DMDW: A set of tools to calculate Debye-Waller factors and other related quantities using dynamical matrices.

DMDW is a set of tools developed to calculate Debye-Waller (DW) factors and other related quantities from a dynamical matrix (matrix of force constants or Hessian matrix) using the Lanczos recursive algorithm.[Refs.] This set includes a module integrated into FEFF, a standalone version that can be used independently of FEFF and a Fortran module that can be integrated into third-party programs. DMDW also includes conversion tools to generate the required input files from different ab initio programs.

This document is divided into the following sections:

* Installing DMDW
  ** Installing as a FEFF module
  ** Creating and installing the standalone version
  ** Using as a DW factor engine

* Using DMDW
  ** Using dym2feffinp
  ** Using within a XANES or EXAFS calculation in FEFF
  ** Calculating DW factors using the standalone version
  ** The "dym" dynamical matrix file format

* Examples
  ** XANES and EXAFS calculations
  ** Calculating DW factors with the standalone version
  ** Creating a FEFF input file from a dym file using dym2feffinp
  ** Creating dynamical matrix files from third-party programs

* Troubleshooting common problems
  ** Structure problems
  ** Lanczos problems

* Future developments
  ** Expected changes in FEFF input format
  ** Expected changes in DMDW input format
  ** Expected changes in dynamical matrix file format

----

* Installing DMDW
  ** Installing as a FEFF module

The installation of DMDW within FEFF is straightforward. Please refer to the FEFF installation instructions. After the FEFF installation is completed a module called "dmdw" should be located under the FEFF "bin" directory structure.

  ** Creating and installing the standalone version

Within the "src/DMDW" directory in the FEFF distribution, execute the following command:

make standalone

This will create a directory "dmdw_standalone" under "src/DMDW". Edit "Makefile" inside the directory "dmdw_standalone/src". Change the "F90" variable to your fortran 90 compiler of choice. Then execute the following commands:

```
make
make install
make examples
```

If everything worked correctly the reference results located in "dmdw_standalone/examples/Reference_Results" should agree with those generated in "dmdw_standalone/examples".

  ** Using as a DW factor engine

[NOT WRITTEN YET]

----

* Using DMDW

  ** Using dym2feffinp

Before explaining how to include dynamical matrix DW factors in EXAFS and XANES calculations, it is important that the user becomes familiar with some constraints/limitations that are present in the current implementation. These limitations stem from the fact that both the dynamical matrix and FEFF input files contain structural information. These structures must match for the DW values to be correct. Since FEFF internally sorts the atoms according to distance to the absorber, special care must be taken to avoid mismatching the structural information coming from the FEFF input with that from the dym file. dym2feffinp is a utility that helps in the generation of FEFF input files with structures that match those in the dynamical matrix files. The usage of dym2feffinp is as follows:

dym2feffinp [Options] dymfile

where dymfile is the name of the file containing the dynamical matrix. This command creates two files, feff.dym and feff.inp, which contain correctly matched structures. (NOTE OF WARNING: If dymfile is named "feff.dym", then dym2feffinp will APPEND the updated dym information to it. We recommended that a different name is used for dymfile. Future version will check that dymfile doesn't use the "feff.dym" name.)

The default behavior of dym2feffinp can be modified with the following options:

```
--c  iAbs   Use atom iAbs as absorber
--f  fname  Write feff input to file fname
--d  dname  Write adjusted dym file to file dname
--j         Skip header and only write POTENTIALS + ATOMS cards
--s  spec   Write feff input for spec=XANES or spec=EXAFS
```

The --c options allows the user to choose different absorbers. The usual approach of editing a FEFF input file and changing the potential type of a certain atom to 0 will result in mismatched FEFF and dym structures. This should

be avoided. It is recommended that different input files be generated using the
--c option.

The --f and --d change the default output filenames from "feff.inp" and
"feff.dym" to fname and dname, respectively.

   ** Using within a XANES or EXAFS calculation in FEFF

The inclusion of dynamical matrix DW factors in XANES and EXAFS calculations is
analogous to the use of correlated-Debye DW factors in FEFF84. In the XANES
case, single-scattering DW factors are calculated for each pair of atoms in the
cluster. For EXAFS calculations, the DW factors are calculated only for the
selected paths (for instance, selected with the RPATH card). For both cases the
DEBYE card input is only slightly different than in previous versions:

DEBYE Temp Debye_Temp [DW_Opt [dym_File DMDW_Order DMDW_Type DMDW_Route]]

where:
        Temp   Temperature at which the DW factors are calculated
        Debye_Temp Debye Temperature of the material
        DW_Opt   Option that controls the type of DW factors used.
                    The possible values are:
                        0   Correlated-Debye method
                        1   Eqs. of Motion method
                        2   Recursion method
                        3   CL [?? Need to check]
                        4   Read from "sig2.dat" file
                        5   Dynamical-Matrix method
                        <0   Do not calculate DW factors

Options 0-4 are explained in the FEFF manual. When DW_Opt=5, the following
parameters can be included:
        dym_File   Name of the dynamical matrix information file. The
                    default value is "feff.dym"
        DMDW_Order Lanczos recursion order to be used in the calculation.
                    The default value is 2. Well converged results are
                    usually obtained for DMDW_Order=6-10. For small size
                    systems, these values might be too large. As a rule
                    of thumb, DMDW_Order should be less than
                    3*(Number of atoms)-6. Some paths, within systems with
                    high symmetry, might require a lower DMDW_Order. The
                    user should always check for convergence with this
                    parameter.
        DMDW_Type   Type of DW calculation.
                    The possible values are:
                        0   Parallel s^2
                    [NOTE: the meaning of this parameter might change in a
                    future release]
                    The default value is 0.
        DMDW_Route Which paths to use in the dmdw module. These paths do
                    not affect the path selection in the XAS calculations,
                    they are used for the generation of an input file for
                    the independent dmdw module.
                    The possible values are:
                        0   Skip dmdw module

```
                  1     All SS paths from absorber
                  2     Same as 1 + all DS paths from absorber
                  3     Same as 2 + all TS paths from absorber
                 11     All SS paths
                 12     Same as 1 + all DS paths
                 13     Same as 2 + all TS paths
            The default value is 0.
```

  ** Calculating DW factors using the standalone version

Other capabilities of DMDW can be accessed by means of the "dmdw" module or by
compiling the standalone version (which generates a "dmdw" module without
generating the rest of the FEFF code). All the details described below apply to
the input used by both the "dmdw" module and the standalone version. During the
execution of a normal FEFF run using ab initio DW factors, an input for the
"dmdw" module is automatically generated based on the options used in the DEBYE
card. This autogenerated input can be used "as is" with the standalone version,
or further edited to access other capabilities.

The "dmdw" input is very simple, with the first three lines determining the main
parameters of the calculation. The rest of the input depends on the content of
these first lines.

```
Lanczos_Order
nT T_Min T_Max
DW_Type
```

where:

Line 1 – Lanczos_Order: Number of Lanczos iterations (integer).

  This parameter is equivalent to the DMDW_Order parameter described above for
  the DEBYE card. It corresponds to the number of Lanczos iterations to be used
  in the calculation. Well converged results are usually obtained for
  DMDW_Order=6-10. For small size systems, these values might be too large. As a
  rule of thumb, this value should be less than 3*(Number of atoms)-6. Some
  paths, within systems with high symmetry, might require a lower recursion
  order. The user should always check for convergence with this parameter.

Line 2 – nT: Number of temperature values in grid (integer)
          T_Min, T_Max: Minimum and maximum temperature values (real, in K)

  Define a grid of temperatures in which to calculate the DW factors. This
  option is very efficient in the generation of whole temperature curves since
  it performs the Lanczos procedure only once and then calculates the DW for
  each temperature.

Line 3 – DMDW_Type: Type of DW calculation (integer).

  This parameter is equivalent to the one described above for the DEBYE card,
  but more values are available.
  The possible values are:
```
      0     Parallel s^2
      1     Vibrational free energy
       2        Self Energy/Spectral function
```

```
        3      Crystallographic u^2
        4      Perpendicular s^2 (Not available yet)
```

   The parallel s^2 is the usual mean-square relative displacement (MSRD) along a
   path. The perpendicular s^2 is the MSRD orthogonal to a path. The
   crystallographic u^2 is the mean-square displacement of a given atom with
   respect to its stationary position. Finally, the vibrational free energy
   associated with that crystallographic u^2 can also be calculated.

   [NOTE: Options 1 and 4 are not fully activated in this release. Also notice
          that the meaning of this parameter might change in a future release.]

The rest of the input depends on DMDW_Type. Here we list each possible case:

If DMDW_Type = 0 or 3, the rest of the "dmdw" input file should have the form:

```
Filename
nPathDesc
PathDesc1
PathDesc2
.
.
```

where

Line 4 – Filename: Name of file containing the dynamical matrix (string)

   The file must be present in the same directory as the DMDW input and be in
   "dym" format (see below).

Line 5 – nPathDesc: Number of path descriptors (integer)

   Define the number of path descriptors to use for the generation of paths.

Lines 6... – PathDescN: Nth path descriptor used to generate a list of paths
                        (integer and real, see below)

   A path descriptor has the following form:

     nAt At(1)...At(nAt) Path_Length

   where:

     nAt: Number of atoms in the path (integer)
     At(i): Index of atom that must be included in the path (integer)

            These indices correspond to the ones used in the "dym" file. The
            number 0 is a wildcard representing any atom in the structure.
            For instance, the atom indices "1 0 2" represent a double
            scattering paths starting at atom 1, ending at atom 2 and
            passing through every other allowed atom in the system. The
            paths are generated in such a way that no consecutive repeated
            indices are allowed.

     Path_Length: Effective path length cutoff (real, in Bohr)

This parameter helps fine-tune the generated path list, removing paths that are longer than necessary.

If the number of atoms in the path is 1 (nAt=1), then only crystallographic u^2 values are computed for the single atom in the path (for all cartesian displacements of that atom). DMDW will skip any multi-atom path for u^2 calculations (DMDW_Type = 3) and any single atom path for s^2 calculations (DMDW_Type = 0).

If DMDW_Type = 1 or 2, the rest of the "dmdw" input file should have the form:

[Shauna, please include here the file format you use for the self-energy calculations and VFE].

** The "dym" dynamical matrix file format

A "dym" file contains the information required by the Lanczos algorithm. This includes the atomic masses, structure and force constants. Two conversion scripts are included in the "bin" directory to convert Gaussian 03 formatted checkpoint ("fchk") files (fchk2dym) and Quantum Espresso dynamical matrix files (dynG2dym) into our "dym" dynamical matrix format. The "fchk2dym" command has been thoroughly tested, but the "dynG2dym" has not. The current format of the "dym" files is as follows:

Line 1 – dym_Type: Dynamical matrix file type (integer)

This value is for future use. Set to 1 for now.

[Shauna, please include here your modifications to the dym format.]

Line 2 – nAt: Number of atoms (integer)

Number of atoms in the system.

Lines 2..2+nAt – Atomic numbers (integer)

Atomic numbers of atoms in the system.

Lines 2+nAt+1..2+2*nAt – Atomic masses (real, in AMU)

Atomic masses of the atoms in the system.

Lines 2+2*nAt+1..2+3*nAt – Atomic coordinates (real, in Bohr)

Cartesian coordinates ("x y z") of the atoms in the system.

Lines 2+3*nAt+1..End – Dynamical matrix in atom pair block format (integer and real, see below,in atomic units):

The force constants in the system are stored for each pair of atoms in the system using the following block format:

    i j
    d2E/dxidxj d2E/dxidyj d2E/dxidzj

```
    d2E/dyidxj d2E/dyidyj d2E/dyidzj
    d2E/dzidxj d2E/dzidyj d2E/dzidzj

  where:

    i, j: Indices defining the atomic pair
    d2E/daidbj: Second derivative of the energy (i.e. force constant) with
              respect to the a coordinate of atom i and the b coordinate of
         atom j, where a,b={x,y,z}.

--------------------------------------------------------------------------
* Examples
  ** Creating a FEFF input file from a dym file using dym2feffinp

Here we demonstrate how to convert a dym file, in this case created from a
Gaussian fchk file, into matched pairs of feff.inp and feff.dym files, for
different absorbing centers.

The dym file for a CO2 molecule (CO2.dym), converted from the formatted
checkpoint file looks like:

###########################################################################
   1
   3
   8
   6
   8
    15.99491460
    12.00000000
    15.99491460
   0.00000000    0.00000000    2.20979482
   0.00000000    0.00000000    0.00000000
   0.00000000    0.00000000   -2.20979482
    1    1
  3.501599e-02 -7.311989e-13 -8.941376e-12
 -7.311989e-13  3.501599e-02  3.206256e-11
 -8.941376e-12  3.206256e-11  1.042343e+00
    1    2
 -7.001817e-02 -5.485621e-12  2.501278e-11
 -3.211930e-12 -7.001817e-02 -2.341738e-11
 -3.124223e-11 -3.615378e-11 -9.594793e-01
    1    3
  3.500217e-02 -8.681691e-13 -1.846564e-11
  8.681691e-13  3.500217e-02 -1.245331e-11
 -1.846599e-11  1.245327e-11 -8.286417e-02
    2    1
 -7.001817e-02 -3.211930e-12 -3.124223e-11
 -5.485621e-12 -7.001817e-02 -3.615378e-11
  2.501278e-11 -2.341738e-11 -9.594793e-01
    2    2
  1.400363e-01  1.883207e-12  2.058909e-11
  1.883207e-12  1.400363e-01  4.005329e-11
  2.058909e-11  4.005329e-11  1.918959e+00
    2    3
 -7.001817e-02  2.586772e-12  5.500370e-12
```

```
   4.227571e-12 -7.001817e-02  3.602353e-12
   3.495310e-11  1.591451e-11 -9.594793e-01
     3    1
   3.500217e-02  8.681691e-13 -1.846599e-11
  -8.681691e-13  3.500217e-02  1.245327e-11
  -1.846564e-11 -1.245331e-11 -8.286417e-02
     3    2
  -7.001817e-02  4.227571e-12  3.495310e-11
   2.586772e-12 -7.001817e-02  1.591451e-11
   5.500370e-12  3.602353e-12 -9.594793e-01
     3    3
   3.501599e-02  7.311989e-13 -8.940090e-12
   7.311989e-13  3.501599e-02 -3.206153e-11
  -8.940090e-12 -3.206153e-11  1.042343e+00
######################################################################
```

The dym files are not required to be sorted in any particular order, they retain
the atom order of the program that generated the dynamical matrix. In this case,
the order is O, C and O, with the C atom at the origin. Since FEFF internally
sorts the atoms according to their distance to the absorber, if this dym file is
used as is to compute the EXAFS/XANES for the C atom, the results would be
incorrect. We can generate the appropriate FEFF input file and associated dym
file with the following command:

dym2feffinp --c 2 --f CO2_C_feff.inp --d CO2_C_feff.dym CO2.dym

This creates the following CO2_C_feff.dym file:

```
######################################################################
     1
     3
     6
     8
     8
   12.000000
   15.994915
   15.994915
     0.00000000     0.00000000     0.00000000
     0.00000000     0.00000000     2.20979482
     0.00000000     0.00000000    -2.20979482
     1    1
   1.400363E-01  1.883207E-12  2.058909E-11
   1.883207E-12  1.400363E-01  4.005329E-11
   2.058909E-11  4.005329E-11  1.918959E+00
     1    2
  -7.001817E-02 -3.211930E-12 -3.124223E-11
  -5.485621E-12 -7.001817E-02 -3.615378E-11
   2.501278E-11 -2.341738E-11 -9.594793E-01
     1    3
  -7.001817E-02  2.586772E-12  5.500370E-12
   4.227571E-12 -7.001817E-02  3.602353E-12
   3.495310E-11  1.591451E-11 -9.594793E-01
     2    1
  -7.001817E-02 -5.485621E-12  2.501278E-11
  -3.211930E-12 -7.001817E-02 -2.341738E-11
```

```
   -3.124223E-11 -3.615378E-11 -9.594793E-01
       2     2
    3.501599E-02 -7.311989E-13 -8.941376E-12
   -7.311989E-13  3.501599E-02  3.206256E-11
   -8.941376E-12  3.206256E-11  1.042343E+00
       2     3
    3.500217E-02 -8.681691E-13 -1.846564E-11
    8.681691E-13  3.500217E-02 -1.245331E-11
   -1.846599E-11  1.245327E-11 -8.286417E-02
       3     1
   -7.001817E-02  4.227571E-12  3.495310E-11
    2.586772E-12 -7.001817E-02  1.591451E-11
    5.500370E-12  3.602353E-12 -9.594793E-01
       3     2
    3.500217E-02  8.681691E-13 -1.846599E-11
   -8.681691E-13  3.500217E-02  1.245327E-11
   -1.846564E-11 -1.245331E-11 -8.286417E-02
       3     3
    3.501599E-02  7.311989E-13 -8.940090E-12
    7.311989E-13  3.501599E-02 -3.206153E-11
   -8.940090E-12 -3.206153E-11  1.042343E+00
################################################################################
```

This dym file is now centered on the C atom and the atoms are sorted correctly.
The associated CO2_C_feff.inp FEFF input file has the following structure
section:

```
################################################################################
POTENTIALS
     0     6     C
     1     8     O

ATOMS
    0.00000     0.00000     0.00000     0     C   0.00000     0
    0.00000     0.00000     1.16937     1     O   1.16937     1
    0.00000     0.00000    -1.16937     1     O   1.16937     2
END
################################################################################
```

which is correctly centered and has the same structure as the dym file.

  ** XANES and EXAFS calculations

  A typical FEFF input file that uses ab initio DW factors in a XANES
  calculation looks as follows:

```
################################################################################
* This feff9 input file was generated by dym2feffinp

 TITLE absorbing atom:    0

 EDGE        K
 S02         1.0000
```

```
*               pot    xsph     fms    paths  genfmt  ff2chi
CONTROL          1       1       1       1       1       1
PRINT            1       0       0       0       0       0

*          ixc  [ Vr   Vi ]
EXCHANGE    0

*          r_scf  [ l_scf   n_scf    ca ]
SCF        4.000

*           kmax   [ delta_k  delta_e ]
XANES      4.000

*           r_fms      l_fms
FMS        6.000

DEBYE    500.0  1073.0  5 feff.dym  6  0  1

POTENTIALS
    0    8    O
    1    1    H

ATOMS
    0.00000    0.00000    0.00000    0    O  0.00000    0
    0.96141   -0.12674    0.00000    1    H  0.96972    1
   -0.12674    0.96141    0.00000    1    H  0.96972    2
END
################################################################################
```

This input file results in the XANES O K edge spectrum of a single water
molecule. (If an EXAFS calculation is required, the same DEBYE card parameters
apply, but the XANES card should be substituted by the EXAFS one.) It uses ab
initio DW factors at 500K and a dynamical matrix stored in the file
"feff.dym". The number of Lanczos recursion iterations is set to 6, the type
of DW calculation is to calculate parallel s^2, and it asks that all single
scattering paths from the absorber be calculated independently in the "dmdw"
module. The input generated for this module is:

```
################################################################################
    6
    1    500.000    500.000
    0
feff.dym
    1
    2    1    0            3.20
################################################################################
```

The first line corresponds to the number of Lanczos iterations. The second
defines the temperature, in this case a grid with a single point. The third
defines the type of DW calculation and the fourth the name of the dynamical
matrix file. The fifth line declares that the input contains a single path
descriptor, which is included in the next line. This descriptor defines all
single scattering paths from the absorber that are less than 3.2 Bohr long.

A dynamical matrix file for this calculation looks like this:

```
##########################################################################
     1
     3
     8
     1
     1
   15.994915
    1.007825
    1.007825
    0.00000000     0.00000000     0.00000000
    1.81679640    -0.23950080     0.00000240
   -0.23950080     1.81679640     0.00000240
     1     1
  5.398996E-01 -1.171079E-01  5.031484E-07
 -1.171079E-01  5.399060E-01  9.690730E-07
  5.031484E-07  9.690730E-07 -1.841479E-03
     1     2
 -4.941835E-01  3.022460E-02 -6.064138E-07
  8.687800E-02 -4.571081E-02 -1.155657E-07
 -6.583932E-07  7.894155E-08  9.207451E-04
     1     3
 -4.571614E-02  8.688332E-02  1.032683E-07
  3.022992E-02 -4.941952E-01 -8.535212E-07
  1.552287E-07 -1.048028E-06  9.207340E-04
     2     1
 -4.941835E-01  8.687800E-02 -6.583932E-07
  3.022460E-02 -4.571081E-02  7.894155E-08
 -6.064138E-07 -1.155657E-07  9.207451E-04
     2     2
  5.034834E-01 -7.711698E-02  6.431492E-07
 -7.711698E-02  5.501543E-02 -7.759238E-08
  6.431492E-07 -7.759238E-08 -8.716053E-04
     2     3
 -9.299924E-03 -9.761022E-03  1.524317E-08
  4.689238E-02 -9.304625E-03 -1.349708E-09
 -3.672524E-08  1.931636E-07 -4.913982E-05
     3     1
 -4.571614E-02  3.022992E-02  1.552287E-07
  8.688332E-02 -4.941952E-01 -1.048028E-06
  1.032683E-07 -8.535212E-07  9.207340E-04
     3     2
 -9.299924E-03  4.689238E-02 -3.672524E-08
 -9.761022E-03 -9.304625E-03  1.931636E-07
  1.524317E-08 -1.349708E-09 -4.913982E-05
     3     3
  5.501607E-02 -7.712230E-02 -1.185055E-07
 -7.712230E-02  5.034998E-01  8.548785E-07
 -1.185055E-07  8.548785E-07 -8.715942E-04
##########################################################################

  ** Calculating DW factors with the standalone version

[NOT WRITTEN YET]
```

** Creating dynamical matrix files from third-party programs

[NOT WRITTEN YET]

----
* Troubleshooting common problems
  ** Structure problems

[NOT WRITTEN YET]

  ** Lanczos problems

* If the code warns that there are less poles than Lanczos iterations, it
  usually means that the iteration order is to high. Try with a smaller
  number.

* When the structure associated with a dynamical matrix is not sufficiently
  optimized, the program is likely to report that certain paths result in
  poles associated with imaginary frequencies. The code currently ignores
  these poles by setting their weight to zero. Usually this doesn't affect the
  results significantly, but they should be considered very carefully anyway.

* The code checks the symmetry of the dynamical matrix. If isn't sufficiently
  symmetric, the results should be examined carefully.

----
* Future developments
  ** Performance improvements

[NOT WRITTEN YET]
Parallelization of calculation of DW factors in XANES, if running under MPI.

  ** Expected changes in FEFF input format

[NOT WRITTEN YET]

  ** Expected changes in DMDW input format

[NOT WRITTEN YET]

  ** Expected changes in dynamical matrix file format

Inclusion of forces (to use with less than optimal structures)
Inclusion of a title (for bookkeeping purposes)

[NOT WRITTEN YET]