
Important Note: Any blue color text below is a clickable link to a pdf or log file.

Outline

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i. *Preliminaries*

The nomenclature in the MESRA output is made clear by simply transposing the one used in presentation [P] and in Ref. [15], unless the contrary is explicitly stated. Few advices are given in paragraph **vii** of this manual.

The MESRA software comes after his predecessor, NANCY_EX 2.0 (link), which solely aimed at producing unrelaxed detachment/attachment density matrices, natural and canonical transition orbitals, as well as unrelaxed density-based descriptors of molecular electronic transitions.

ii. *Requirements*

MESRA is written in Fortran 90, currently interfaced with multiple versions of the Gaussian software (link).

Requirements for MESRA to work are

- Unix operating system (Linux/Mac OS) with bash environment
- Fortran compiler installed (Intel or GNU compilers like gfortran are recommended; if Intel compiler is used, it is advised to use the mkl libraries indicated in the makefile)
- The gmake build automation tool installed (MESRA is compiled using a makefile)

- BLAS and LAPACK mathematical libraries installed
- Gaussian software is installed and sourced
- The formchk, rwfdump, and cubegen utilities of Gaussian are sourced
- Permissions to modify and source your *$HOME/.bashrc* file

iii. *Downloading and installing* MESRA

1. Place the mesra.tar.bz2 archive in the directory where you wish to store the mesra software.

2. Untar the compressed file

tar -jxvf mesra.tar.bz2 && rm mesra.tar.bz2

3. Go inside the mesra directory

cd mesra

4. Modify the makefile according to your installation

vi src/makefile

In that file, FC stands for Fortran Compiler, and LFLAGS stands for Libraries flags; make sure the $() and -o tags are correctly placed according to the compiler you use. When you are done, save and exit the file by typing "*:wq"*.

5. Install mesra

./install_mesra

Important: when typing this command, you will be prompted an answer (y/n) for allowing MESRA to add the path to its executables in your $HOME/.bashrc file, and to source the .bashrc file. If you do not have the permissions for these operations, please type '*n'* and contact your administrator. In case you have the permissions for this and type '*y'*, a new « PATH=$PATH: » line should have appeared in your $HOME/.bashrc file with the location of MESRA software and executables ($PATH/mesra/bin). You might wish to check that this operation was successful by typing

grep 'mesra' $HOME/.bashrc

If you get an error message when running the *./install_mesra* command due to a problem with your compiler, try to modify again the *src/makefile* and relaunch the installation, or contact your administrator. If the problem persists, use the e-mail address in the *Contact* section of this web site to report the problem.

MESRA installation generates an *installation.log* file that you might wish to compare with our reference one, downloadable by clicking here.

Installing MESRA created a *test* directory in mesra/. This directory contains sub-directories that you can use for testing MESRA before moving to your own calculations. The *test* directory contains three sub-directories

cubes

contains two cube files for performing numerical integration and/or cube manipulations.

restricted

contains a directory with the outcome of a TDDFT calculation, and one with the outcome of a CIS calculation, both for closed-shell molecules.

unrestricted

is equivalent but for open-shell molecules. In particular, each sub-directory (*tddft* and *cis*) contains two sub-sub-directories, *form* (unrestricted SCF with both alpha and beta electrons) and *H2* (unrestricted SCF with only alpha electrons).

6. Open a new tab, and check that the installation of the MESRA environment was successful by typing *mesra_man*. An in-line manual should be displayed on your screen. If not, check your ~/.bashrc file, or re-open your terminal.

Other utilities installed in the *mesra/bin* directory are

clean_mesra

cleans the files and directories after a MESRA calculation in case of trouble

test_mesra

launches the quick test that has been launched after installing MESRA.

uninstall_mesra (for developers)

uninstalls MESRA. This can also be useful if you misused the makefile when trying to install MESRA, and wish to restart the installation with the proper parameters in the makefile.

reinstall_mesra (for developers)

reinstalls MESRA, accounting for the modifications the developer made in the Fortran source files (*mesra/src/*) and executables (*mesra/src/executables/*), and launches the test with *test_mesra.*

recompile_mesra (for developers)

simply recompiles the Fortran sources without performing *test_mesra a posteriori.* Useful and fast if you did not modify executable files from *mesra/src/executables/*. The equivalent if you modified executable files from *mesra/src/executables/* is not necessary: you simply need to copy/paste the modified file(s) directly in *mesra/bin/.* Never modify files in the */mesra/bin/* directory: your modifications will be discarded when reinstalling (*reinstall_mesra*) or recompiling (*recompile_mesra*).

iv. *Preparation of the Gaussian inputs, and pre-treatment of the Gaussian outputs*

iv.A Preparing the Gaussian excited-state calculation input

These two lines should be placed at the beginning of your Gaussian input:

%chk = chk_filename.chk

%rwf = rwf_filename.rwf

(simply replace « chk_filename » and « rwf_filename » by the name you want)

The MESRA software is compatible with the *CIS, TDA* and *TD* keywords in Gaussian. The minimum number of roots (*Nstates=J* option to the *CIS, TDA* or *TD* keyword) to be computed is *J=3*.

If you wish to compute « relaxed » quantities, you should add the *density=all* keyword and option to your Gaussian excited-state calculation input.

iv.B Pre-treatment of Gaussian's output files

After Gaussian's calculation is performed, you should use the formchk and rwfdump utilities to produce files that will be used by MESRA

formchk chk_filename.chk

rwfdump rwf_filename.rwf overlap 514r

rwfdump rwf_filename.rwf density 633r

Caution: When relaxing the hole-particle pair with the *density=all* key, i.e., using the Z-vector method, Gaussian's default excited state for the relaxation is the first one. If you wish to compute the relaxation-related features on excited states of higher energy, you should relaunch a Gaussian job adding the *read* and *root=N* options to those originally used with the excited state keyword (*CIS, TDA, TD*), where *N* is the number of your excited state of interest.

v. *Use of the* MESRA *software: the principle*

Important note 1: unless you simply wish to process cube files, you should create a working directory with files related to the only one Gaussian calculation you target with MESRA. This directory should **solely** contain the following files: the .fchk file of the calculation, the "overlap" and "density" files. The quotation marks mean that these files should have this **exact**, lower cased, file name: *overlap* and *density.*

Important note 2: all the keywords and options given to MESRA except file names should be **lower cased!**

Using MESRA is extremely simple. There are two situations:

- You are in a directory with cube files that you want to analyze or manipulate

Then you just need to type *mesra*, followed by the appropriate series of arguments (details below under the **utilities** title)

- You are in the working directory depicted above (specific to each Gaussian excited-state calculation, and contains solely the .fchk, *overlap* and *density* files) and wish to perform one of the **main tasks** listed below

Then you just need to start by "preparing" the use of MESRA by typing

mesra prep $soft $fchk_file $roots

$soft is the software name you used (g03, g09, and g16 only are accepted)

$fchk_file is the name of your .fchk file

$roots is the number of transitions that were computed by Gaussian. Please note that if you are using g16, MESRA will automatically detect the number of transitions that were computed, so the last argument is not necessary in that case, and that case only.

Example of use:

mesra prep g16 pp3.fchk

Another example:

mesra prep g09 butadiene.fchk 6

Now that you generated a "general information file" with the *prep* keyword, you can use MESRA, that will read this general information file, so you just need to provide information on the current job you want to perform. If we continue with the butadiene example, we can type

mesra dau 2

which will cause the computation and storage of the detachment/attachment density matrices, and the evaluation of density-based descriptors using Löwdin-like detachment/attachment population. A directory "*mesra-t2*" will be created in the working directory, and MESRA's output files will be stored there.

Jobs can be done consecutively: the general information file remains in the working directory. For instance, one can type

mesra dau 2

then

mesra orbsxy 3

then

...

without any unsafe interference between past and current MESRA jobs.

The outcome of MESRA calculations for the *x*th excited state of a molecule is a set of files, gathered in the *mesra-tx* directory. Here are the file types that can be produced by MESRA:

.log

collects the information printed on screen, and some additional, secondary information for developers (see below).

.fchk

MESRA produces two types of *.fchk* files: those that will contain a density matrix, which can be visualized by using the *cubegen* utility with the *fdensity=scf*. These files have explicit names (*detachmentU.fchk*, *DeltaR.fchk*, etc.) with Delta being the (unrelaxed or relaxed) difference density matrix. In this context, *DeltaZ* stands for the Z-vector (*gamma^Z* matrix). The other type of *.fchk* that MESRA outputs contains orbitals (*p*NTOs, *a*NTOs, CTOs). Those can be visualized by creating a cube using the *cubegen* utility with the *mo=1,2[,3,4,...]*. The numbers between square brackets are optional. The orbitals are paired in the *.fchk* file, so the couples are arranged as *occ1*, *virt1*, *occ2*, *virt2*, etc. which means that using the *mo=1,2* keyword and option with the *cubegen* utility will produce a cube with the first couple *(occ1/virt1)* of transition orbitals. Using the *mo=1,2,3,4* keyword and option will produce a cube with the first two couples.

.eig

When performing a matrix diagonalization, MESRA produces a file with the eigenvalues. Again, the nomenclature of these files is made very explicit. For instance *daU.eig* will contain the eigenvalues of the unrelaxed difference density matrix, used for producing the unrelaxed detachment/attachment density matrices.

C.orth

contains the diagonal entries of (C^dagger)SC, to check that the LCAO coefficients are properly read and that there is no orthogonality problem between the canonical orbitals.

.ac

The *.ac* files arise from the *a*diabatic *c*onnection (*ac*) of the Z-vector. There are two of them: *adiabZ.ac* which stores the numerical results (evolution of the relative amplitude of the relaxation, relaxed descriptors) along the adiabatic connection. The second file, *acVec_Z.ac* stores the auto-correlation of the *natural difference orbitals* (the eigenvectors of the difference density matrix) along the adiabatic connection.

.cube

The outcome of cube manipulations is another cube file.

vi. *Keywords list and options*

Note 1: the list of keywords and options is visible from anywhere in the terminal by simply typing

mesra_man

They are written so that the MESRA software can be executed as

mesra argument1 argument2 [...]

Note 2: some features can be accompanied by a population analysis (PA) of the detachment/attachment density matrices. This means that one of the arguments to the *mesra* command should be an integer between 0 and 100, that will be converted into a percentage (*x*, decimal number between 0 and 1). For example, the default value (*x = 1/2*) corresponds to 50. The full DS (*x* = 0) to SD (*x = 1*) and SA to AS spectrum can be scanned using the *scanpa* option.

The keywords labelled with an asterisk (*) are compatible with population analysis to produce approximation of the density-based descriptors; the operation can be discarded by using the *nopa* option. Two asterisks (**) mean that population analysis is mandatory. Three asterisks (***) means that population analysis is mandatory, and that the *scanpa* option is forbidden.

The keywords marked by a circle (°) require cube files to be in the *mesra-tx* repository (x is the target transition number). These cube files can be obtained by using the command

cubegen 0 fdensity=scf formchk_filename.fchk formchk_filename.cube -X h

by replacing *X* by 3 for a numerical integration analysis of the density or for producing figures with a good density resolution. *X* can alternatively be replaced by 2 to provide a coarse grid, for a quick visualization of the density.

Note that when using the cubegen command above for producing cubes that are to be used for numerical integration, it is important to keep consistency between the fchk and cube base names, so that only the extension (.fchk, .cube) differ.

Keywords marked by a double circle (°°) require a "U" or "XY" .log file(s) from a *qmniu* or *qmnixy* calculation in the *mesra-tx* directory (x is the target transition number). This simply means that prior to a qmnirlx calculation, you should obviously have performed a qmniu or a qmnixy calculation.

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1. Main tasks - Processing files in the working directory

Reminder: Every keyword except file names should be lower cased.

Optional arguments are indicated below by their default value between square brackets.

Post-processing of the Quantum Package is being implemented, and will concern unrelaxed detachment/attachment (dau) construction and population analysis approximation to density-based descriptors, for closed-shell molecules only.

prep *- Preparation for the use of* MESRA

Argument 1: *prep*

Argument 2: Software (g03, g09, g16)

Argument 3: Fchk file name (if applicable - Gaussian postprocessing)

Argument 4: Total number of transitions computed (if Software is different from g16)

dau* - *Detachment/attachment from the* ***u****nrelaxed difference density matrix.*

Argument 1: *dau*

Argument 2: Number of the transition of interest

Argument 3: [50] statement about the population analysis : can be "*nopa*" (no population analysis), "*scanpa*" or any integer between 0 and 100

daxy* - *Unrelaxed detachment/attachment density matrices for CIS, TDHF, TDA, TDDFT (XY methods) using appropriately the properties of the difference density matrix (no matrix diagonalization is necessary, hence the calculation is faster but does not produce the eigenvalues.*

Argument 1: *daxy*

Argument 2: Number of the transition of interest

Argument 3: [50] statement about the population analysis : can be "*nopa*" (no population analysis), "*scanpa*" or any integer between 0 and 100

daz* - *Detachment/attachment related to the Z-vector transformation (diagonalizes the Z-vector and produces its detachment/attachment)*

Argument 1: *daz*

Argument 2: Number of the transition of interest

Argument 3: [50] statement about the population analysis : can be "*nopa*" (no population analysis), "*scanpa*" or any integer between 0 and 100

dar* - *Relaxed detachment/attachment, obtained by diagonalizing the relaxed difference density matrix. The use of this keyword is highly discouraged.*

Argument 1: *dar*

Argument 2: Number of the transition of interest

Argument 3: [50] statement about the population analysis : can be "*nopa*" (no population analysis), "*scanpa*" or any integer between 0 and 100

rlxypa** - *Relaxed density-based descriptors are produced using population analysis*

Argument 1: *rlxypa*

Argument 2: Number of the transition of interest

Argument 3: [50] statement about the population analysis : can be "*scanpa*", or any integer between 0 and 100

! *nopa* not authorized

alphaddagger** - *Approximates the alpha^ddagger integrals using population analysis*

Argument 1: *alphaddagger*

Argument 2: Number of the transition of interest

Argument 3: [50] statement about the population analysis : can be "*scanpa*", or any integer between 0 and 100

! *nopa* not authorized

adiabz -*** *Adiabatic connection of the Z-vector*

Argument 1: *adiabz*

Argument 2: Number of the transition of interest

Argument 3: [50] statement about the population analysis : can be any integer between 0 and 100

! *scanpa* not authorized

! *nopa* not authorized

orbsxy *- Transition orbitals for CIS, TDHF, TDA, TDDFT (XY methods).* *p*NTOs, *a*NTOs, *and* CTOs *are computed.*

Argument 1: *orbsxy*

Argument 2: Number of the transition of interest

! For the ***orbsxy***, ***pntos***, ***antos***, and ***ctos*** keywords, in the MESRA output when "*x"* and "*y"* are employed (for instance, in the (*x^dagger*)*x* expression), it is the *x* and *y* TDDFT vectors that are pointed.

pntos *- Projected Natural Transition Orbitals*

Argument 1: *pntos*

Argument 2: Number of the transition of interest

antos - *Natural Transition Orbitals corresponding to a TDDFT auxiliary wave function*

Argument 1: *antos*

Argument 2: Number of the transition of interest

ctos - *Canonical Transition Orbitals*

Argument 1: *ctos*

Argument 2: Number of the transition of interest

qmniu° *- Computes density-based descriptors from the unrelaxed detachment/attachment cubes constructed using the outcome of a* MESRA *dau calculation.*

Argument 1: *qmniu*

Argument 2: Number of the transition of interest

! *detachmentU.cube* and *attachmentU.cube* files should be in the *mesra-tx* directory, *where x is number of the transition of interest*

qmnixy° *- Computes density-based descriptors from the unrelaxed detachment/attachment cubes constructed using the outcome of a* MESRA *daxy calculation.*

Argument 1: *qmnixy*

Argument 2: Number of the transition of interest

! *detachment_XY.cube* and *attachment_XY.cube* files should be in the *mesra-tx* directory, *where x is number of the transition of interest*

qmniz° *- Computes density-based descriptors from the unrelaxed detachment/attachment cubes constructed using the outcome of a* MESRA *daz calculation.*

Argument 1: *qmniz*

Argument 2: Number of the transition of interest

! *detachmentZ.cube* and *attachmentZ.cube* files should be in the *mesra-tx* directory, *where x is number of the transition of interest*

qmnir° *- Computes density-based descriptors from the unrelaxed detachment/attachment cubes constructed using the outcome of a* MESRA *dar calculation.*

Argument 1: *qmnir*

Argument 2: Number of the transition of interest

! *detachmentR.cube* and *attachmentR.cube* files should be in the *mesra-tx* directory, *where x is number of the transition of interest*

qmnirlx°° **-** *Computes relaxed density-based descriptors from the* MESRA *.log file from a qmniu or a qmnixy calculation.*

Argument 1: *qmnirlx*

Argument 2: Number of the transition of interest

! *qmNIU.log* or *qmNI_XY.*log *file should be in the mesra-tx directory, where x is the number of the transition of interest*

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2. Utilities - Processing cube files directly in any directory

qmni **-** *Computes density overlap, normalized charge displacement, and centroids from two cube files*

Argument1: *qmni*

Argument2: cube1 file name

Argument3: cube2 file name

split **-** *Splits the entries of a cube file according to their sign, and integrates*

Argument 1: *split*

Argument 2: cube file name

cubeop **-** *Operations on cubes : op1*cube1 + op2*cube2 = cube3*

Argument 1: *cubeop*

Argument 2: cube1 file name

Argument 3: cube2 file name

Argument 4: cube3 file name

Argument 5: op1 (*p* or *m*, standing for plus or minus)

Argument 6: op2 (*p* or *m*, standing for plus or minus)

incrcube **-** *Increase of a cube size*

Argument 1: *incrcube*

Argument 2: cube file name

Argument 3: percentage of size increase (each dimension will be increased with the same percentage)

Comments

dau outputs the 1-DDM eigenvalues, while *daxy* does not: it simply produces the detachment/attachment density matrices.

When performing a detachment/attachment analysis on the Z-vector, one notices that the equivalent of chi and phi for the unrelaxed detachment/attachment analysis in this case are the zeta^Z and phi^Z quantities. However, these are still labelled chi and phi when performing the Z-vector detachment/attachment calculation and population analysis (*daz* keyword) or numerical integration (*qmniz* keyword). One can also obtain zeta^Z by constructing the cube with the z-vector density (stored in a DeltaZ file with .fchk extension) and using MESRA with the *split* keyword. This is also true for finding the (unrelaxed) *chi* by building a cube from the Delta (U or _XY) file with .fchk extension and using MESRA with the *split* keyword.

vii. *Advices*

When performing detachment/attachment population analysis, $x = 1/2$ is the recommended scheme (which explains why "50" is usually the default value), as the Löwdin-like detachment/attachment population analysis is the only one that ensures populations higher than zero and lower than one.

For the numerical integration, we recommend the use of the "-3" key when constructing the cube using Gaussian utility.

viii. *The* .log *files*

The most useful information is printed on screen, and in a .log file. The .log file also contains information helpful to developers for bug tracking or for detecting when the excited-state calculation itself is problematic, or when MESRA software has been misused.

Here are few keys for reading the .log files:

- "p" is used for canonical space ground-state density matrix
- "pK" is for atomic space ground-state density matrix
- "px" and "pxK" are standing for excited-state density matrices
- Lower "t" is used for canonical space transition density matrix
- Upper "T" is for atomic space transition density matrix
- S is the atomic basis overlap matrix (equation 5 in Ref. [15])
- During population analysis, $y = 1-x$

ix. *Quantities, with their original reference*

The quantities that are computable using MESRA are listed below, with their original reference, i.e. the one in which it has first been published, and the name they get in the code output.

ix.A *From Ref.* [15]

The following quantities are reported using in Ref. [15] and will be referred as follows:

[Original Ref.] Description of the quantity (name in the code output, equation in [15])

[6] The integral of detachment/attachment density (theta, eq. 22)

[6] The hole/particle spatial overlap (phiS, eq. 25)

[7] The amount of transferred charge (chi, eq. 26)

[8] The fraction of D/A contributing to the net charge displacement (phi, eq. 26)

[8] The joint measure of locality and normalized charge displacement (psi, eq. 27)

[12] The relaxed-unrelaxed detachment/attachment integral difference (lambda^dagger, eq. 34)

[12] Integral of the relaxation-induced detachment/attachment alteration (alpha^ddager, eq. 35)

[12] The amount of transferred charge during the relaxation (chi, eq. 36)

ix.B *From presentation* [P]

The following quantities are reported using in [P] and will be referred as follows:

[Original Ref.] Description of the quantity (name in the code output, section in [P])

[7] The D/A and n+/n- inter-centroid distances (zeta, II.1.C)

[Unpublished] Normalized relaxation-induced charge displacement (phi, II.1.D)

[Unpublished] Relaxed phiS, phi, and psi descriptors (explicit, II.1.E)

+ Two quantities related to wave function-based analysis (XY methods)

[9] Amplitude of the particle-hole correlation (III.3.A)

[9] CTOs residue: sum of the absolute value of the negative theta_eta entries (item 3 of section III.3.C, sum of Psi_ia - theta_ia in eq. 73 of Ref. [9])

References - Any green color text below is a direct link to the document web page.

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