The first number is the frequency, the second the LAO ellipticity and the third is the non-LAO ellipticity. A corresponding file is generated called MCDspectra.dat using standard units (cm^{-1} for frequencies and molar ellipticity for the ellipticity). The individual \mathcal{B} term contribution to the MCD spectra is written to the files BtermAU.dat and Bterm.dat. Per default 5000 points are used for the simulated spectrum. The standard units for the \mathcal{B} term are given as $\frac{D^2\mu_B}{cm^{-1}}$, where D is the unit Debye and μ_B is the Bohr magneton. The conversion factor between atomic units and the standard units is 5.8876410^{-5} . The standard unit for the \mathcal{A} term is given as $D^2\mu_B$, with a conversion factor of 12.920947806163007.
4. Perform damped calculations based on the standard MCD calculation. A number of points around each individual MCD peak (default value: 10) are determined for which to calculate the damped spectra. The result is printed to the files dampedMCDspectraRAU.dat (atomic units) and dampedMCDspectraR.dat.

Test case: LSresponse/LSresponse_mcd_calc, LSresponse/LSresponse_mcd
LSresponse/LSresponse_mcd2, LSresponse/LSresponse_mcd3

Note that only the LSresponse/LSresponse_mcd_calc test case is a good example for a general MCD calculation.

.MCDEXCIT

<Number of excited states to consider>

The \mathcal{B} terms will be calculated for all states, unless they are zero due to selection rules (dipole forbidden)

.DEGENERATE

This keyword must be set in input if the molecule has a degenerate state so that \mathcal{A} terms are possible, otherwise all states are assumed non-degenerate and no \mathcal{A} terms will be calculated. When this keyword is set, the \mathcal{A} terms are calculated and a derivative Lorentzian lineshape function is used to simulate the individual \mathcal{A} term contributions to the MCD spectrum (See Ref. [67]). The individual \mathcal{A} terms contributions to the MCD spectrum are written to the files AtermAU.dat and Aterm.dat

.DAMPEDXCOOR

<Number of frequencies>

<Freq1, freq2, ... , freqN>

The frequencies for which to calculate the damped MCD spectra (in atomic units).

.DAMPEDRANGE

<Freq1>

<FreqN>

<Number of frequencies in range between Freq1 and Freq2>

The frequencies for which to calculate the damped MCD spectra (in atomic units), here specified as an interval.

.NO LONDON

Deactivates the use of LAOs (i.e., only standard, non-LAO, basis is used)

.NO NOLONDON

Deactivates the use of non-LAOs (i.e., only LAO are used)

.NO SIMULATE

Deactivates the simulation of the MCD spectrum from the individual MCD terms

.NO ATERM

Deactivates the calculation of \mathcal{A} terms

.NO BTERM

Deactivates the calculation of \mathcal{B} terms

.NO DAMPED

Deactivates the execution of damped MCD spectra

.GAUSSIAN

Uses Gaussian lineshape functions (with a lineshape parameter of 0.0070851079363103793) instead of the default Lorentzian lineshape functions.

.LINESHAPEPARAM

<lineshape parameter>

Changes the lineshape parameter (default value is 0.005 a.u. for Lorentzian, and 0.0070851079363103793 a.u. for Gaussian) used to simulate the spectrum

.NSTEPS

<number of frequencies used for the simulated MCD spectra>

Changes the number of frequencies used for the simulation of the MCD spectra from the individual \mathcal{A} and \mathcal{B} terms' sticks (default 5000).

.NVECFORPEAK

<number of frequencies used around each MCD peak>

Changes the number of frequencies used around each MCD peak (default 10) in the damped response calculation.

Note that the keyword **.DTHR** under ***SOLVER** (see section 3.8.1) can be used to define the threshold below which an excited state is considered degenerate

3.8.6 *SHIELD

Nuclear magnetic shielding tensors and chemical shift can be calculated with this keyword

Test case: LSresponse/LSresponse_NMR_SHIELD

ESDIPOLE

Permanent dipole moment for excited states. **Always requires specification of .NEXCIT!**

If .EXSTATES is not specified, the excited state dipole moments for all excited states from 1 to NEXCIT are calculated.

Test case: LSresponse/LSresponse_HF_esd

.EXSTATES

<Number of specific excited states to consider>

<Specific excited states to consider>

Only calculate excited state gradient for selected excited states. The first line after .EXSTATES contains the number of excited states for which the excited state dipole moment is to be calculated, and the second line specifies such states (identified by their index in the .NEXCIT list). **Important:** The position of the highest lying excited state specified by .EXSTATES must be smaller than or equal to the total number of excited states specified by .NEXCIT!

3.8.7 *ESGRAD

Calculation of the molecular gradient for excited states. **Always requires specification of .NEXCIT!** If .EXSTATES is not specified, excited state gradients for all excited states from 1 to NEXCIT are calculated.

Test case: LSresponse/LSresponse_HF_esg

.EXSTATES

<Number of specific excited states to consider>

<Specific excited states to consider>

Input is identical to .EXSTATES under *ESDIPOLE.

For example, the following input is used to calculate excited state gradients for excited states number 3 and 6:

```
**RESPONS
.NEXCIT
6
*ESGRAD
.EXSTATES
2
3 6
```

3.8.8 *GAMMA

Calculation of the (possibly complex) second electric-dipole hyperpolarizability tensor γ_{ABCD} and the corresponding averages γ_{\parallel} and γ_{\perp} . The second hyperpolarizability tensor equals minus the cubic response function $\langle\langle\mu_A; \mu_B, \mu_C, \mu_D\rangle\rangle_{\omega_B, \omega_C, \omega_D}$, where the frequencies are in general allowed to be complex – i.e. $\omega_B = \omega_B^R + i\omega_B^I$, $\omega_C = \omega_C^R + i\omega_C^I$, and $\omega_D = \omega_D^R + i\omega_D^I$. The input is analogous to those for *ALPHA and *BETA. Unspecified frequencies are set to zero by default, i.e. if no frequencies are specified the static second hyperpolarizability is calculated.

Test case: LSresponse/LSresponse_HF_gamma

```
.BFREQ
  <Number of real frequencies for B operator>
  <Freq1, freq2, ... , freqN>
  Real frequencies  $\omega_B^R$  in the corresponding cubic response function. Input as for
  .BFREQ under *ALPHA.

.IMBFREQ
  <Number of imaginary frequencies for B operator>
  <Freq1, freq2, ... , freqN>
  Imaginary frequencies  $\omega_B^I$  in the corresponding cubic response function. Input as for
  .BFREQ under *ALPHA.

.CFREQ
  <Number of real frequencies for C operator>
  <Freq1, freq2, ... , freqN>
```


Real frequencies ω_C^R in the corresponding cubic response function. Input as for .BFREQ under *ALPHA.

.IMCFREQ

<Number of imaginary frequencies for C operator>

<Freq1, freq2, ... , freqN>

Imaginary frequencies ω_C^I in the corresponding cubic response function. Input as for .IMBFREQ under *ALPHA.

.DFREQ

<Number of real frequencies for D operator>

<Freq1, freq2, ... , freqN>

Real frequencies ω_D^R in the corresponding cubic response function. Input as for .BFREQ under *ALPHA.

.IMDFREQ

<Number of imaginary frequencies for D operator>

<Freq1, freq2, ... , freqN>

Imaginary frequencies ω_D^I in the corresponding cubic response function. Input as for .IMBFREQ under *ALPHA.

3.8.9 *MOLGRA

Single point calculation of the molecular gradient.

Test case: LSresponse/LSresponse_HF_molgra

3.8.10 *TPA

Two-photon absorption where both individual photons have the same energy (= half the excitation energy). **Always requires specification of .NEXCIT!** If .EXSTATES is not specified, two-photon absorption for all excited states from 1 to NEXCIT are calculated.

Test case: LSresponse/LSresponse_HF_tpa

.EXSTATES

<Number of specific excited states to consider>

<Specific excited states to consider>

Input is identical to .EXSTATES under *ESDIPOLE.

3.9 **DEC and **CC

Correlated coupled-cluster (CC) calculations using the Divide-Expand-Consolidate (DEC) scheme [69, 70, 71, 72, 73, 74], where local orbitals are used to carry out the correlated cal-

ulation on a large molecular system in terms of many small local calculations. Formally, the computational time for the DEC scheme scales linearly with system size. Currently only second-order Møller-Plesset (MP2) calculations (energy, density, and geometry optimization) are available using the DEC scheme. DEC calculations are invoked using the `**DEC` keyword.

Furthermore, conventional coupled-cluster energies for the MP2, CC2, and CCSD models are available using the `**CC` keyword. The computational time for these implementations scale with the system size to the fifth, fifth, and sixth power for MP2, CC2, and CCSD, respectively.

The `**DEC` and `**CC` implementations employ massive parallelism and will be highly effective only if many computing nodes are available.

Special note: It is highly recommended that the memory available for the calculation is specified in the input, see `.MEMORY` keyword below.

The `**DEC` section uses local orbitals by default, while the `**CC` section uses canonical orbitals by default. Below keywords for the `**DEC` section and `**CC` section and relevant test cases are given.

****DEC input keywords** (only MP2 model):

`.FOT`

`<FOT level>`

Level for fragment optimization threshold (FOT). The FOT defines the precision of a DEC calculation compared to a conventional calculation [69, 70, 71, 72, 73, 74]. The input is an integer which defines the negative power of the FOT; e.g. if FOT level=5, then the FOT= 10^{-5} a.u. Thus, the higher the FOT, the smaller is the error of the DEC calculation compared to a conventional calculation (and of course, the more expensive is the calculation). Possible values: 1,2,3,4,5,6,7,8. Default value: 4.

`.MEMORY`

`<Memory in gigabytes>`

It is highly recommended to specify the memory (in gigabytes) available for the calculation using this keyword! For an MPI run this is the memory available for each MPI process. If this keyword is not set, the program will try to estimate the available memory using a system call. While this will usually work fine it might fail on some architectures. (This keyword can also be used in `**CC` section).

`.PAIRTHR`

`<Pair distance threshold (in a.u.)>`

Pair distance threshold (in a.u.) beyond which pair fragments are omitted from the calculation. By default this value is adapted to the FOT.

.PAIRTHRANGSTROM

<Pair distance threshold (in Angstrom)>

Pair distance threshold (in Å) beyond which pair fragments are omitted from the calculation. By default this value is adapted to the FOT.

.RESTART

Restart unfinished DEC calculation. Requires that HF files *dens.restart*, *fock.restart*, *lcm_orbitals.u*, and *overlapmatrix* are present in the folder where the calculation is restarted. Additionally, if .info files are present it means that some of the fragment calculations have been carried out and the .RESTART keyword will read information about the finished fragment calculations from file and calculate the missing fragments. Specifically, if the files *atomicfragments.info* and *atomicfragmentsdone.info* are present, it means that some (or all) of the atomic fragment calculations are finished. If, in addition, the file *fragenenergies.info* (energy calculation) *or* *mp2grad.info* (MP2 density or gradient calculation) is also present, it means that some (or all) of the pair fragments are also done.

Note 1: This keyword should NOT be combined with .RESTART in the *DENSOPT section.

Note 2: This keyword cannot be used for a DEC-MP2 geometry optimization. The only way to "restart" a DEC-MP2 geometry optimization is use the current geometry in a new DEC-MP2 geometry optimization – i.e., copy the most recently generated MOLECULE.xxx file to MOLECULE.INP and run the calculation again using the same LSDALTON.INP.

.NOTABSORBH

By default orbitals originally assigned to hydrogen atoms are reassigned to the nearest heavy atom. This reassigning can be turned off by invoking this keyword.

.FROZENCORE

Use the frozen core approximation (can also be used in **CC section).

.DENSITY

Calculate DEC-MP2 density matrix [73] (stored in MP2.dens). The MP2 electric dipole moment is also calculated if this keyword is invoked.

.GRADIENT

Calculate MP2 molecular gradient [73] at input geometry (for geometry optimization,

see test case examples below). The MP2 density and electric dipole moment is also calculated if this keyword is invoked.

.KAPPATHR

<THR>

Threshold for $\bar{\kappa}$ multiplier equations solved when DEC-MP2 molecular gradient is calculation. Default value is 10^{-4} .

.CANONICAL

Use canonical orbitals. This is only recommended for advanced users for testing purposes. In general, the DEC scheme is only meaningful for local orbitals.

.MPIGROUPSIZE

<Size>

Size of local MPI groups (integer) in massively parallel DEC scheme [74]. The default settings should suffice for most purposes, and use of the keyword is only recommended for advanced users.

Example test cases for **DEC calculations:

These test cases illustrate the main features of the DEC scheme. The test cases are located in LSDALTON/test/dectests.

- *decmp2_energy*: Calculate DEC-MP2 energy.
- *decmp2_density*: Calculate DEC-MP2 density matrix and electric dipole moment.
- *decmp2_gradient*: Calculate DEC-MP2 molecular gradient.
- *decmp2_geopt*: Carry out DEC-MP2 geometry optimization. Note that the geometry optimization is invoked by the **OPTIMIZE section, while the **DEC section specifies that the geometry optimization should use DEC-MP2 energies and molecular gradients. The DEC-MP2 geometry optimization will automatically estimate the intrinsic energy error of the DEC calculation. If this error is larger than the difference between two geometry, the FOT level will be increased to get a more accurate energy and gradient in the next iteration.

****CC input keywords:**

.MP2

Use MP2 model. This gives the canonical MP2 energy and is not optimized for parallel performance. It is only intended to be used for benchmarking DEC-MP2 calculations on relatively small molecular systems.

.CC2

Use CC2 model which is not an optimized code, but rather uses the CCSD optimized code with some contributions removed. See CCSD documentation for details.

.CCSD

Use CCSD model. The code employed is a massively parallel version and flexible with respect to memory. Due to the use of one-sided communication in these models it is recommended to run CCSD with an asynchronous progress engine switched on (how to do that can be found in the documentation of the respective MPI library you are using). When running a CCSD calculation make sure that at least one quantity of size V^2O^2 (O = number of occupied orbitals, V = number of virtual orbitals) fits into memory in double precision floating point numbers (with some additional space of course). Using this keyword automatically triggers checkpointing after each iteration. The calculation can be restarted with the usual `..RESTART` keyword.

.FROZENCORE

Use the frozen core approximation (can also be used in `**DEC` section).

.MEMORY

<Memory in gigabytes>

It is highly recommended to specify the memory (in gigabytes) available for the calculation using this keyword! For an MPI run this is the memory available for each MPI process. If this keyword is not set, the program will try to estimate the available memory using a system call. While this will usually work fine it might fail on some architectures. (This keyword can also be used in `**DEC` section).

.CCMAXITER

Maximum number of iterations in CC solver.

.CCTHR

Convergence threshold for residual norm in CC solver.

.SUBSIZE

Number of previous vectors to store in CROP scheme [43] for CC solver.

.CCSDNOSAFE

Prevent saving of CCSD amplitudes as checkpoint files.

Example test cases for **CC calculations:

The test cases are located in LSDALTON/test/dectests.

- *fullmp2_energy*: Calculate conventional canonical MP2 energy.
- *fullccsd_high*: Calculate conventional canonical CCSD energy.

3.10 **PLT

Generation of .plt files which may be used to visualize densities, orbitals, and electrostatic potentials by calculating these at specific points in space. The .plt files can be visualized e.g. using the Chimera program [1].

Important note: This section assumes that an LSDALTON calculation has already been carried out to generate files containing density matrix elements or molecular orbital coefficients. The .plt files can then be generated by running a new calculation where the LSDALTON.INP file has been modified as exemplified below.

The density matrix from HF and DFT calculation are saved in a file *dens.restart*, while the MP2 density is saved in the file *MP2.dens* (if requested, see **DEC section). The canonical MO coefficients are saved in the file *cmo_orbitals.u*, while localized molecular orbitals are saved in a file *lcm_orbitals.u* (if requested). The definition of the grid points is described in the **PLTGRID section.

Note that it is also possible to generate .plt files for orbitals on the run as described in Section 3.7.

.INPUT

<Name of input file>

The name of the input file containing density matrix elements or orbital coefficients. Possible input files include *dens.restart*, *MP2.dens*, *cmo_orbitals.u*, and *lcm_orbitals.u*.

.OUTPUT

<Name of output file>

The name of the output plt-file where the calculated values at each grid point are saved. Examples are given below.

.DENS

Construct .plt file for electron density at grid points. For example to calculate electron density from the file *dens.restart* and save information in file *dens.plt*, insert the following section in the LSDALTON.INP file used to generate the *dens.restart* file in the first place:

```
**PLT
```

```
.INPUT
dens.restart
.OUTPUT
dens.plt
.DENS
```

.EP

Construct .plt file for electrostatic potential grid points based on input density matrix. For example to calculate electrostatic potential from the density in the file *dens.restart* and save information in file *ep.plt*, insert the following section in the LSDALTON.INP file used to generate the *dens.restart* file in the first place:

```
**PLT
.INPUT
dens.restart
.OUTPUT
ep.plt
.EP
```

.ORB

<Orbital index>

Construct .plt file for specific orbital at grid points. For example to calculate values of orbital number 8 at grid points from the file *lcm_orbitals.u* and save information in file *orb8.plt*, insert the following section in the LSDALTON.INP file used to generate the *lcm_orbitals.u* file in the first place:

```
**PLT
.INPUT
lcm_orbitals.u
.OUTPUT
orb8.plt
.ORB
8
```

.CHARGEDIST

<Orbital index 1 Orbital index 2>

Construct .plt file for charge distribution of two orbitals at grid points. For example to calculate charge distribution between orbitals 5 and 8 at grid points from the file *lcm_orbitals.u* and save information in file *cd.5.8.plt*, insert the following section in the LSDALTON.INP file used to generate the *lcm_orbitals.u* file in the first place::

```

**PLT
.INPUT
lcm_orbitals.u
.OUTPUT
cd_5_8.plt
.CHARGEDIST
5 8

```

3.11 **PLTGRID

Definition of 3-dimensinal grid used for generation of .plt files in **PLT section. The default grid choice should suffice for most visualization purposes. This section is only for the advanced user who wishes to modify the default choice of grid. This also modifies the grid used when .plt files for local orbitals are generated on the run, see Section 3.7.

The grid box is defined in the following manner:

- The first point in the grid box is (X1,Y1,Z1).
- The remaining grid points are then defined by going out in the X, Y, and Z directions with step sizes *deltax*, *deltay*, and *deltaz*, until there are *nX*, *nY*, and *nZ* points in the X,Y, and Z directions (giving a total number of gridpoints $nX \times nY \times nZ$).

There are two options to define the grid box: (i) manual gridbox where X1, Y1, Z1, *deltax*, *deltay*, *deltaz*, *nX*, *nY*, *nZ* are defined explicitly in the input file; (ii) molecule-specific gridbox where all atoms are contained within the grid box AND there is an additional buffer zone around the outermost atoms in the X, Y, and Z directions. Option (ii) thus requires that the *deltax*, *deltay*, *deltaz*, and buffer values are defined by the input, which implicitly defines X1, Y1, Z1, *nX*, *nY*, and *nZ* based on the molecular structure.

The default gridbox uses option (ii) with *deltax*=*deltay*=*deltaz*=0.3 a.u. and *buffer*=6.0 a.u. User-defined grid box based on options (i) and (ii) use the following inputs:

```
.MANUAL
```

```

<X1  Y1  Z1>
<deltax  deltay  deltaz>
<nX  nY  nZ>

```

Manual definition of gridbox as described above. All input values are in a.u.

```
.MOLECULE
```

```

<buffer>
<deltax  deltay  deltaz>

```

Molecule-specific definition of gridbox as described above. All input values are in a.u.

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