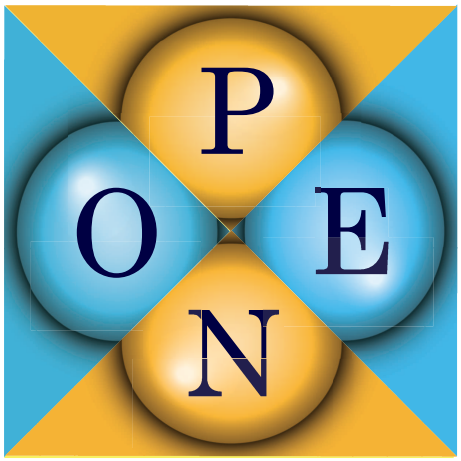
User's manual of OpenMX Ver. 3.7



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1 About OpenMX

OpenMX (Open source package for Material eXplorer) is a software package for nano-scale material simulations based on density functional theories (DFT) [1], norm-conserving pseudopotentials [19, 20, 21, 22, 23], and pseudo-atomic localized basis functions [28]. The methods and algorithms used in OpenMX and their implementation are carefully designed for the realization of large-scale *ab initio* electronic structure calculations on parallel computers based on the MPI or MPI/OpenMP hybrid parallelism. The efficient implementation of DFT enables us to investigate electronic, magnetic, and geometrical structures of a wide variety of materials such as biological molecules, carbon-based materials, magnetic materials, and nanoscale conductors. Systems consisting of 1000 atoms can be treated using the conventional diagonalization method if several hundreds cores on a parallel computer are used. Even *ab initio* electronic structure calculations for systems consisting of more than 10000 atoms are possible with the O(N) method implemented in OpenMX if several thousands cores on a parallel computer are available. Since optimized pseudopotentials and basis functions, which are well tested, are provided for many elements, users may be able to quickly start own calculations without preparing those data by themselves. Considerable functionalities have been implemented for calculations of physical properties such as magnetic, dielectric, and electric transport properties. Thus, we expect that OpenMX can be a useful and powerful theoretical tool for nano-scale material sciences, leading to better and deeper understanding of complicated and useful materials based on quantum mechanics. The development of OpenMX has been initiated by the Ozaki group in 2000, and from then onward many developers listed in the top page of the manual have contributed for further development of the open source package. The distribution of the program package and the source codes follow the practice of the GNU General Public License (GPL) [59], and they are downloadable from http://www.openmx-square.org/

Features and capabilities of OpenMX Ver. 3.7 are listed below:

- total energy and forces by cluster, band, O(N), and low-order scaling methods
- local density approximation (LDA, LSDA) [2, 3, 4] and generalized gradient approximation (GGA) [5] to the exchange-correlation potential
- LDA+U methods [16]
- norm-conserving pseudopotentials [2, 20, 21, 23]
- variationally optimized pseudo-atomic basis functions [28]
- fully and scalar relativistic treatment within pseudopotential scheme [10, 19, 13]
- non-collinear DFT [6, 7, 8, 9]
- constraint DFT for non-collinear spin and orbital orientation [11]
- macroscopic polarization by Berry's phase [12]
- Divide-conquer (DC) method [37] and Krylov subspace method for O(N) eigenvalue solver
- Parallel eigensolver by ELPA [26]

- simple, RMM-DIIS [40], GR-Pulay [39], Kerker [41], and RMM-DIIS with Kerker's metric [40] charge mixing schemes
- exchange coupling parameter [14, 15]
- effective screening medium (ESM) method [81, 84]
- scanning tunneling microscope (STM) simulation [52]
- nudged elastic band (NEB) method [53]
- charge doping
- uniform electric field
- full and constrained geometry optimization
- electric transport calculations by a non-equilibrium Green's function (NEGF) method [54]
- construction of maximally localized wannier functions
- NVE ensemble molecular dynamics
- NVT ensemble molecular dynamics by a velocity scaling [17] and the Nose-Hoover methods [18]
- Mulliken, Voronoi, and ESP fitting analysis of charge and spin densities
- analysis of wave functions and electron (spin) densities
- dispersion analysis by the band calculation
- density of states (DOS) and projected DOS
- flexible data format for the input
- Interface to XCrySDen for visualizing data such as charge density [61]
- completely dynamic memory allocation
- parallel execution by Message Passing Interface (MPI)
- parallel execution by OpenMP
- useful user interface for developers

The collinear and non-collinear (NC) DFT methods are implemented including scalar and fully relativistic pseudopotentials, respectively. The constraint NC-DFT is also supported to control spin and orbital magnetic moments. These methods will be useful to investigate complicated NC magnetic structures and the effect of spin-orbit coupling. The diagonalization of the conventional calculations is performed by a ELPA based parallel eigensolver [26] which scales up to several thousands cores. The feature may allow us to investigate systems consisting of 1000 atoms using the conventional diagonalization. Not only the conventional diagonalization scheme is provided for clusters, molecules, slab, and solids, but also linear scaling and a low-order scaling methods are supported as eigenvalue solver. With a proper choice for the eigenvalue solvers, systems consisting of more than 10000 atoms

can be treated with careful consideration to balance between accuracy and efficiency. As one of the other important features of OpenMX Ver. 3.7, it is worth mentioning that electronic transport calculations based on the NEGF method are supported not only for the collinear DFT method, but also the NC-DFT method with fully relativistic pseudopotentials and the constraint schemes.

We are continuously working toward development. Motivated contributors who want to develop the open source codes are always welcome.

2 Installation

2.1 Including libraries

OpenMX can be installed under linux environment where three library packages are available as listed below:

- LAPACK (and BLAS) (http://www.netlib.org/)
- FFTW (http://www.fftw.org/)
- MPI library such as MPICH2 and OpenMPI

If these library packages are not installed on your machine, you are required to install them before the installation of OpenMX. Note that a MPI library such as MPICH2 and OpenMPI has to be available for the installation of OpenMX Ver. 3.7. Without a MPI library, OpenMX Ver. 3.7 cannot be installed. If these libraries packages are available on your machine, you can proceed the following procedure for the installation. Then, after downloading 'openmx3.7.tar.gz', decompress it as follows:

```
% tar zxvf openmx3.7.tar.gz
```

When it is completed, you can find three directories 'source', 'work', 'DFT_DATA13' under the directory 'openmx3.7'. The directories 'source', 'work', and 'DFT_DATA13' contain source files, input files, and data files for optimized pseudo-atomic basis functions and pseudopotentials of Ver. 2013, respectively.

2.2 Serial version

The installation of the serial version is not supported for OpenMX Ver. 3.7.

2.3 MPI version

To proceed the installation of the MPI version, move to the directory 'source', and modify 'makefile' in 'source' to specify the compiler and libraries by **CC**, **FC**, and **LIB**. The default for the specification of **CC** and **LIB** in 'makefile' is as follows:

```
CC    = mpicc -Dnoomp -O3 -I/usr/local/include
FC    = mpif90 -Dnoomp -O3 -I/usr/local/include
LIB   = -L/usr/local/lib -lfftw3 -llapack -lblas -lg2c -static
```

CC and **FC** are the specification for C and FORTRAN compilers, respectively, and **LIB** is the specification for libraries which are linked. Although the specification of **FC** is not required up to and including Ver. 3.6, **FC** must be specified in Ver. 3.7 due to the introduction of the ELPA based parallel eigensolver [26]. The option '-Dnoomp' should be added under environment that OpenMP is not available. You need to set the **CC**, **FC** and **LIB** appropriately on your computer environment so that the compilation and linking can be properly performed and the executable file can be well optimized, while the specification largely depends on your computer environment. After specifying **CC**, **FC** and **LIB** appropriately, then install as follows:

```
% make install
```

When the compilation is completed normally, then you can find the executable file 'openmx' in the directory 'work'. To make the execution of OpenMX efficient, you can change a compiler and compile options appropriate for your computer environment, which can generate an optimized executable file. Several examples for **CC**, **FC** and **LIB** can be found in 'makefile' in the directory 'source' for your convenience.

2.4 OpenMP/MPI version

To generate the OpenMP/MPI hybrid version, all you have to do is to include a compiler option for OpenMP parallelization for **CC** and **FC** in 'makefile' in the directory 'source'. To proceed the installation of the OpenMP/MPI version, move to the directory 'source', and specify **CC**, **FC** and **LIB** in 'makefile', for example, as follows:

For icc

```
CC    = mpicc -openmp -O3 -I/usr/local/include
FC    = mpif90 -openmp -O3 -I/usr/local/include
LIB   = -L/usr/local/lib -lfftw3 -llapack -lblas -lg2c -static
```

For pgcc

```
CC    = mpicc -mp -O3 -I/usr/local/include
FC    = mpif90 -mp -O3 -I/usr/local/include
LIB   = -L/usr/local/lib -lfftw3 -llapack -lblas -lg2c -static
```

The compiler option for OpenMP depends on compiler. Also, it is noted that older versions of icc and pgcc do not support the compiler option for OpenMP. After specifying **CC**, **FC**, and **LIB** appropriately, then install as follows:

```
% make install
```

When the compilation is completed normally, then you can find the executable file 'openmx' in the directory 'work'. To make the execution of OpenMX efficient, you can change a compiler and compile options appropriate for your computer environment, which can generate an optimized executable file.

2.5 FFTW3

OpenMX Ver. 3.7 supports only FFTW3, while older versions up to Ver. 3.6 also support FFTW2 as well as FFTW3. Then, you may link FFTW3 in your makefile as follows:

```
LIB      = -L/usr/local/lib -fftw3 -llapack -lblas -lg2c -static
```

2.6 Other options

2.6.1 -Dblaswrap and -lI77

In some environment, adding two options -Dblaswrap and -lI77 is required, while we do not fully understand why such a dependency exists. In such a case, add two options for **CC**, **FC**, and **LIB** as follows:

```
CC    = mpicc -openmp -O3 -Dblaswrap -I/usr/local/include
FC    = mpif90 -mp -openmp -Dblaswrap -I/usr/local/include
LIB   = -L/usr/local/lib -lfftw3 -llapack -lblas -lg2c -lI77 -static
```

2.6.2 Df77, -Df77_, -Df77__, -DF77, -DF77_, -DF77__

When lapack and blas libraries are linked, the specification of routines could depend on the machine environment. The variation could be capital or small letter, or with or without of the underscore. To choose a proper name of lapack and blas routines on your computer environment, you can specify an option by -Df77, -Df77_, -Df77__, -DF77, -DF77_, or -DF77__. If the capital letter is needed in calling the lapack routines, then choose 'F', and choose a type of the underscore by none, '_', or '__'. The default set is -Df77_.

2.6.3 -Dnosse

Since the routine (Krylov.c) for the O(N) Krylov subspace method has been optimized using Streaming SIMD Extensions (SSE), the code will be compiled including SSE on default compilation. If your processors do not support SSE, then include '-Dnosse' as compilation option for **CC**.

2.6.4 -Dkcomp

For SPARC processors developed by FUJITSU Ltd., include -Dkcomp as compilation option for **CC** and **FC**.

2.7 Platforms

So far, we have confirmed that OpenMX Ver. 3.7 runs normally on the following machines:

- Sandy Bridge Xeon clusters
- Opteron cluster
- CRAY-XC30
- Fujitsu FX10
- K at RIKEN

2.8 Tips for installation

Most problems in installation of OpenMX are caused by the linking of LAPACK and BLAS or its alternative. We would recommend users to link ACML and MKL in most cases, while ACML seems to be slightly better than MKL with respect to computational speed and numerical stability. Examples on how to link them can be found in 'makefile' in the directory 'source'.

Also, we provide a couple of tips for the installation on popular platforms below. OpenMX requires C and FORTRAN compilers, LAPACK and BLAS libraries, and FFT library. In addition, as the C compiler is used for linking, the corresponding FORTRAN library of the compiler should be explicitly specified. Here we provide some sample settings for installation on platforms with several popular

compilers and LAPACK and BLAS libraries, with the assumption that the FFT library is installed in /usr/local/fftw3/.

- Intel C and FORTRAN compilers (icc, ifort) and the MKL library for LAPACK and BLAS

  MKLROOT=/opt/intel/mkl
  CC=mpicc -O3 -xHOST -openmp -I/usr/local/fftw3/include -I/$MKLROOT/include
  FC=mpiifort -O3 -xHOST -openmp -I/$MKLROOT/include
  LIB= -L/usr/local/fftw3/lib -lfftw3 -L/$MKLROOT/lib/intel64/ -lmkl_intel_lp64 -lmkl_intel_thread -lmkl_core -lpthread -lifcore

- PGI C and FORTRAN compilers (pgcc, pgCC, pgf77, pgf90) and the ACML library for LAPACK and BLAS

  CC=mpicc -fast -mp -Dnosse -I/usr/local/fftw3/include -I/usr/local/acml/gnu64/include
  FC=mpif90 -fast -mp -I/usr/local/acml/gnu64/include
  LIB= -L/usr/local/fftw3/lib -lfftw3 /usr/local/acml/gnu64/lib/libacml.a /usr/lib64/libg2c.a -pgf90libs

  Important: The preprocessor option -Dnosse must be specified with the PGI C compiler when -mp is used for enabling OpenMP.

- GNU C and FORTRAN compilers (gcc, g++, gfortran) and the MKL library for LAPACK and BLAS

  MKLROOT=/opt/intel/mkl
  CC=mpicc -O3 -ffast-math -fopenmp -I/usr/local/fftw3/include -I/$MKLROOT/include
  FC=mpif90 -O3 -ffast-math -fopenmp -I/$MKLROOT/include
  LIB= -L/usr/local/fftw3/lib -lfftw3 -L/$MKLROOT/lib/intel64/ -lmkl_intel_lp64 -lmkl_intel_thread -lmkl_core -lpthread -lgfortran

- GNU C and FORTRAN compilers (gcc, g++, gfortran) and the ACML library for LAPACK and BLAS

  CC=mpicc -O3 -ffast-math -fopenmp -I/usr/local/fftw3/include -I/usr/local/acml/gnu64/include
  FC=mpif90 -O3 -ffast-math -fopenmp -I/usr/local/acml/gnu64/include
  LIB= -L/usr/local/fftw3/lib -lfftw3 /usr/local/acml/gnu64/lib/libacml.a -lgfortran

Other combinations of the compiler and LAPACK and BLAS libraries can be done in the same fashion. The following commands can be used to show information about the compiler (Intel, PGI, GNU, etc.) used by MPI.

```
%mpicc -compile-info (with MPICH)
%mpicc -help  (with OpenMPI)
```

In some cases, the location of the FORTRAN library is unknown to the C compiler, resulting in the following link errors:

```
/usr/bin/ld: cannot find -lifcore
```

with the Intel compiler,

```
/usr/bin/ld: cannot find -lpgf90
```

with the PGI compiler, or

```
-lpgf90_rpm1, -lpgf902, -lpgf90rtl, -lpgftnrtl
```

as the "-pgf90libs" flag is just a shortcut for them,

```
/usr/bin/ld: cannot find -lgfortran
```

with the GNU compiler.

To solve this link-time problem, the location of the FORTRAN library must be explicitly specified as follows. First, the location of the FORTRAN compiler can be identified with the following commands.

```
%which ifort (with the Intel compiler)
/opt/intel/fce/10.0.026/bin/ifort

%which pgf90 (with the PGI compiler)
/opt/pgi/linux86-64/7.0/bin/pgf90

%which gfortran (with the GNU compiler)
/usr/bin/gfortran
```

Then, the location of the FORTRAN library usually resides in /lib of the parent folder of /bin, and must be specified in LIB.

```
LIB= ... -L/opt/intel/fce/10.0.026/lib -lifcore (with the Intel compiler)
LIB= ... -L/opt/pgi/linux86-64/7.0/lib -pgf90libs (with the PGI compiler)
LIB= ... -L/usr/lib -lgfortran (with the GNU compiler)
```

3 Test calculation

If the installation is completed normally, please move to the directory 'work' and perform the program 'openmx' using an input file 'Methane.dat' which can be found in the directory 'work' as follows:

```
% mpirun -np 1 openmx Methane.dat > met.std &
```

Or if you use the MPI/OpenMP version:

```
% mpirun -np 1 openmx Methane.dat -nt 1 > met.std &
```

The test input file 'Methane.dat' is for performing the SCF calculation of a methane molecule with a fixed structure (No MD). The calculation is performed in only about 12 seconds by using a 2.6 GHz Xeon machine, although it is dependent on a computer. When the calculation is completed normally, 11 files and one directory

```
met.std              standard output of the SCF calculation
met.out              input file and standard output
met.xyz              final geometrical structure
met.ene              values computed at every MD step
met.md               geometrical structures at every MD step
met.md2              geometrical structure of the final MD step
met.cif              cif file of the initial structure for Material Studio
met.tden.cube        total electron density in the Gaussian cube format
met.v0.cube          Kohn-Sham potential in the Gaussian cube format
met.vhart.cube       Hartree potential in the Gaussian cube format
met.dden.cube        difference electron density measured from atomic density
met_rst/             directory storing restart files
```

are output to the directory 'work'. The output data to a standard output is stored to the file 'met.std' which is helpful to know the computational flow of the SCF procedure. The file 'met.out' includes computed results such as the total energy, forces, the Kohn-Sham eigenvalues, Mulliken charges, the convergence history for the SCF calculation, and analyzed computational time. A part of the file 'met.out' is shown below. It is found that the eigenvalues energy converges by 11 iterations within 1.0e-10 Hartree.

```
*******************************************************
*******************************************************
                  SCF history at MD= 1
*******************************************************
*******************************************************

   SCF=   1  NormRD=  1.000000000000  Uele= -3.523143659974
   SCF=   2  NormRD=  0.567253699744  Uele= -4.405605131921
   SCF=   3  NormRD=  0.103433490729  Uele= -3.982266241934
   SCF=   4  NormRD=  0.024234990593  Uele= -3.906896836134
```

```
 SCF=   5  NormRD=  0.011006215697  Uele= -3.893084558820
 SCF=   6  NormRD=  0.006494145332  Uele= -3.890357113476
 SCF=   7  NormRD=  0.002722267527  Uele= -3.891669816209
 SCF=   8  NormRD=  0.000000672350  Uele= -3.889285164733
 SCF=   9  NormRD=  0.000000402419  Uele= -3.889285102456
 SCF=  10  NormRD=  0.000000346348  Uele= -3.889285101128
 SCF=  11  NormRD=  0.000000515395  Uele= -3.889285101063
```

Also, the total energy, chemical potential, Kohn-Sham eigenvalues, the Mulliken charges, dipole moment, forces, fractional coordinate, and analysis of computational time are output in 'met.out' as follows:

```
*****************************************************
        Total energy (Hartree) at MD = 1
*****************************************************

  Uele.         -3.889285101063

  Ukin.          5.533754016241
  UH0.         -14.855520072374
  UH1.           0.041395625260
  Una.          -5.040583803800
  Unl.          -0.134640939010
  Uxc0.         -1.564720823137
  Uxc1.         -1.564720823137
  Ucore.         9.551521413583
  Uhub.          0.000000000000
  Ucs.           0.000000000000
  Uzs.           0.000000000000
  Uzo.           0.000000000000
  Uef.           0.000000000000
  UvdW           0.000000000000
  Utot.         -8.033515406373

  Note:

  Utot = Ukin+UH0+UH1+Una+Unl+Uxc0+Uxc1+Ucore+Uhub+Ucs+Uzs+Uzo+Uef+UvdW

  Uene:   band energy
  Ukin:   kinetic energy
  UH0:    electric part of screened Coulomb energy
  UH1:    difference electron-electron Coulomb energy
  Una:    neutral atom potential energy
  Unl:    non-local potential energy
  Uxc0:   exchange-correlation energy for alpha spin
```

```
  Uxc1:   exchange-correlation energy for beta spin
  Ucore:  core-core Coulomb energy
  Uhub:   LDA+U energy
  Ucs:    constraint energy for spin orientation
  Uzs:    Zeeman term for spin magnetic moment
  Uzo:    Zeeman term for orbital magnetic moment
  Uef:    electric energy by electric field
  UvdW:   semi-empirical vdW energy

  (see also PRB 72, 045121(2005) for the energy contributions)



  Chemical potential (Hartree)       0.000000000000

************************************************************
************************************************************
          Eigenvalues (Hartree) for SCF KS-eq.
************************************************************
************************************************************

   Chemical Potential (Hartree) =   0.00000000000000
   Number of States             =   8.00000000000000
   HOMO =  4
   Eigenvalues
                Up-spin            Down-spin
         1  -0.69897190537228  -0.69897190537228
         2  -0.41522646150979  -0.41522646150979
         3  -0.41522645534084  -0.41522645534084
         4  -0.41521772830844  -0.41521772830844
         5   0.21218282298348   0.21218282298348
         6   0.21218282358344   0.21218282358344
         7   0.21227055734372   0.21227055734372
         8   0.24742493684297   0.24742493684297

************************************************************
************************************************************
                  Mulliken populations
************************************************************
************************************************************

  Total spin S =  0.000000000000

                   Up spin      Down spin     Sum           Diff
```

```
    1    C      2.509755704  2.509755704   5.019511408   0.000000000
    2    H      0.372561098  0.372561098   0.745122197   0.000000000
    3    H      0.372561019  0.372561019   0.745122038   0.000000000
    4    H      0.372561127  0.372561127   0.745122254   0.000000000
    5    H      0.372561051  0.372561051   0.745122102   0.000000000

Sum of MulP: up   =     4.00000 down          =     4.00000
             total=     8.00000 ideal(neutral)=     8.00000

 Decomposed Mulliken populations

   1    C          Up spin      Down spin     Sum           Diff
           multiple
 s           0    0.681752967  0.681752967   1.363505935   0.000000000
  sum over m      0.681752967  0.681752967   1.363505935   0.000000000
  sum over m+mul  0.681752967  0.681752967   1.363505935   0.000000000
 px           0    0.609349992  0.609349992   1.218699985   0.000000000
 py           0    0.609302752  0.609302752   1.218605504   0.000000000
 pz           0    0.609349993  0.609349993   1.218699985   0.000000000
  sum over m      1.828002737  1.828002737   3.656005474   0.000000000
  sum over m+mul  1.828002737  1.828002737   3.656005474   0.000000000

   2    H          Up spin      Down spin     Sum           Diff
           multiple
 s           0    0.372561098  0.372561098   0.745122197   0.000000000
  sum over m      0.372561098  0.372561098   0.745122197   0.000000000
  sum over m+mul  0.372561098  0.372561098   0.745122197   0.000000000

   3    H          Up spin      Down spin     Sum           Diff
           multiple
 s           0    0.372561019  0.372561019   0.745122038   0.000000000
  sum over m      0.372561019  0.372561019   0.745122038   0.000000000
  sum over m+mul  0.372561019  0.372561019   0.745122038   0.000000000

   4    H          Up spin      Down spin     Sum           Diff
           multiple
 s           0    0.372561127  0.372561127   0.745122254   0.000000000
  sum over m      0.372561127  0.372561127   0.745122254   0.000000000
  sum over m+mul  0.372561127  0.372561127   0.745122254   0.000000000

   5    H          Up spin      Down spin     Sum           Diff
           multiple
 s           0    0.372561051  0.372561051   0.745122102   0.000000000
  sum over m      0.372561051  0.372561051   0.745122102   0.000000000
```

```
   sum over m+mul  0.372561051  0.372561051   0.745122102   0.000000000

************************************************************
************************************************************
                    Dipole moment (Debye)
************************************************************
************************************************************

 Absolute D        0.00000071

                      Dx               Dy               Dz
 Total              0.00000046       0.00000000      -0.00000054
 Core               0.00000000       0.00000000       0.00000000
 Electron           0.00000046       0.00000000      -0.00000054
 Back ground       -0.00000000      -0.00000000      -0.00000000

************************************************************
************************************************************
       xyz-coordinates (Ang) and forces (Hartree/Bohr)
************************************************************
************************************************************

<coordinates.forces
  5
    1     C     0.00000   0.00000   0.00000   0.000000000327 -0.000...
    2     H    -0.88998  -0.62931   0.00000  -0.064883705001 -0.045...
    3     H     0.00000   0.62931  -0.88998   0.000000043463  0.045...
    4     H     0.00000   0.62931   0.88998   0.000000045939  0.045...
    5     H     0.88998  -0.62931   0.00000   0.064883635459 -0.045...
coordinates.forces>

************************************************************
************************************************************
       Fractional coordinates of the final structure
************************************************************
************************************************************

     1      C     0.00000000000000   0.00000000000000   0.00000000000000
     2      H     0.91100190000000   0.93706880000000   0.00000000000000
     3      H     0.00000000000000   0.06293120000000   0.91100190000000
     4      H     0.00000000000000   0.06293120000000   0.08899810000000
     5      H     0.08899810000000   0.93706880000000   0.00000000000000

************************************************************
```

```
************************************************************
               Computational Time (second)
************************************************************
************************************************************

   Elapsed.Time.        11.725

                                Min_ID   Min_Time       Max_ID   Max_Time
   Total Computational Time =     0       11.725          0       11.725
   readfile                 =     0        8.987          0        8.987
   truncation               =     0        0.155          0        0.155
   MD_pac                   =     0        0.000          0        0.000
   OutData                  =     0        0.452          0        0.452
   DFT                      =     0        2.130          0        2.130

*** In DFT ***

   Set_OLP_Kin              =     0        0.127          0        0.127
   Set_Nonlocal             =     0        0.104          0        0.104
   Set_ProExpn_VNA          =     0        0.132          0        0.132
   Set_Hamiltonian          =     0        0.741          0        0.741
   Poisson                  =     0        0.351          0        0.351
   Diagonalization          =     0        0.004          0        0.004
   Mixing_DM                =     0        0.000          0        0.000
   Force                    =     0        0.200          0        0.200
   Total_Energy             =     0        0.296          0        0.296
   Set_Aden_Grid            =     0        0.022          0        0.022
   Set_Orbitals_Grid        =     0        0.026          0        0.026
   Set_Density_Grid         =     0        0.120          0        0.120
   RestartFileDFT           =     0        0.003          0        0.003
   Mulliken_Charge          =     0        0.000          0        0.000
   FFT(2D)_Density          =     0        0.000          0        0.000
   Others                   =     0        0.003          0        0.003
```

The files 'met.tden.cube', 'met.v0.cube', 'met.vhart.cube', and 'met.dden.cube', are the total electron density, the Kohn-Sham potential, the Hartree potential, and the difference electron density taken from the superposition of atomic densities of constituent atoms, respectively, which are output in the Gaussian cube format. Since the Gaussian cube format is one of well used grid formats, you can visualize the files using free molecular modeling software such as Molekel [60] and XCrySDen [61]. The visualization will be illustrated in the latter section.

4 Automatic running test

In addition to a running test of the Section 'Test calculation', if you want to check whether most functionalities of OpenMX have been successfully installed on your computer or not, we recommend for you to perform an automatic running test. To do this, you can run OpenMX as follows:

For the MPI parallel running

```
% mpirun -np 8 openmx -runtest
```

For the OpenMP/MPI parallel running

```
% mpirun -np 8 openmx -runtest -nt 2
```

In the parallel execution, you can specify other options for mpirun. Then, OpenMX will run with 14 test files, and compare calculated results with the reference results which are stored in 'work/input_example'. The comparison (absolute difference in the total energy and force) is stored in a file 'runtest.result' in the directory 'work'. The reference results were calculated using a single processor of a 2.6 GHz Xeon machine. If the difference is within last seven digits, we may consider that the installation is successful. As an example, 'runtest.result' generated by the automatic running test is shown below:

1	input_example/Benzene.dat	Elapsed time(s)= 4.78	diff Utot= 0.000000000000	diff Force= 0.000000000002
2	input_example/C60.dat	Elapsed time(s)= 14.96	diff Utot= 0.000000000019	diff Force= 0.000000000004
3	input_example/CO.dat	Elapsed time(s)= 9.86	diff Utot= 0.000000000416	diff Force= 0.000000000490
4	input_example/Cr2.dat	Elapsed time(s)= 10.70	diff Utot= 0.000000000000	diff Force= 0.000000000044
5	input_example/Crys-MnO.dat	Elapsed time(s)= 19.98	diff Utot= 0.000000004126	diff Force= 0.000000001888
6	input_example/GaAs.dat	Elapsed time(s)= 26.39	diff Utot= 0.000000001030	diff Force= 0.000000000007
7	input_example/Glycine.dat	Elapsed time(s)= 5.48	diff Utot= 0.000000000001	diff Force= 0.000000000000
8	input_example/Graphite4.dat	Elapsed time(s)= 5.00	diff Utot= 0.000000002617	diff Force= 0.000000015163
9	input_example/H2O-EF.dat	Elapsed time(s)= 4.88	diff Utot= 0.000000000000	diff Force= 0.000000000113
10	input_example/H2O.dat	Elapsed time(s)= 4.60	diff Utot= 0.000000000008	diff Force= 0.000000013375
11	input_example/HMn.dat	Elapsed time(s)= 13.44	diff Utot= 0.000000000001	diff Force= 0.000000000001
12	input_example/Methane.dat	Elapsed time(s)= 3.64	diff Utot= 0.000000000001	diff Force= 0.000000002263
13	input_example/Mol_MnO.dat	Elapsed time(s)= 9.43	diff Utot= 0.000000003714	diff Force= 0.000000000540
14	input_example/Ndia2.dat	Elapsed time(s)= 5.67	diff Utot= 0.000000000004	diff Force= 0.000000000001

Total elapsed time (s) 138.79

The comparison was made using 8 processes by MPI with 2 treads by OpenMP on the same Xeon cluster machine. Since the floating point operation depends on not only computer environment, but also the number of processors used in parallel execution, we see in the above example that there is a small difference even using the same machine. The elapsed time of each job is also output, so it is helpful in comparing the computational speed depending on computer environment. In the directory 'work/input_example', you can find 'runtest.result' files generated on several platforms.

If you want to make reference files by yourself, please execute OpenMX as follows:

```
% ./openmx -maketest
```

Then, for input files '*.dat' in the directory 'work/input_example', OpenMX will generate the output files '*.out' in 'work/input_example'. So, you can add a new dat file which is used in the next running test. But, please make sure that the previous out files in 'work/input_example' will be overwritten by this procedure. For advanced testers for checking the reliability of code, see also the Sections 'Automatic force tester' and 'Automatic memory leak tester'.

5 Automatic running test with large-scale systems

In some cases, one may want to know machine performance for more time consuming calculations. For this purpose, an automatic running test with relatively large-scale systems can be performed by

For the MPI parallel running

```
% mpirun -np 128 openmx -runtestL
```

For the OpenMP/MPI parallel running

```
% mpirun -np 128 openmx -runtestL -nt 2
```

Then, OpenMX will run with 16 test files, and compare calculated results with the reference results which are stored in 'work/large_example'. The comparison (absolute difference in the total energy and force) is stored in a file 'runtestL.result' in the directory 'work'. The reference results were calculated using 16 MPI processes of a 2.6 GHz Xeon cluster machine. If the difference is within last seven digits, we may consider that the installation is successful. As an example, 'runtestL.result' generated by the automatic running test is shown below:

1	large_example/5_5_13COb2.dat	Elapsed time(s)= 39.43	diff Utot= 0.000000000013	diff Force= 0.000000000046
2	large_example/B2C62_Band.dat	Elapsed time(s)= 572.22	diff Utot= 0.000000000025	diff Force= 0.000000013928
3	large_example/CG15c-Kry.dat	Elapsed time(s)= 40.71	diff Utot= 0.000000002112	diff Force= 0.000000001090
4	large_example/DIA512-1.dat	Elapsed time(s)= 37.93	diff Utot= 0.000000169524	diff Force= 0.000000033761
5	large_example/FeBCC.dat	Elapsed time(s)= 81.55	diff Utot= 0.000000000649	diff Force= 0.000000001349
6	large_example/GEL.dat	Elapsed time(s)= 47.05	diff Utot= 0.000000000066	diff Force= 0.000000000002
7	large_example/GFRAG.dat	Elapsed time(s)= 24.05	diff Utot= 0.000000000122	diff Force= 0.000000000015
8	large_example/GGFF.dat	Elapsed time(s)= 639.31	diff Utot= 0.000000000051	diff Force= 0.000000000243
9	large_example/MCCN.dat	Elapsed time(s)= 53.72	diff Utot= 0.000000009994	diff Force= 0.000000016474
10	large_example/Mn12_148_F.dat	Elapsed time(s)= 76.58	diff Utot= 0.000000000096	diff Force= 0.000000000090
11	large_example/N1C999.dat	Elapsed time(s)= 97.56	diff Utot= 0.000000006902	diff Force= 0.000000007356
12	large_example/Ni63-O64.dat	Elapsed time(s)= 78.00	diff Utot= 0.000000000782	diff Force= 0.000000000047
13	large_example/Pt63.dat	Elapsed time(s)= 60.40	diff Utot= 0.000000002147	diff Force= 0.000000000059
14	large_example/SialicAcid.dat	Elapsed time(s)= 47.80	diff Utot= 0.000000000005	diff Force= 0.000000000003
15	large_example/ZrB2_2x2.dat	Elapsed time(s)= 143.16	diff Utot= 0.000000000030	diff Force= 0.000000000003
16	large_example/nsV4Bz5.dat	Elapsed time(s)= 104.20	diff Utot= 0.000000010770	diff Force= 0.000000000605

Total elapsed time (s) 2143.68

The comparison was made using 128 MPI processes and 4 OpenMP threads (totally 256 cores) on CRAY-XC30. Since the automatic running test requires large memory, you may encounter a segmentation fault in case that a small number of cores are used. Also the above example implies that the total elapsed time is about 36 minutes even using 256 cores. See also the Section 'Large-scale calculation' for another large-scale benchmark calculation.

6 Input file

6.1 An example: methane molecule

An input file 'Methane.dat' in the directory 'work' is shown below. The input file has a flexible data format in such a way that a parameter is given behind a keyword, the order of keywords is arbitrary, and a blank and a comment can be also described freely. For the keywords and options, both capital, small letters, and the mixture are acceptable, although these options in below example are written in a specific form.

```
#
# File Name
#

System.CurrrentDirectory         ./    # default=./
System.Name                      met
level.of.stdout                   1    # default=1 (1-3)
level.of.fileout                  1    # default=1 (0-2)

#
# Definition of Atomic Species
#

Species.Number       2
<Definition.of.Atomic.Species
 H   H5.0-s1          H_PBE13
 C   C5.0-s1p1        C_PBE13
Definition.of.Atomic.Species>

#
# Atoms
#

Atoms.Number         5
Atoms.SpeciesAndCoordinates.Unit   Ang # Ang|AU
<Atoms.SpeciesAndCoordinates
 1  C      0.000000    0.000000    0.000000     2.0  2.0
 2  H     -0.889981   -0.629312    0.000000     0.5  0.5
 3  H      0.000000    0.629312   -0.889981     0.5  0.5
 4  H      0.000000    0.629312    0.889981     0.5  0.5
 5  H      0.889981   -0.629312    0.000000     0.5  0.5
Atoms.SpeciesAndCoordinates>
Atoms.UnitVectors.Unit             Ang # Ang|AU
<Atoms.UnitVectors
  10.0   0.0   0.0
   0.0  10.0   0.0
   0.0   0.0  10.0
Atoms.UnitVectors>

#
# SCF or Electronic System
```

```
#

scf.XcType                 GGA-PBE     # LDA|LSDA-CA|LSDA-PW|GGA-PBE
scf.SpinPolarization        off        # On|Off|NC
scf.ElectronicTemperature  300.0       # default=300 (K)
scf.energycutoff           120.0       # default=150 (Ry)
scf.maxIter                 100        # default=40
scf.EigenvalueSolver        cluster    # DC|Cluster|Band
scf.Kgrid                  1 1 1       # means n1 x n2 x n3
scf.Mixing.Type           rmm-diis     # Simple|Rmm-Diis|Gr-Pulay|Kerker|Rmm-Diisk
scf.Init.Mixing.Weight     0.30        # default=0.30
scf.Min.Mixing.Weight      0.001       # default=0.001
scf.Max.Mixing.Weight      0.400       # default=0.40
scf.Mixing.History          7          # default=5
scf.Mixing.StartPulay       5          # default=6
scf.criterion             1.0e-10      # default=1.0e-6 (Hartree)

#
# MD or Geometry Optimization
#

MD.Type                     nomd       # Nomd|Opt|NVE|NVT_VS|NVT_NH
                                     # Constraint_Opt|DIIS
MD.maxIter                    1        # default=1
MD.TimeStep                  1.0       # default=0.5 (fs)
MD.Opt.criterion          1.0e-4       # default=1.0e-4 (Hartree/Bohr)
```

6.2 Keywords

The specification of each keyword is given below. The list does not include all the keywords in OpenMX, and those keywords will be explaned in each corresponding section.

File name

System.CurrrentDir
The output directory of output files is specified by this keyword. The default is './'.

System.Name
The file name of output files is specified by this keyword.

DATA.PATH
The path to the VPS and PAO directories can be specified in your input file by the following keyword:

```
DATA.PATH    ../DFT_DATA13     # default=../DFT_DATA13
```

Both the absolute and relative specifications are available. The default is '../DFT_DATA13'.

level.of.stdout

The amount of the standard output during the calculation is controlled by the keyword 'level.of.stdout'. In case of 'level.of.stdout=1', minimum information. In case of 'level.of.stdout=2', additional information together with the minimum output information. 'level.of.stdout=3' is for developers. The default is 1.

level.of.fileout
The amount of information output to the files is controlled by the keyword 'level.of.fileout'. In case of 'level.of.fileout=0', minimum information (no Gaussian cube and grid files). In case of 'level.of.fileout=1', standard output. In case of 'level.of.fileout=2', additional information together with the standard output. The default is 1.

Definition of Atomic Species

Species.Number
The number of atomic species in the system is specified by the keyword 'Species.Number'.

Definition.of.Atomic.Species
Please specify atomic species by giving both the file name of pseudo-atomic basis orbitals and pseudopotentials which must be existing in the directories 'DFT_DATA13/PAO' and 'DFT_DATA13/VPS', respectively. For example, they are specified as follows:

```
<Definition.of.Atomic.Species
 H   H5.0-s1>1p1>1      H_CA13
 C   C5.0-s1>1p1>1      C_CA13
Definition.of.Atomic.Species>
```

The beginning of the description must be '<Definition.of.Atomic.Species', and the last of the description must be 'Definition.of.Atomic.Species>'. In the first column, you can give any name to specify the atomic species. The name is used in the specification of atomic coordinates by 'Atoms.SpeciesAndCoordinates'. In the second column, the file name of the pseudo-atomic basis orbitals without the file extension and the number of primitive orbitals and contracted orbitals are given. Here we introduce an abbreviation of the basis orbital we used as H4.0-s1>1p1>1, where H4.0 indicates the file name of the pseudo-atomic basis orbitals without the file extension which must exist in the directory 'DFT_DATA13/PAO', s1>1 means that one optimized orbitals are constructed from one primitive orbitals for the s-orbital, which means no contraction. Also, in case of s1>1, corresponding to no contraction, you can use a simple notation 's1' instead of 's1>1'. Thus, 'H4.0-s1p1' is equivalent to 'H4.0-s1>1p1>1'. In the third column, the file name for the pseudopotentials without the file extension is given. Also the file must exist in the directory 'DFT_DATA13/VPS'. It can be possible to assign as the different atomic species for the same atomic element by specifying the different basis orbitals and pseudopotentials. For example, you can define the atomic species as follows:

```
<Definition.of.Atomic.Species
 H1   H5.0-s1p1         H_CA13
 H2   H5.0-s2p2d1       H_CA13
 C1   C5.0-s2p2         C_CA13
 C2   C5.0-s2p2d2       C_CA13
```

```
Definition.of.Atomic.Species>
```

The flexible definition may be useful for the decrease of computational efforts, in which only high level basis functions are used for atoms belonging to the essential part which determines the electric properties in the system, and lower level basis functions are used for atoms in the other inert parts.

Atoms

Atoms.Number
The total number of atoms in the system is specified by the keyword 'Atoms.Number'.

Atoms.SpeciesAndCoordinates.Unit
The unit of the atomic coordinates is specified by the keyword 'Atoms.SpeciesAndCoordinates.Unit'. Please specify 'Ang' when you use the unit of Angstrom, and 'AU' when the unit of atomic unit. The fractional coordinate is also available by 'FRAC'. Then, please specify the coordinates spanned by **a**, **b**, and **c**-axes given in 'Atoms.UnitVectors'. In the fractional coordinates, the coordinates can range from -0.5 to 0.5, and the coordinates beyond its range will be automatically adjusted after the input file is read.

Atoms.SpeciesAndCoordinates
The atomic coordinates and the number of spin charge are given by the keyword 'Atoms.SpeciesAndCoordinates' as follows:

```
<Atoms.SpeciesAndCoordinates
  1   C      0.000000    0.000000    0.000000     2.0  2.0
  2   H     -0.889981   -0.629312    0.000000     0.5  0.5
  3   H      0.000000    0.629312   -0.889981     0.5  0.5
  4   H      0.000000    0.629312    0.889981     0.5  0.5
  5   H      0.889981   -0.629312    0.000000     0.5  0.5
Atoms.SpeciesAndCoordinates>
```

The beginning of the description must be '<Atoms.SpeciesAndCoordinates', and the last of the description must be 'Atoms.SpeciesAndCoordinates>'. The first column is a sequential serial number for identifying atoms. The second column is given to specify the atomic species which must be given in the first column of the specification of the keyword 'Definition.of.Atomic.Species' in advance. In the third, fourth, and fifth columns, x-, y-, and z-coordinates are given. When 'FRAC' is chosen for the keyword 'Atoms.SpeciesAndCoordinates.Unit', the third, fourth, and fifth columns are fractional coordinates spanned by **a**, **b**, and **c**-axes, where the coordinates can range from -0.5 to 0.5, and the coordinates beyond its range will be automatically adjusted after the input file is read. The sixth and seventh columns give the number of initial charges for up and down spin states of each atom, respectively. The sum of up and down charges must be the number of valence electrons for the atomic element. When you calculate spin-polarized systems using 'LSDA-CA' or 'LSDA-PW', you can give the initial spin charges for each atom, which might be those of the ground state, to accelerate the SCF convergence.

Atoms.UnitVectors.Unit
The unit of the vectors for the unit cell is specified by the keyword 'Atoms.UnitVectors.Unit'. Please specify 'Ang' when you use the unit of Angstrom, and 'AU' when the unit of atomic unit.

Atoms.UnitVectors
The vectors, **a**, **b**, and **c** of the unit cell are given by the keyword 'Atoms.UnitVectors' as follows:

```
<Atoms.UnitVectors
  10.0   0.0   0.0
   0.0  10.0   0.0
   0.0   0.0  10.0
Atoms.UnitVectors>
```

The beginning of the description must be '<Atoms.UnitVectors', and the last of the description must be 'Atoms.UnitVectors>'. The first, second, and third rows correspond to the vectors, **a**, **b**, and **c** of the unit cell, respectively. If the keyword is absent in the cluster calculation, a unit cell is automatically determined so that the isolated system cannot overlap with the image systems in the repeated cells. See also the Section 'Automatic determination of the cell size'.

SCF or Electronic System

scf.XcType
The keyword 'scf.XcType' specifies the exchange-correlation potential. Currently, 'LDA', 'LSDA-CA', 'LSDA-PW', and 'GGA-PBE' are available, where 'LSDA-CA' is the local spin density functional of Ceperley-Alder [2], 'LSDA-PW' is the local spin density functional of Perdew-Wang, in which the gradient of density is set to zero in their GGA formalism [4]. Note: 'LSDA-CA' is faster than 'LSDA-PW'. 'GGA-PBE' is a GGA functional proposed by Perdew et al [5].

scf.SpinPolarization
The keyword 'scf.SpinPolarization' specifies the non-spin polarization or the spin polarization for the electronic structure. If the calculation for the spin polarization is performed, then specify 'ON'. If the calculation for the non-spin polarization is performed, then specify 'OFF'. When you use 'LDA' for the keyword 'scf.XcType', the keyword 'scf.SpinPolarization' must be 'OFF'. In addition to these options, 'NC' is supported for the non-collinear DFT calculation. For this calculation, see also the Section 'Non-collinear DFT'.

scf.partialCoreCorrection
The keyword 'scf.partialCoreCorrection' is a flag for a partial core correction (PCC) in calculations of exchange-correlation energy and potential. 'ON' means that PCC is made, and 'OFF' is none. In any cases, the flag should be 'ON', since pseudopotentials generated with PCC should be used with PCC, and also PCC does not affect the result for pseudopotentials without PCC because of zero PCC charge in this case.

scf.Hubbard.U
In case of the LDA+U or GGA+U calculation, the keyword 'scf.Hubbard.U' should be switched 'ON' (ON|OFF). The default is 'OFF'.

scf.Hubbard.Occupation
In the LDA+U method, three occupation number operators 'onsite', 'full', and 'dual' are available which can be specified by the keyword 'scf.Hubbard.Occupation'.

Hubbard.U.values
An effective U-value on each orbital of species is defined by the following keyword:

```
<Hubbard.U.values                  #  eV
 Ni  1s 0.0 2s 0.0 1p 0.0 2p 0.0 1d 4.0 2d 0.0
 O   1s 0.0 2s 0.0 1p 0.0 2p 0.0 1d 0.0
Hubbard.U.values>
```

The beginning of the description must be '<Hubbard.U.values', and the last of the description must be 'Hubbard.U.values>'. For all the basis orbitals specified by the 'Definition.of.Atomic.Species', you have to give an effective U-value in the above format. The '1s' and '2s' mean the first and second s-orbital, and the number behind '1s' is the effective U-value (eV) for the first s-orbital. The same rule is applied to p- and d-orbitals.

scf.Constraint.NC.Spin
The keyword 'scf.Constraint.NC.Spin' should be switched 'ON' (ON|OFF) when the constraint DFT method for the non-collinear spin orientation is performed.

scf.Constraint.NC.Spin.v
The keyword 'scf.Constraint.NC.Spin.v' gives a prefactor (eV) of the penalty functional in the constraint DFT for the non-collinear spin orientation.

scf.ElectronicTemperature
The electronic temperature (K) is given by the keyword 'scf.ElectronicTemperature'. The default is 300 (K).

scf.energycutoff
The keyword 'scf.energycutoff' specifies the cutoff energy which is used in the calculation of matrix elements associated with difference charge Coulomb potential and exchange-correlation potential and the solution of Poisson's equation using fast Fourier transform (FFT). The default is 150 (Ryd).

scf.Ngrid
The keyword 'scf.Ngrid' gives the number of grids to discretize the **a**-, **b**-, and **c**-axes. Although 'scf.energycutoff' is usually used for the discretization, the numbers of grids are specified by 'scf.Ngrid', they are used for the discretization instead of those by 'scf.energycutoff'.

scf.maxIter
The maximum number of SCF iterations is specified by the keyword 'scf.maxIter'. The SCF loop is terminated at the number specified by 'scf.maxIter' even if a convergence criterion is not satisfied. The default is 40.

scf.EigenvalueSolver
The solution method for the eigenvalue problem is specified by the keyword 'scf.EigenvalueSolver'. An O(N) divide-conquer method 'DC', an O(N) Krylov subspace method 'Krylov', a numerically exact low-order scaling method 'ON2', the cluster calculation 'Cluster', and the band calculation 'Band' are

available.

scf.Kgrid
When you specify the band calculation 'Band' for the keyword 'scf.EigenvalueSolver', then you need to give a set of numbers (n1,n2,n3) of grids to discretize the first Brillouin zone in the k-space by the keyword 'scf.Kgrid'. For the reciprocal vectors $\tilde{\mathbf{a}}$, $\tilde{\mathbf{b}}$, and $\tilde{\mathbf{c}}$ in the k-space, please provide a set of numbers (n1,n2,n3) of grids as n1 n2 n3. The k-points in OpenMX are generated according to the Monkhorst-Pack method [25].

scf.ProExpn.VNA
Switch on the keyword 'scf.ProExpn.VNA' in case that the neutral atom potential VNA is expanded by projector operators [29]. Otherwise turn off. The default is 'ON'.

```
scf.ProExpn.VNA      ON      # ON|OFF, default = ON
```

In case that 'scf.ProExpn.VNA=OFF', the matrix elements for the VNA potential are evaluated by using the regular mesh in real space.

scf.Mixing.Type
A mixing method of the electron density (or the density matrix) to generate an input electron density at the next SCF step is specified by keyword 'scf.Mixing.Type'. A simple mixing method ('Simple'), 'GR-Pulay' method (Guaranteed-Reduction Pulay method) [39], 'RMM-DIIS' method [40], 'Kerker' method [41], and 'RMM-DIISK' method [40] are available. The simple mixing method used here is modified to accelerate the convergence, referring to a convergence history. When 'GR-Pulay', 'RMM-DIIS', 'Kerker', or 'RMM-DIISK' is used, the following recipes are helpful to obtain faster convergence of SCF calculations:

- Use a rather larger value for 'scf.Mixing.StartPulay'. Before starting the Pulay-like mixing, achieve a convergence at some level. An appropriate value may be 10 to 30 for 'scf.Mixing.StartPulay'.
- Use a rather larger value for 'scf.ElectronicTemperature' in case of metallic systems. When 'scf.ElectronicTemperature' is small, numerical instabilities appear often.
- Use a large value for 'scf.Mixing.History'. In most cases, 'scf.Mixing.History=20' can be a good value.

Among these mixing schemes, the robustest one might be 'RMM-DIISK'.

scf.Init.Mixing.Weight
The keyword 'scf.Init.Mixing.Weight' gives the initial mixing weight used by the simple mixing, the GR-Pulay, the RMM-DIIS, the Kerker, and the RMM-DIISK methods. The valid range is 0 <scf.Init.Mixing.Weight< 1. The default is 0.3.

scf.Min.Mixing.Weight
The keyword 'scf.Min.Mixing.Weight' gives the lower limit of a mixing weight in the simple and Kerker mixing methods. The default is 0.001.

scf.Max.Mixing.Weight
The keyword 'scf.Max.Mixing.Weight' gives the upper limit of a mixing weight in the simple and Kerker mixing methods. The default is 0.4.

scf.Kerker.factor
The keyword gives a Kerker factor which is used in the Kerker and RMM-DIISK mixing methods. If the keyword is not given, a proper value is automatically determined. For further details, see the Section 'SCF convergence'.

scf.Mixing.History
In the GR-Pulay method [39], the RMM-DIIS method [40], the Kerker method [41], and the RMM-DIISK method [40], the input electron density at the next SCF step is estimated based on the output electron densities in the several previous SCF steps. The keyword 'scf.Mixing.History' specifies the number of previous SCF steps which are used in the estimation. For example, if 'scf.Mixing.History' is specified to be 3, and when the SCF step is 6th, the electron densities at 5, 4, and 3 SCF steps are taken into account. Around 30 is a better choice.

scf.Mixing.StartPulay
The SCF step which starts the GR-Pulay, the RMM-DIIS, the Kerker, and the RMM-DIISK methods is specified by the keyword 'scf.Mixing.StartPulay'. The SCF steps before starting these Pulay-type methods are then performed by the simple or Kerker mixing methods. The default is 6.

scf.Mixing.EveryPulay
The residual vectors in the Pulay-type mixing methods tend to become linearly dependent each other as the mixing steps accumulate, and the linear dependence among the residual vectors makes the convergence difficult. A way of avoiding the linear dependence is to do the Pulay-type mixing occasionally during the Kerker mixing. With this prescription, you can specify the frequency using the keyword 'scf.Mixing.EveryPulay'. For example, in case of 'scf.Mixing.EveryPulay=5', the Pulay-mixing is made at every five SCF iterations, while the Kerker mixing is used at the other steps. 'scf.Mixing.EveryPulay=1' corresponds to the conventional Pulay-type mixing. It is noted that the keyword 'scf.Mixing.EveryPulay' is supported for only 'RMM-DIISK', and the default value is 1.

scf.criterion
The keyword 'scf.criterion' specifies a convergence criterion (Hartree) for the SCF calculation. The SCF iteration is ended when a condition, dUele<scf.criterion, is satisfied, where dUele is defined as the absolute deviation between the eigenvalue energy at the current and previous SCF steps. The default is 1.0e-6 (Hartree).

scf.Electric.Field
give The keyword 'scf.Electric.Field' gives the strength of a uniform external electric field given by a sawtooth waveform. For example, when an electric field of 1.0 GV/m (10^9 V/m) is applied along the **a**-axis, specify in your input file as follows:

```
scf.Electric.Field   1.0 0.0 0.0   # default=0.0 0.0 0.0 (GV/m)
```

The sign of electric field is taken as that applied to electrons. The default is 0.0 0.0 0.0.

scf.system.charge
The keyword 'scf.system.charge' gives the amount of the electron and hole dopings. The plus and minus signs correspond to hole and electron dopings, respectively. The default is 0.

scf.SpinOrbit.Coupling

When the spin-orbit coupling is included, the keyword should be 'ON', otherwise please set to 'OFF'. In case of the inclusion of the spin-orbit coupling, you have to use j-dependent pseudopotentials. See also the Section 'Relativistic effects' as for the j-dependent pseudopotentials.

1D FFT

1DFFT.EnergyCutoff
The keyword '1DFFT.EnergyCutoff' gives the energy range to tabulate the Fourier transformed radial functions of pseudo-atomic orbitals and of the projectors for non-local potentials. The default is 3600 (Ryd).

1DFFT.NumGridK
The keyword '1DFFT.NumGridK' gives the the number of radial grids in the k-space. The values of the Fourier transformation for radial functions of pseudo-atomic orbitals and of the projectors for non-local potentials are tabulated on the grids, ranging from zero to 1DFFT.EnergyCutoff, as a function of radial axis in the **k**-space. The default is 900.

1DFFT.NumGridR
The keyword '1DFFT.NumGridR' gives the the number of radial grids in real space which is used in the numerical grid integrations of the Fourier transformation for radial functions of pseudo-atomic orbitals and of the projectors for non-local potentials. The default is 900.

Orbital Optimization

orbitalOpt.Method
The keyword 'orbitalOpt.Method' specifies a method for the orbital optimization. When the orbital optimization is not performed, then choose 'OFF'. When the orbital optimization is performed, the following two options are available: 'atoms' in which basis orbitals on each atom are fully optimized, 'species' in which basis orbitals on each species are optimized. In 'atoms', the radial functions of basis orbitals are optimized with a constraint that the radial wave function R is independent on the magnetic quantum number, which guarantees the rotational invariance of the total energy. However, the optimized orbital on all the atoms can be different from each other. In the 'species', basis orbitals in atoms with the same species name, that you define in 'Definition.of.Atomic.Species', are optimized as the same orbitals. If you want to assign the same orbitals to atoms with almost the same chemical environment, and optimize these orbitals, this scheme is useful.

orbitalOpt.scf.maxIter
The maximum number of SCF iterations in the orbital optimization is specified by the keyword 'orbitalOpt.scf.maxIter'.

orbitalOpt.Opt.maxIter
The maximum number of iterations for the orbital optimization is specified by the keyword 'orbitalOpt.Opt.maxIter'. The iteration loop for the orbital optimization is terminated at the number specified by 'orbitalOpt.Opt.maxIter' even if a convergence criterion is not satisfied.

orbitalOpt.Opt.Method

Two schemes for the optimization of orbitals are available: 'EF' which is an eigenvector following method, 'DIIS' which is the direct inversion method in iterative subspace. The algorithms are basically the same as for the geometry optimization. Either 'EF' or 'DIIS' is chosen by the keyword 'orbitalOpt.Opt.Method'.

orbitalOpt.StartPulay
The quasi Newton method 'EF' and 'DIIS' starts from the optimization step specified by the keyword 'orbitalOpt.StartPulay'.

orbitalOpt.HistoryPulay
The keyword 'orbitalOpt.HistoryPulay' specifies the number of previous steps to estimate the next input contraction coefficients used in the quasi Newton method 'EF' and 'DIIS'.

orbitalOpt.SD.step
The orbital optimization at optimization steps before moving to the quasi Newton method 'EF' or 'DIIS' is performed by the steepest decent method. The prefactor used in the steepest decent method is specified by the keyword 'orbitalOpt.SD.step'. In most cases, 'orbitalOpt.SD.step' of 0.001 can be a good prefactor.

orbitalOpt.criterion
The keyword 'orbitalOpt.criterion' specifies a convergence criterion ((Hartree/borh)^2) for the orbital optimization. The iterations loop is finished when a condition, Norm of derivatives<orbitalOpt.criterion, is satisfied.

CntOrb.fileout
If you want to output the optimized radial orbitals to files, then the keyword 'CntOrb.fileout' must be 'ON'.

Num.CntOrb.Atoms
The keyword 'Num.CntOrb.Atoms' gives the number of atoms whose optimized radial orbitals are output to files.

Atoms.Cont.Orbitals
The keyword 'Atoms.Cont.Orbitals' specifies the atom number, which is given by the first column in the specification of the keyword 'Atoms.SpeciesAndCoordinates' for the output of optimized orbitals as follows:

```
<Atoms.Cont.Orbitals
 1
 2
Atoms.Cont.Orbitals>
```

The beginning of the description must be '<Atoms.Cont.Orbitals', and the last of the description must be 'Atoms.Cont.Orbitals>'. The number of lines should be consistent with the number specified in the keyword 'Atoms.Cont.Orbitals'. For example, the name of files are C_1.pao and H_2.pao, where the symbol corresponds to that given by the first column in the specification of the keyword 'Definition.of.Atomic.Species' and the number after the symbol means that of the first column in the specification of the keyword 'Atoms.SpeciesAndCoordinates'. These output files 'C_1.pao' and

'H_2.pao' can be an input data for pseudo-atomic orbitals as is.

SCF Order-N

orderN.HoppingRanges
The keyword 'orderN.HoppingRanges' defines the radius of a sphere which is centered on each atom. The physically truncated cluster for each atom is constructed by picking up atoms inside the sphere with the radius in the DC and Krylov subspace O(N) methods.

orderN.KrylovH.order
The dimension of the Krylov subspace of Hamiltonian in each truncated cluster is given by the 'orderN.KrylovH.order'.

orderN.KrylovS.order
In case of 'orderN.Exact.Inverse.S=off', the inverse is approximated by a Krylov subspace method for the inverse, where the dimension of the Krylov subspace of overlap matrix in each truncated cluster is given by the keyword 'orderN.KrylovS.order'. The default value is 'orderN.KrylovH.order'×4.

orderN.Exact.Inverse.S
In case of 'orderN.Exact.Inverse.S=on', the inverse of overlap matrix for each truncated cluster is exactly evaluated. Otherwise, see the keyword 'orderN.KrylovS.order'. The default is 'on' (on|off).

orderN.Recalc.Buffer
In case of 'orderN.Recalc.Buffer=on', the buffer matrix is recalculated at every SCF step. Otherwise, the buffer matrix is calculated at the first SCF step, and fixed at subsequent SCF steps. The default is 'on' (on|off).

orderN.Expand.Core
In case of 'orderN.Expand.Core=on', the core region is defined by atoms within a sphere with radius of $1.2 \times r_{\min}$, where $r_{\min}$ is the distance between the central atom and the nearest atom. The core regsion defines a set of vectors used for the first step in the generation of the Krylov subspace for each truncated cluster. In case of 'orderN.Expand.Core=off', the central atom is considered as the core region. The default is 'on' (on|off).

MD or Geometry Optimization

MD.Type
Please specify the type of the molecular dynamics calculation or the geometry optimization. Currently, NO MD (Nomd), MD with the NVE ensemble (NVE), MD with the NVT ensemble by a velocity scaling scheme (NVT_VS)[17], MD with the NVT ensemble by a Nose-Hoover scheme (NVT_NH) [18], MD with multi-heat bath (NVT_VS2 or NVT_VS4), the geometry optimization by the steepest decent (SD) method (Opt), DIIS optimization method (DIIS), the eigenvector following (EF) method (EF) [45], and the rational function (RF) method (RF) [46] are available. For the details, see the Sections 'Geometry optimization' and 'Molecular dynamics'.

MD.Fixed.XYZ

In the geometry optimization and the molecular dynamics simulations, it is possible to separately fix the x-, y-, and z-coordinates of the atomic position to the initial position in your input file by the following keyword:

```
<MD.Fixed.XYZ
  1  1 1 1
  2  1 0 0
MD.Fixed.XYZ>
```

The example is for a system consisting of two atoms. If you have N atoms, then you have to provide N rows in this specification. The 1st column is the same sequential number to specify atom as in the specification of the keyword 'Atoms.SpeciesAndCoordinates'. The 2nd, 3rd, and 4th columns are flags for the x-, y-, and z-coordinates, respectively. '1' means that the coordinate is fixed, and '0' relaxed. In the above example, the x-, y-, and z-coordinates of the atom '1' are fixed, only the x-coordinate of the atom '2' is fixed. The default setting is that all the coordinates are relaxed. The fixing of atomic positions are valid all the geometry optimizers and molecular dynamics schemes.

MD.maxIter
The keyword 'MD.maxIter' gives the number of MD iterations.

MD.TimeStep
The keyword 'MD.TimeStep' gives the time step (fs).

MD.Opt.criterion
When any of the geometry optimizers is chosen for the keyword 'MD.Type', then the keyword 'MD.Opt.criterion' specifies a convergence criterion (Hartree/Bohr). The geometry optimization is finished when a condition, the maximum force on atom is smaller than 'MD.Opt.criterion', is satisfied.

MD.Opt.DIIS.History
The keyword 'MD.Opt.DIIS.History' gives the number of previous steps to estimate the optimized structure used in the geometry optimization by 'DIIS', 'EF', and 'RF'. The default value is 3.

MD.Opt.StartDIIS
The geometry optimization step at which 'DIIS', 'EF', or 'RF' starts is specified by the keyword 'MD.Opt.StartDIIS'. The geometry optimization steps before starting the DIIS-type method is performed by the steepest decent method. The default value is 5.

MD.TempControl
The keyword specifies temperature for atomic motion in MD of the NVT ensembles. In 'NVT_VS', the temperature for nuclear motion can be controlled by

```
<MD.TempControl
  3
  100   2  1000.0  0.0
  400  10   700.0  0.4
  700  40   500.0  0.7
MD.TempControl>
```

The beginning of the description must be '<MD.TempControl', and the last of the description must be 'MD.TempControl>'. The first number '3' gives the number of the following lines to control the temperature. In this case, you can see that there are three lines. Following the number '3', in the consecutive lines the first column means MD steps and the second column gives the interval of MD steps that the velocity scaling is made. For the above example, a velocity scaling is performed at every two MD steps until 100 MD steps, at every 10 MD steps from 100 to 400 MD steps, and at every 40 MD steps from 400 to 700 MD steps. The third and fourth columns give a given temperature (K) and a scaling parameter α in the interval. For further details see the Section 'Molecular dynamics'. On the other hand, in NVT_NH, the temperature for nuclear motion can be controlled by

```
<MD.TempControl
  4
  1    1000.0
  100  1000.0
  400   700.0
  700   600.0
MD.TempControl>
```

The beginning of the description must be '<MD.TempControl', and the last of the description must be 'MD.TempControl>'. The first number '4' gives the number of the following lines to control the temperature. In this case you can see that there are four lines. Following the number '4', in the consecutive lines the first and second columns give the MD steps and a given temperature for nuclear motion. The temperature between the MD steps explicitly specified by the keyword is given by linear interpolation.

NH.Mass.HeatBath

In 'NVT_NH', a mass of heat bath is given by the keyword. The default mass is 20, where we use the unified atomic mass unit that the principal isotope of carbon atom is 12.0.

MD.Init.Velocity

For molecular dynamics simulations, it is possible to provide the initial velocity of each atom by the following keyword:

```
<MD.Init.Velocity
 1    3000.000  0.0  0.0
 2   -3000.000  0.0  0.0
MD.Init.Velocity>
```

The example is for a system consisting of two atoms. If you have N atoms, then you have to provide N rows in this specification. The 1st column is the same sequential number to specify atom as in the specification of the keyword 'Atoms.SpeciesAndCoordinates'. The 2nd, 3rd, and 4th columns are x-, y-, and z-components of the velocity of each atom. The unit of the velocity is m/s. The keyword 'MD.Init.Velocity' is compatible with the keyword 'MD.Fixed.XYZ'.

Band dispersion

Band.dispersion
When you evaluate the band dispersion, please specify 'ON' for the keyword 'Band.dispersion'.

Band.KPath.UnitCell
The keyword 'Band.KPath.UnitCell' gives unit vectors, which are used in the calculation of the band dispersion, as follows:

```
<Band.KPath.UnitCell
 3.56 0.0 0.0
 0.0 3.56 0.0
 0.0 0.0 3.56
Band.KPath.UnitCell>
```

The beginning of the description must be '<Band.KPath.UnitCell', and the last of the description must be 'Band.KPath.UnitCell>'. If 'Band.KPath.UnitCell' exists, the reciprocal lattice vectors for the calculation of the band dispersion are calculated by the unit vectors specified in 'Band.KPath.UnitCell'. If 'Band.KPath.UnitCell' is not found, the reciprocal lattice vectors, which are calculated by the unit vectors specified in 'Atoms.UnitVectors', is employed for the calculation of the band dispersion. In case of fcc, bcc, base centered cubic, and trigonal cells, the reciprocal lattice vectors for the calculation of the band dispersion should be specified using the keyword 'Band.KPath.UnitCell' based on the consuetude in the band calculations.

Band.Nkpath
The keyword 'Band.Nkpath' gives the number of paths for the band dispersion.

Band.kpath
The keyword 'Band.kpath' specifies the paths of the band dispersion as follows:

```
<Band.kpath
  15  0.0 0.0 0.0   1.0 0.0 0.0   g X
  15  1.0 0.0 0.0   1.0 0.5 0.0   X W
  15  1.0 0.5 0.0   0.5 0.5 0.5   W L
  15  0.5 0.5 0.5   0.0 0.0 0.0   L g
  15  0.0 0.0 0.0   1.0 1.0 0.0   g X
Band.kpath>
```

The beginning of the description must be '<Band.kpath', and the last of the description must be 'Band.kpath>'. The number of lines should be consistent with 'Band.Nkpath'. The first column is the number of grids at which eigenvalues are evaluated on the path. The following (n1, n2, n3) and (n1', n2', n3'), spanned by the reciprocal lattice vectors, specifies the starting and ending **k**-points of the path in the first Brillouin zone. If 'Band.KPath.UnitCell' is found, the reciprocal lattice vectors for the calculation of the band dispersion are calculated by the unit vectors specified in 'Band.KPath.UnitCell'. If 'Band.KPath.UnitCell' is not found, the reciprocal lattice vectors, which

are calculated by the unit vectors specified in 'Atoms.UnitVectors' is employed for the calculation of the band dispersion. The final two alphabets give the name of the starting and ending **k**-points of the path.

Restarting

scf.restart
If you want to restart the SCF calculation using a previous file '*_rst/*' which should be generated in the previous calculation, then set the keyword 'scf.restart' to 'ON'.

Output of molecular orbitals (MOs)

MO.fileout
If you want to output molecular orbitals (MOs) to files, then set the keyword 'MO.fileout' to 'ON'.

num.HOMOs
The keyword 'num.HOMOs' gives the number of the highest occupied molecular orbitals (HOMOs) that you want to output to files.

num.LUMOs
The keyword 'num.LUMOs' gives the number of the lowest unoccupied molecular orbitals (LUMOs) that you want to output to files.

MO.Nkpoint
When you have specified 'MO.fileout=ON' and 'scf.EigenvalueSolver=Band', the keyword 'MO.Nkpoint' gives the number of the **k**-points at which you output MOs to files.

MO.kpoint
The keyword 'MO.kpoint' specifies the **k**-point, at which MOs are evaluated for the output to files, as follows:

```
<MO.kpoint
  0.0  0.0  0.0
MO.kpoint>
```

The beginning of the description must be '<MO.kpoint', and the last of the description must be 'MO.kpoint>'. The k-points are specified by (n1, n2, n3) which is spanned by the reciprocal lattice vectors, where the the reciprocal lattice vectors are determined in the same way as 'Band.kpath'.

DOS and PDOS

Dos.fileout
If you want to evaluate density of states (DOS) and projected partial density of states (PDOS), please set in 'Dos.fileout=ON'.

Dos.Erange
The keyword 'Dos.Erange' determines the energy range for the DOS calculation as

```
Dos.Erange                -10.0  10.0
```

The first and second values are the lower and upper bounds of the energy range (eV) for the DOS calculation, respectively.

Dos.Kgrid
The keyword, Dos.Kgrid, gives a set of numbers (n1,n2,n3) of grids to descretize the first Brillouin zone in the **k**-space, which is used in the DOS calculation.

Interface for developers

HS.fileout
If you want to use Kohn-Sham Hamiltonian, overlap, and density matrices, please set in 'HS.fileout=ON'. Then, these data are stored to '*.scfout' in a binary form, where '*' is the file name specified by the keyword 'System.Name'. The utilization of these data is illustrated in the Section 'Interface for developers'.

Voronoi charge

Voronoi.charge
If you want to calculate Voronoi charges, then set the keyword 'Voronoi.charge' in 'ON'. The result is found in '*.out', '*' is the file name specified by the keyword 'System.Name'.

7 Output files

In case of 'level.of.fileout=0', the following files are generated. In the following, '*' is the file name specified by the keyword 'System.Name'.

- *.out

  The history of SCF calculations, the history of geometry optimization, Mulliken charges, the total energy, and the dipole moment.

- *.xyz

  The final geometrical structure obtained by MD or the geometry optimization, which can be read in xmakemol and XCrySDen.

- *.bulk.xyz

  If 'scf.EigenvalueSolver=Band', atomic coordinates including atoms in copied cells are output, which can be read in xmakemol and XCrySDen.

- *_rst/

  The directory storing restart files.

- *.md

  Geometrical coordinates at every MD step, which can be read in xmakemol and XCrySDen.

- *.md2

  Geometrical coordinates at the final MD step with the species names that you specified .

- *.cif

  Initial geometrical coordinates in the cif format suited for Material Studio.

- *.ene

  Values computed at every MD step. The values are found in the routine 'iterout.c'.

In case of 'level.of.fileout=1', the following Gaussian cube files are generated, in addition to files generated in 'level.of.fileout=0', In the following, '*' is the file name specified by the keyword 'System.Name'.

- *.tden.cube

  Total electron density in a form of the Gaussian cube format.

- *.sden.cube

  If the spin-polarized calculation using 'LSDA-CA', 'LSDA-PW', or 'GGA-PBE' is performed, then spin electron density is output in a Gaussian cube format.

- *.dden.cube

  Difference electron density taken from superposition of atomic densities of constituent atoms in a form of the Gaussian cube format.

- *.v0.cube

  The Kohn-Sham potential excluding the non-local potential for up-spin in a Gaussian cube format.

- *.v1.cube

  The Kohn-Sham potential excluding the non-local potential for down-spin in a Gaussian cube format in the spin-polarized calculation.

- *.vhart.cube

  The Hartree potential in a Gaussian cube format.

In case of 'level.of.fileout=2', the following files are generated in addition to files generated in level.of.fileout=1, In the following, '*' is the file name specified by the keyword 'System.Name'.

- *.vxc0.cube

  The exchange-correlation potential for up-spin in a Gaussian cube format.

- *.vxc1.cube

  The exchange-correlation potential for down-spin in a Gaussian cube format.

- *.grid

  The real space grids which are used numerical integrations and the solution of Poisson's equation.

If 'MO.fileout=ON' and 'scf.EigenvalueSolver=Cluster', the following files are also generated:

- *.homo0_0.cube, *.homo0_1.cube, ...

  The HOMOs are output in a Gaussian cube format. The first number below 'homo' means a spin state (up=0, down=1). The second number specifies the eigenstates, i.e., 0, 1, and 2 correspond to HOMO, HOMO-1, and HOMO-2, respectively.

- *.lumo0_0.cube, *.lumo0_1.cube, ...

  The LUMOs are output in a Gaussian cube format. The first number below 'lumo' means a spin state (up=0, down=1). The second number specifies the eigenstates, i.e., 0, 1, and 2 correspond to LUMO, LUMO+1, and LUMO+2, respectively.

If 'MO.fileout=ON' and 'scf.EigenvalueSolver=Band', the following files are also generated:

- *.homo0_0_0_r.cube, *.homo1_0_1_r.cube, ... *.homo0_0_0_i.cube, *.homo1_0_1_i.cube, ...

  The HOMOs are output in a Gaussian cube format. The first number below 'homo' means the k-point number, which is specified by the keyword 'MO.kpoint'. The second number is a spin state (up=0, down=1). The third number specifies the eigenstates, i.e., 0, 1, and 2 correspond to HOMO, HOMO-1, and HOMO-2, respectively. The 'r' and 'i' mean the real and imaginary parts of the wave function.

- *.lumo0_0_0_r.cube, *.lumo1_0_1_r.cube, ... *.lumo0_0_0_i.cube, *.lumo1_0_1_i.cube, ...

  The LUMOs are output in a Gaussian cube format. The first number below 'lumo' means the k-point number, which is specified in the keyword, MO.kpoint. The second number is a spin state (up=0, down=1). The third number specifies the eigenstates, i.e., 0, 1, and 2 correspond to LUMO, LUMO+1, and LUMO+2, respectively. The 'r' and 'i' mean the real and imaginary parts of the wave function.

If 'Band.Nkpath' is not 0 and 'scf.EigenvalueSolver=Band', the following file is also generated:

- *.Band

  A data file for the band dispersion.

If 'Dos.fileout=ON', the following files are also generated:

- *.Dos.val

  A data file of eigenvalues for calculating the density of states.

- *.Dos.vec

  A data file of eigenvectors for calculating the density of states.

If 'scf.SpinPolarization=NC' and 'level.of.fileout=1' or '2', the following files are also generated:

- *.nco.xsf

  A vector file which stores a non-collinear orbital moment projected on each atom by means of Mulliken analysis, which can be visualized using 'Display→Forces' in XCrySDen.

- *.nc.xsf

  A vector file which stores a non-collinear spin moment projected on each atom by means of Mulliken analysis, which can be visualized using 'Display→Forces' in XCrySDen.

- *.ncsden.xsf

  A vector file which stores a non-collinear spin moment on real space grids, which can be visualized using 'Display→Forces' in XCrySDen.

8 Functional

In OpenMX, local density approximations (LDA, LSDA) [2, 3, 4] and a generalized gradient approximation (GGA) [5] to exchange-correlation functional are used. Using a keyword 'scf.XcType', you can choose one of approximations to the exchange-correlation functional:

```
scf.XcType                  LDA         # LDA|LSDA-CA|LSDA-PW|GGA-PBE
```

Currently, 'LDA', 'LSDA-CA', 'LSDA-PW', and 'GGA-PBE' are available, where 'LSDA-CA' is the local spin density functional of Ceperley-Alder [2], 'LSDA-PW' is the local spin density functional of Perdew-Wang, in which the gradient of density is set in zero in their GGA formalism [4]. Note: 'LSDA-CA' is faster than 'LSDA-PW'. 'GGA-PBE' is GGA proposed by Perdew, Burke, and Ernzerhof [5]. The GGA is implemented by using the first order finite difference method in real space. In addition, LDA+U (or GGA+U) functionals are also available. For the details, see the Section 'LDA+U'. The relevant keyword to specify the spin (un)polarized and non-collinear calculations is 'scf.SpinPolarization'.

```
scf.SpinPolarization        off         # On|Off|NC
```

If the calculation for the spin polarization is performed, then specify 'ON'. If the calculation for the non-spin polarization is performed, then specify 'OFF'. When you use 'LDA' for the keyword 'scf.XcType', the keyword 'scf.SpinPolarization' must be off. In addition to these options, 'NC' is supported for the non-collinear DFT calculation. For this calculation, see also the Section 'Non-collinear DFT'.

9 Basis sets

9.1 General

OpenMX uses numerical pseudo-atomic orbitals (PAOs) χ as basis function to expand one-particle Kohn-Sham wave functions. The PAO function is given by a product of a radial function R and a real spherical harmonic function Y as

$$\chi(\mathbf{r}) = R(r)Y(\hat{\mathbf{r}}),$$

where the radial function R is a numerically defined one, and finite within a cutoff radius in real space. In other words, the function R becomes zero beyond a pre-defined cutoff radius. The PAO function calculated by ADPACK is called *primitive* function, and an *optimized* PAO function is obtained by the orbital optimization method in OpenMX starting from the primitive PAO function [28]. They are stored in a file with a file extension of 'pao'. When the OpenMX calculation is performed, the numerical data stored in the file are read, and the value at any r is obtained by an interpolation technique. The files with the file extension of 'pao' should be stored in a directory, e.g., 'DFT_DATA13/PAO', where the directory without 'PAO' can be specified by the following keyword:

```
DATA.PATH    ../DFT_DATA13    # default=../DFT_DATA13
```

Both the absolute and relative specifications are possible, and the default is '../DFT_DATA13'.

In an input file for the OpenMX calculation, The basis set is specified by a keyword 'Definition.of.Atomic.Species' as follows:

```
<Definition.of.Atomic.Species
  H   H5.0-s2p1      H_PBE13
  C   C5.0-s2p1      C_PBE13
Definition.of.Atomic.Species>
```

where an abbreviation, H5.0-s2p1, of the basis function is introduced. H5.0 stands for the file name of the PAO functions without the file extension which must exist in a directory specified by the keyword 'DATA.PATH', e.g., DFT_DATA13/PAO, and 5.0 implies the cutoff radius of the PAO functions. Also, s2p1 means that two s-state radial functions and one p-state radial function stored in the file are used. In this case, totally five PAO basis functions (2x1+1x3=5) are assigned for 'H'.

Since optimized basis functions are available on the web site (http://www.openmx-square.org/) as the database Ver. 2013. We recommend for general users to use these optimized basis functions. But for experts, both the primitive and optimized PAO functions are explained in the subsequent sections.

9.2 Primitive basis functions

The primitive basis functions are generated by ADPACK, and they are the ground and exited states of a pseudo-atom with a confinement pseudopotential [28] as shown in Fig. 1. The functions are numerical table function stored in a file of which file extension is 'pao'. You will see that the ground state is nodeless and the first exited state has one node, and the number of nodes increases in the further excited states. When you use the primitive PAO functions as basis set, the one-particle Kohn-Sham functions are expressed by the linear combination of the pseudo-atomic type basis functions where

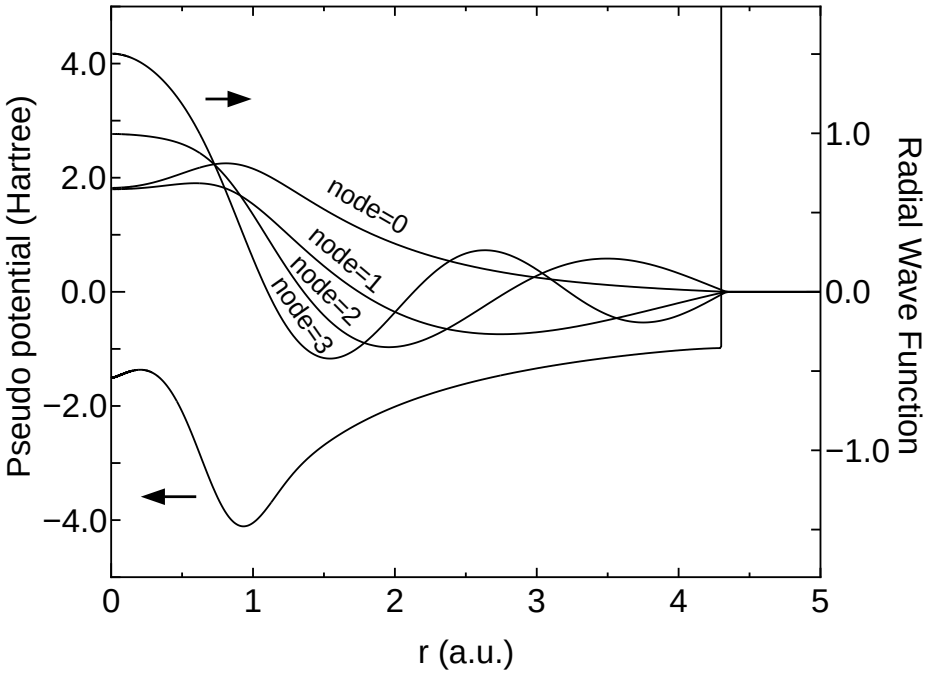

Figure 1: Primitive basis functions for s-orbitals of a carbon pseudo-atom with a confinement pseudopotential.

each basis function is the product of the radial function and a real spherical harmonics function. The accuracy and efficiency of the calculations can be controlled by two parameters: a cutoff radius and the number of basis functions. In general, one can get the convergent results by increasing the cutoff radius and the number of basis functions as shown in Fig. 2. However, it is noted that the use of a large number of basis orbitals with a large cutoff radius requires an extensive computational resource such as memory size and computational time. The general trend to choose the cutoff radius and the number of basis orbitals in a compromise way is discussed in Ref. [28], where you may find that basis orbitals with a higher angular momentum are needed to achieve the sufficient convergence for elements, such as F and Cl, in the right hand side of the periodic table, and that a large cutoff radius of basis orbitals should be used for elements, such as Li and Na, in the left hand side of the periodic table. Since optimized basis functions are available on the web site (http://www.openmx-square.org/) as the database Ver. 2013. We recommend for general users to use these optimized basis functions instead of the primitive PAO functions.

9.3 Optimized basis functions provided by the database Ver. 2013

The optimized PAO functions are provided on the website (http://www.openmx-square.org/) as the database Ver. 2013. This should be the first choice by general users, since they were generated by the orbital optimization method [28], and tested well through a series of benchmark calculations. For most elements in the database Ver. 2013, three systems are chosen as training sets of chemical environment, and the PAO functions were optimized by the orbital optimization method for the chosen systems [28]. Then, those optimized ones are unified to form a single PAO file through a combination scheme of a subspace rotation method and Gram-Schmidt orthogonalization. Thus, the optimized PAO functions

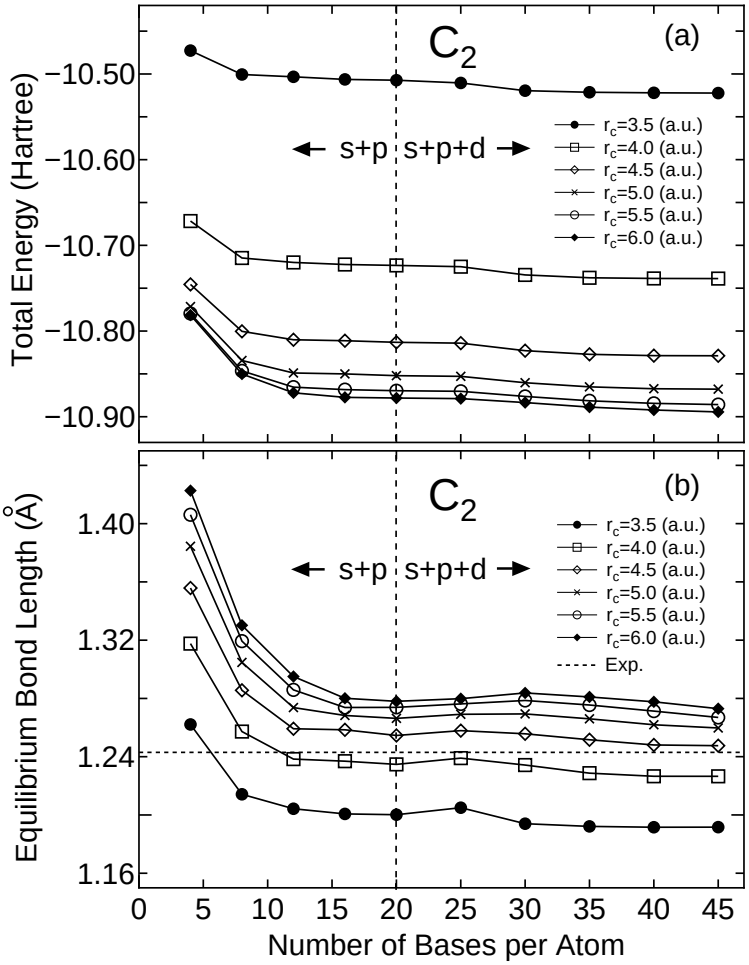

Figure 2: Convergence properties of (a) the total energy and (b) the equilibrium bond length for a carbon dimer with respect to the cutoff radius and the number of basis functions.

have been already optimized for a set of different chemical environments, which may increase the transferability of the optimized PAO functions. In fact, the series of benchmark calculations shown in the web site of the database are in good agreement with corresponding all electron calculations. From the benchmark calculations one may find a proper cutoff radius and the number of basis functions for each element. The input files used for the benchmark calculations are also available on the web site, which may be useful for users to get used to the OpenMX calculations at the initial stage.

The accuracy of the database (2013) was validated by the delta factor [27]. The mean delta factor of 71 elements is 1.538 meV/atom with the standard deviation of 1.423 meV/atom, which implies high accuracy of the database (2013). Users are strongly encouraged to use the new database due to the high accuracy. See also the section 'Calculation of Energy vs. lattice constant'.

9.4 Optimization of PAO by yourself

Starting from the primitive basis functions, you can optimize the radial shape variationally so that the accuracy can be increased. See the details in the Section 'Orbital optimization'.

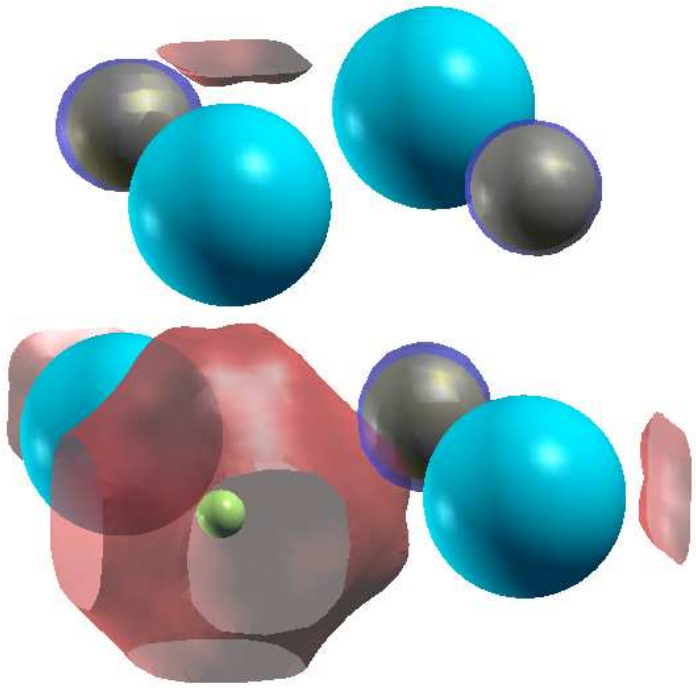

Figure 3: The isosurface map of the highest occupied state at the Γ point for NaCl with a Cl-site vacancy, which shows a F-center in NaCl with a Cl vacancy. The isosurface map was drawn using XCrySDen with the isovalue of 0.042 [61]. The calculation was done with the system charge of -1 using a keyword 'scf.system.charge'. The watery and silver colors correspond to sodium and chlorine atoms,respectively, and the yellow small ball shows the position of empty atom.

9.5 Empty atom scheme

The primitive and optimized PAO functions are usually assigned to atoms. Moreover, it is possible to assign basis functions in any vacant region using an *empty* atom. You will find the empty atom 'E' in the web site of the database (http://www.openmx-square.org/). Using the pseudopotential for the empty atom 'E', though the pseudopotential is a flat zero potential, you can put basis functions at any place independently of atomic position. To do that, you can define empty atoms by

```
<Definition.of.Atomic.Species
  H     H5.0-s2p1       H_PBE13
  C     C5.0-s2p1       C_PBE13
  EH    H5.0-s2p1       E
  EC    C5.0-s2p1       E
Definition.of.Atomic.Species>
```

In the example, two sorts of empty atoms are defined as 'EH' and 'EC' which have basis sets specified by 'H5.0-s2p1' and 'C5.0-s2p1', respectively, which means that one can use any basis functions for an empty atom as shown above. Then 'EH' and 'EC' can be put to any place by the keyword 'Atoms.SpeciesAndCoordinates', where the number of electrons for the empty atom is zero. To define

an empty atom, only thing you have to do is to use 'E.vps' as pseudopotential for the empty atom. The empty atom scheme enables us not only to estimate the basis set superposition error (BSSE) using the counterpoise correction (CP) method [33, 34], but also to treat a vacancy state and a nearly free electron state on metal surfaces within the linear combination of pseudo-atomic orbitals (LCPAO) method. As an example, a calculation of a F-center in NaCl with a Cl vacancy is shown in Fig. 3. We see that the highest occupied state at the Γ point is the F-center state. You can follow the calculation using 'NaCl_FC.dat' in the directory 'work'.

9.6 Specification of a directory storing PAO and VPS files

The path to the VPS and PAO directories can be specified in your input file by the following keyword:

```
DATA.PATH     ../DFT_DATA13     # default=../DFT_DATA13
```

Both the absolute and relative specifications are possible. PAO files in a database should not be used for the VPS in other databases, since semicore states included in several elements are different from each other. So, the consistency in the version of PAO and VPS must be kept. For that reason, it would be better to store PAO and VPS files of each version in different directories. In this case, the keyword is useful.

10 Pseudopotentials

The core Coulomb potential in OpenMX is replaced by a tractable norm-conserving pseudopotential proposed by Morrison, Bylander, and Kleinman [23], which is a norm-conserving version of the ultrasoft pseudopotential by Vanderbilt [24]. Although the pseudopotentials can be generated using ADPACK which is a program package for atomic density functional calculations and available from a web site (http://www.openmx-square.org/), for your convenience, we offer a database (http://www.openmx-square.org/) of the pseudopotentials as the database Ver. 2013. If you want to use pseudopotentials stored in the database, then copy them to the directory, 'openmx3.7/DFT_DATA13/VPS/', while most of data have been already copied in the distributed package of OpenMX Ver. 3.7. You can freely utilize these data in terms of GNU-GPL, but we cannot offer any warranty on these data. The assignation of pseudopotentials can be made using a keyword 'Definition.of.Atomic.Species' as in the case of specification of basis functions as follows:

```
<Definition.of.Atomic.Species
  H   H6.0-s2p1        H_CA13
  C   C6.0-s2p2        C_CA13
Definition.of.Atomic.Species>
```

The pseudopotential file can be specified in the third column, and the file must be existing in the directory 'DFT_DATA13/VPS'. In the specification of atomic coordinates, it is required to give the number of electrons for up- and down-spin states for each atom as follows:

```
<Atoms.SpeciesAndCoordinates
  1   C      0.000000    0.000000    0.000000     2.0  2.0
  2   H     -0.889981   -0.629312    0.000000     0.5  0.5
  3   H      0.000000    0.629312   -0.889981     0.5  0.5
  4   H      0.000000    0.629312    0.889981     0.5  0.5
  5   H      0.889981   -0.629312    0.000000     0.5  0.5
Atoms.SpeciesAndCoordinates>
```

where the sixth and seventh columns give the number of initial charges for up and down spin states for each atom, respectively. The sum of up and down charges for the atomic element should be equivalent to the number of electrons which is taken into account in the pseudopotential generation. Then, the proper number for each pseudopotential can be found in the pseudopotential file '*.vps'. For example, you will see the following line in the file 'C_PBE13.vps' for carbon atom in the database Ver. 2013.

```
 valence.electron            4.0000
```

The number '4.0' corresponds to the number of electrons which is taken into account in the pseudopotential generation. So, we see in the above example that the sum of up (2.0) and down (2.0) spins charges is 4.0 for 'C' in the specification of 'Atoms.SpeciesAndCoordinates'.

When you make pseudopotentials using ADPACK by yourself, you should pay attention to the following points.

- Check whether unphysical calculations have been caused by the ghost states or not. Because of the use of the separable form, the ghost states often appear. You should check whether the pseudopotentials are appropriate or not by performing calculations of simple systems before you calculate systems that you are interested in.
- Make smooth core densities for the partial core correction. If not so, numerical instabilities appear often, since a high energy cutoff is needed for accurate numerical integrations.

You will find the further details in the manual of the program package 'ADPACK'. However, it is noted that generation of good pseudopotentials requires considerable experiences more than what we think at the beginning.

11 Cutoff energy: grid fineness for numerical integrations

11.1 Convergence

The computational effort and accuracy depend on the cutoff energy, which is controlled by the keyword 'scf.energycutoff', for the numerical integrations and the solution of Poisson's equation [29]. Figure 4 shows the convergence of the total energy of a methane molecule with respect to the cutoff energy, where the input file is 'Methane.dat' used in the Section 'Input file'. Since the cutoff energy is not for basis set as in plane wave methods, but for the numerical integrations, the total energy does not have to converge from the upper energy region with respect to the cutoff energy like that of plane wave basis set. In most cases, the cutoff energy of 150-200 Ryd is an optimum choice. However, it should be noted that there is a subtle problem which requires the cutoff energy more than 300 Ryd. Calculations of a very flat potential minimum and a small energy difference among different spin orders could be such a subtle problem.

Structural parameters and the dipole moment of a water molecule, calculated with a different cutoff energy, are shown in Table 1, where the input file is 'H2O.dat' in the directory 'work'. A convergent result is obtained using around 90 Ryd. Although a sufficient cutoff energy depends on elements, 150-200 Ryd might be enough to achieve the convergence for most cases. However, we recommend that you would check physical properties for your system. For the other cutoff energy, 1DFFT.EnergyCutoff, we commonly use 3600 (Ryd) which is quite enough for the convergence with no high computational demands.

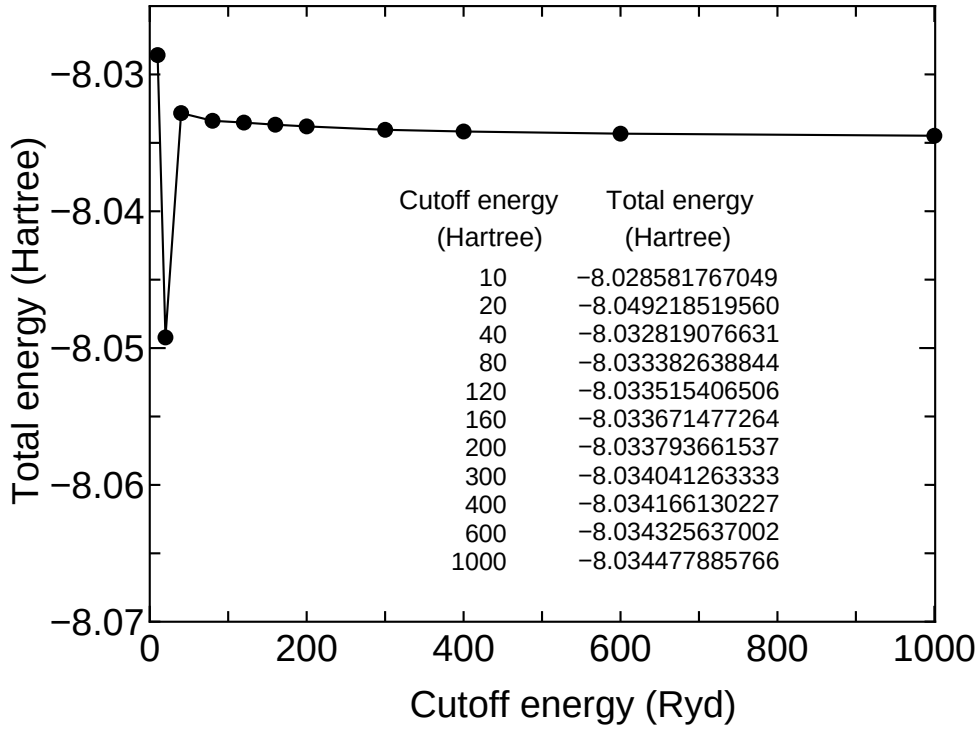

Figure 4: Convergence of the total energy of a methane molecule with respect to the cutoff energy.

Table 1: Convergence of structural parameters, dipole moment of a water molecule with respect to the cutoff energy. The input file is 'H2O.dat' in the directory 'work'.

Ecut(Ryd)	r(H-O) (Å)	∠ (H-O-H) (deg)	Dipole moment (Debye)
60	0.970	103.4	1.838
90	0.971	103.7	1.829
120	0.971	103.7	1.832
150	0.971	103.6	1.829
180	0.971	103.6	1.833
Exp.	0.957	104.5	1.85

11.2 A tip for calculating the energy curve for bulks

When the energy curve for bulk system is calculated as a function of the lattice parameter, a sudden change of the number of real space grids is a serious problem which produces an erratic discontinuity on the energy curve. In fact, we see the discontinuity in cases of 200 and 290 (Ryd) in Fig. 5 when the cutoff energy is fixed. The discontinuity occurs at the lattice parameter where the number of grids changes. To avoid the discontinuity on the energy curve, a keyword 'scf.Ngrid' is available.

```
scf.Ngrid      32 32 32     # n1, n2, and n3 for a-, b-, and c-axes
```

When the number of grids is explicitly specified by the keyword, the axis is discretized by the number without depending on the keyword 'scf.energycutoff'. We see in Fig. 5 that the fixed grids with 32x32x32 gives a smooth curve, while the discontinuity is not so serious even in the cases of 'scf.energycutoff'.

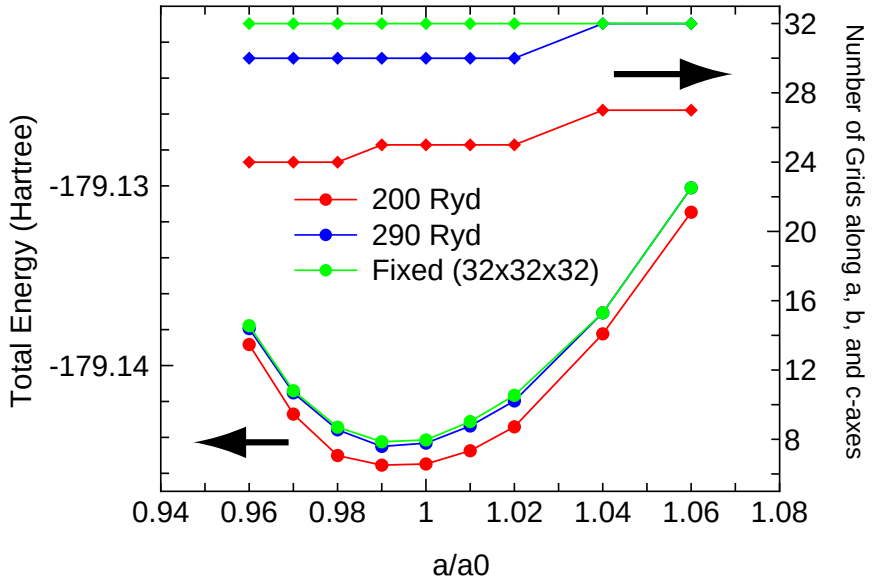

Figure 5: The total energy of bcc iron as a function of the lattice parameter, where the experimental equilibrium lattice constant a_0 is 2.87 Å. A cubic unit cell including two atoms was considered. The input file is 'Febcc2.dat' in the directory 'work'.

11.3 Fixing the relative position of regular grid

OpenMX Ver. 3.7 uses the regular real space grid for the evaluation of Hamiltonian matrix elements associated with the Hartree potential by the difference charge density and exchange-correlation potential, and solution of Poisson's equation. Thus, the total energy depends on the relative position between atomic coordinates and the regular grid. When one calculates an interaction energy or energy curve as a function of atomic coordinates, it is quite important to keep the relative position in all the calculations required for the evaluation of the interaction energy. In the calculation for one of the structures, you will find 'Grid_Origin' in the standard output which gives x-, y-, and z-components of the origin of the regular grid as:

```
Grid_Origin  xxx  yyy  zzz
```

Then, in order to keep the relative position, you have to include the following keyword 'scf.fixed.grid' in your input file for all the systems in the calculations required for the evaluation of the interaction energy:

```
scf.fixed.grid  xxx  yyy  zzz
```

where 'xxx yyy zzz' is the coordinate of the origin you got in the calculation for one of the structures. The procedure largely suppresses the numerical error involved in the use of the regular grid.

In addition, as discussed in the previous subsection 'A tip for calculating the energy curve for bulks', the number of grids should be fixed by the keyword 'scf.Ngrid' when the lattice parameters are also changed in the evaluation of interaction energy.

12 SCF convergence

12.1 General

Five charge mixing schemes in OpenMX Ver. 3.7 are available by the keyword 'scf.Mixing.Type':

- Simple mixing (Simple)

  Relevant keywords: scf.Init.Mixing.Weight, scf.Min.Mixing.Weight, scf.Max.Mixing.Weight

- Residual minimization method in the direct inversion iterative subspace (RMM-DIIS) [40]

  Relevant keywords: scf.Init.Mixing.Weight, scf.Min.Mixing.Weight, scf.Max.Mixing.Weight, scf.Mixing.History, scf.Mixing.StartPulay

- Guaranteed reduction Pulay method (GR-Pulay) [39]

  Relevant keywords: scf.Init.Mixing.Weight, scf.Min.Mixing.Weight, scf.Max.Mixing.Weight, scf.Mixing.History, scf.Mixing.StartPulay

- Kerker mixing (Kerker) [41]

  Relevant keywords: scf.Init.Mixing.Weight, scf.Min.Mixing.Weight, scf.Max.Mixing.Weight, scf.Kerker.factor

- RMM-DIIS with Kerker metric (RMM-DIISK) [40]

  Relevant keywords: scf.Init.Mixing.Weight, scf.Min.Mixing.Weight, scf.Max.Mixing.Weight, scf.Mixing.History, scf.Mixing.StartPulay, scf.Mixing.EveryPulay, scf.Kerker.factor

In the first three schemes density matrices, which are regarded as a quantity in real space, are mixed to generate the input density matrix which can be easily converted into (spin) charge density. On the other hand, the charge mixing is made in Fourier space in the last two schemes. Generally, it is easier to achieve SCF convergence in large gap systems using any mixing scheme. However, it would be difficult to achieve a sufficient SCF convergence in smaller gap and metallic systems, since a charge sloshing problem in the SCF calculations becomes serious often. To handle such difficult systems, two mixing schemes are currently available: Kerker and RMM-DIISK methods. The two mixing schemes could be an effective way for achieving the SCF convergence of metallic systems. When 'Kerker' or 'RMM-DIISK' is used, the following prescriptions are helpful to obtain the convergence of SCF calculations:

- Increase of 'scf.Mixing.History'. A relatively larger vaule 30-50 may lead to the convergence. In addition, 'scf.Mixing.EveryPulay' should be set in 1.

- Use a rather larger value for 'scf.Mixing.StartPulay'. Before starting the Pulay-type mixing, achieve a convergence at some level. An appropriate value may be 10 to 30 for 'scf.Mixing.StartPulay'.

- Use a rather larger value for 'scf.ElectronicTemperature' in case of metallic systems. When 'scf.ElectronicTemperature' is small, numerical instabilities appear often.

In addition, the charge sloshing, which comes from charge components with long wave length, can be significantly suppressed by tuning Kerker's factor α by the keyword 'scf.Kerker.factor', where Kerker's metric is defined by

$$\langle A|B\rangle = \sum_{\mathbf{q}} \frac{A^*_{\mathbf{q}} B_{\mathbf{q}}}{w_{\mathbf{q}}}$$

$$w_{\mathbf{q}} = \frac{|\mathbf{q}|^2}{|\mathbf{q}|^2 + q_0^2}$$

$$q_0 = \alpha |\mathbf{q}_{\min}|$$

where $\mathbf{q}_{\min}$ is the $\mathbf{q}$ vector with the minimum magnitude except 0-vector. A larger α significantly suppresses the charge sloshing, but leads to slower convergence. Since an optimum value depends on system, you may tune an appropriate value for your system.

Furthermore, the behavior of 'RMM-DIISK' can be controlled by the following keyword:

```
scf.Mixing.EveryPulay    5   # default = 1
```

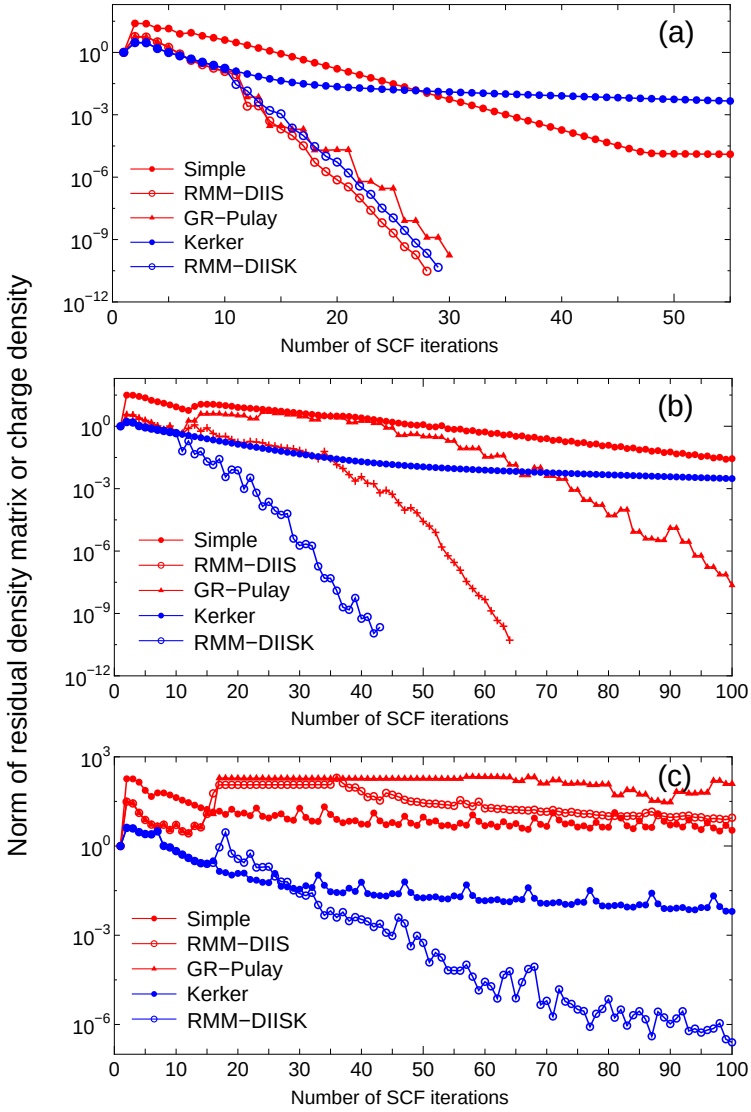

Figure 6: Convergence of the norm of residual density matrix or charge density in the SCF calculations using five mixing schemes of (a) a sialic acid molecule, (b) a Pt_{13} cluster, and (c) a Pt_{63} cluster. The input files are 'SialicAcid.dat', 'Pt13.dat', and 'Pt63.dat' in the directory 'work'.

The residual vectors in the Pulay-type mixing schemes tend to become linearly dependent on each other as the mixing steps accumulate, and the linear dependence among the residual vectors makes the convergence difficult. A way of avoiding the linear dependence is to do the Pulay-type mixing occasionally during the Kerker mixing. With this prescription, you can specify the frequency using the keyword 'scf.Mixing.EveryPulay'. For example, in case of 'scf.Mixing.EveryPulay=5', the Pulay-mixing is made at every five SCF iterations, while the Kerker-type mixing is used at the other steps. 'scf.Mixing.EveryPulay=1' corresponds to the conventional Pulay-type mixing. It is noted that the keyword 'scf.Mixing.EveryPulay' is supported for only 'RMM-DIISK', and the default value is '1'.

The above prescription works in some cases. But the most recommended prescription to accelerate the convergence is the following:

- Increase of 'scf.Mixing.History'. A relatively larger vaule 30-50 may lead to the convergence. In addition, 'scf.Mixing.EveryPulay' should be set in 1.

Since the Pulay-type mixing such as RMM-DIIS and RMM-DIISK is based on a quasi Newton method, the convergence speed is governed by how a good approximate Hessian matrix can be found. As 'scf.Mixing.History' increases, the calculated Hessian may become more accurate.

In Fig. 6 a comparison of five mixing schemes is shown for the SCF convergence for (a) a sialic acid molecule, (b) a Pt_{13} cluster, and (c) a Pt_{63} cluster, where the norm of residual density matrix or charge density can be found as NormRD in the file '*.out' and the input files are 'SialicAcid.dat', 'Pt13.dat', and 'Pt63.dat' in the directory 'work'. We see that 'RMM-DIISK' works with robustness for all the systems shown in Fig. 6. In most cases, 'RMM-DIISK' will be the best choice, while the use of 'Kerker' is required with a large 'scf.Kerker.factor' and a small 'scf.Max.Mixing.Weight' for quite difficult cases in which the convergence is hardly obtained.

12.2 Automatic determination of Kerker's factor

If the keyword 'scf.Kerker.factor' is not given in your input file, OpenMX Ver. 3.7 automatically estimates a proper value of Kerker's factor α by the following equation:

$$\alpha = \frac{0.5}{|\mathbf{b}_{\rm min}|^2} \left(4 \frac{Dq}{Aq} + 1.0 \right)$$

with

$$Aq = \frac{1}{3} \left(|\mathbf{b}_1|^2 + |\mathbf{b}_2|^2 + |\mathbf{b}_3|^2 \right),$$

$$Dq = \frac{1}{3} \sum_{i<j} \left| |\mathbf{b}_i|^2 - |\mathbf{b}_j|^2 \right|,$$

where $\mathbf{b}_i (i = 1, 2, 3)$ is a reciprocal vector, and $\mathbf{b}_{\rm min}$ is the smallest vector among $\{\mathbf{b}\}$. The equation takes account of the dependency of α on the size and anisotropy of the system. From a series of numerical calculations it is found that the estimated value works well in most cases.

12.3 On-the-fly control of SCF mixing parameters

During the SCF calculation, it is possible to change the following parameters for the SCF mixing:

```
scf.maxIter
scf.Min.Mixing.Weight
scf.Max.Mixing.Weight
scf.Kerker.factor
scf.Mixing.StartPulay
```

For example, when you specify the following two keywords in your input file as

```
System.CurrrentDirectory          ./    # default=./
System.Name                       c60
```

then make a file whose name is 'c60_SCF_keywords' in the directory './', and write in it as

```
scf.maxIter               100
scf.Min.Mixing.Weight     0.01
scf.Max.Mixing.Weight     0.10
scf.Kerker.factor         10.0
scf.Mixing.StartPulay     30
```

OpenMX will try to read the file 'c60_SCF_keywords' at every SCF step, and show the following message in the standard output, if the file is successfully read by OpenMX.

```
The keywords for SCF iteration are renewed by ./c60_SCF_keywords.
```

Also, if a minus value is given for the keyword, scf.maxIter, then OpenMX will be terminated. The on-the-fly control of SCF mixing parameters may be useful when large-scale calculations are performed.

13 Restarting

13.1 General

After finishing your first calculation or achieving the self consistency, you may want to continue the calculation or to calculate density of states, band dispersion, molecular orbitals, and etc. using the self consistent charge in order to save the computational time. To do this, a keyword 'scf.restart' is available.

```
scf.restart            on        # on|off,default=off
```

When the keyword 'scf.restart' is switched on, restart files generated by your first calculation will be used as the input Hamiltonian or charge density in the second calculation, while 'System.Name' in the second calculation should be the same as in the first calculation. The restart files are stored in a directory '*_rst' below the 'work' directory, where * means 'System.Name'. The restart files in the '*_rst' contain all the information for both the density matrix mixing schemes and k-space mixing schemes. So, it is also possible to use another mixing scheme in the second calculation. As an example, we illustrate the restarting procedure using an input file *C60.dat* which can be found in the directory 'work'. In Fig. 7, we see that the second calculation is accelerated due to the use of the restart file.

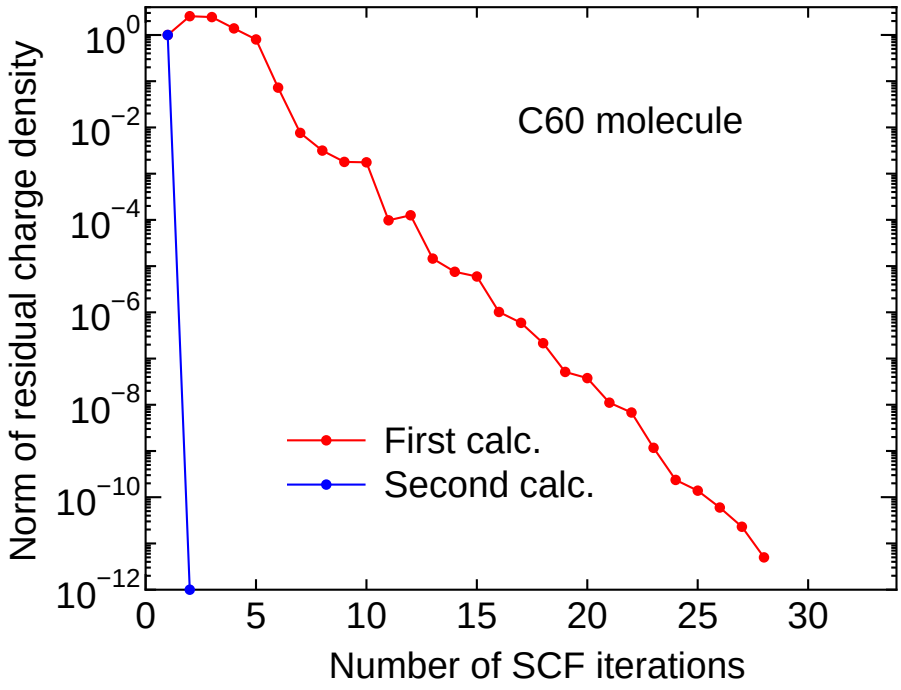

Figure 7: SCF convergence of a C_{60} molecule. In the second calculation, the restart files generated by the first calculation were used. The input file is 'C60.dat' in the directory 'work'.

13.2 Extrapolation scheme during MD and geometry optimization

In the geometry optimization and molecular dynamics simulations, the restart files generated at the previous steps are automatically utilized at the next step to accelerate the convergence using an

extrapolation scheme [42, 43]. In the extrapolation scheme, the number of previous MD or geometry optimization steps can be controlled by a keyword:

```
scf.ExtCharge.History      2        # default=2
```

From a series of benchmark calculations, 'scf.ExtCharge.History' of 2 works well and a larger number tends to be numerically unstable. So, users are recommended to use the default setting of 2.

13.3 Input file for the restart calculation

An input file '*.dat#' is generated at every MD step for the restart calculation with the final structure and the same 'Grid_Origin' explained in the Section 'Fixing the relative position of regular grid'. Using the file '*.dat#', it can be possible to continue MD calculations and geometry optimization from the last step.

14 Geometry optimization

14.1 Steepest decent optimization

An example of the geometry optimization is illustrated in this Section. As an initial structure, let us consider the methane molecule given in the Section 'Input file', but the x-coordinate of the carbon atom of the methane molecule is moved to 0.3 Å as follows:

```
<Atoms.SpeciesAndCoordinates
  1   C      0.300000    0.000000    0.000000     2.0  2.0
  2   H     -0.889981   -0.629312    0.000000     0.5  0.5
  3   H      0.000000    0.629312   -0.889981     0.5  0.5
  4   H      0.000000    0.629312    0.889981     0.5  0.5
  5   H      0.889981   -0.629312    0.000000     0.5  0.5
Atoms.SpeciesAndCoordinates>
```

Then, a keyword 'MD.type' is specified as 'Opt', and set to 200 for a keyword 'MD.maxIter'. The 'Opt' is based on a simple steepest decent method with a variable prefactor. Figure 8 (a) shows the convergence history of the norm of the maximum force on atom as a function of the number of the optimization steps. We see that the norm of the maximum force on atom converges after the structure overshot the stationary point because of change of the prefactor. Using 'Methane2.dat' in the directory 'work', you can trace the calculation. As well as the case of the methane molecule, a similar behavior can be seen for the silicon diamond as shown in Fig. 8(b).

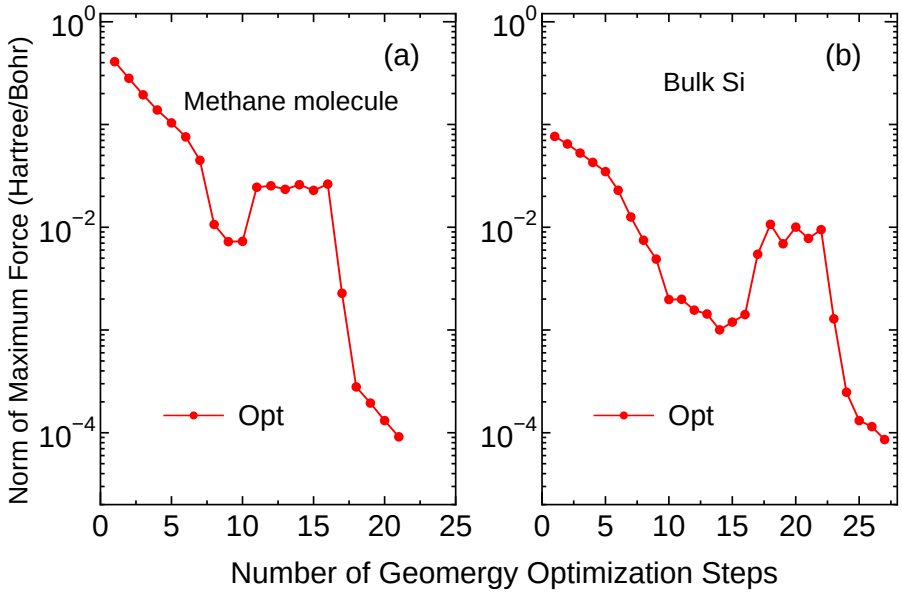

Figure 8: The norm of the maximum force on atom of (a) a methane molecule (b) silicon in the diamond structure as a function of geometry optimization steps. The initial structures are ones distorted from the the equilibrium structures. The input files are 'Methane2.dat' and 'Si8.dat' in the directory 'work', respectively.

14.2 EF, BFGS, RF, and DIIS optimizations

Although 'Opt' is a robust scheme, the convergence speed can be slow in general. Faster schemes based on quasi Newton methods are available for the geometry optimization. They are the eigenvector following (EF) method [45], the Broyden-Fletcher-Goldfarb-Shanno (BFGS) method [47], the rational function (RF) method [46], and a direct inversion iterative sub-space (DIIS) method [44], implemented in Cartesian coordinate. In the EF and RF methods, the approximate Hessian is updated by the BFGS method. Thus, five geometry optimizers, Opt, EF, BFGS, RF and DIIS, are available in OpenMX Ver. 3.7, which can be specified by 'MD.Type'. The relevant keywords are listed below:

```
MD.Type                    EF         # Opt|DIIS|BFGS|RF|EF
MD.Opt.DIIS.History         3         # default=3
MD.Opt.StartDIIS            5         # default=5
MD.Opt.EveryDIIS          200         # default=200
MD.maxIter                100         # default=1
MD.Opt.criterion        1.0e-4        # default=0.0003 (Hartree/Bohr)
```

Especially, you can control these schemes by two keywords:

```
MD.Opt.DIIS.History     3       # default=3
MD.Opt.StartDIIS        5       # default=5
```

The keyword 'MD.Opt.DIIS.History' specifies the number of the previous steps to update an optimum Hessian matrix. The default value is 3. Also, the geometry optimization step at which 'EF', 'BFGS', 'RF', or 'DIIS' starts is specified by the keyword 'MD.Opt.StartDIIS'. The geometry optimization steps before starting these methods is performed by the steepest decent method as in 'Opt'. The default value is 5.

The initial step in the optimization is automatically tuned by monitoring the maximum force in the initial structure. As shown in Fig. 9 which shows the number of geometry steps to achieve the maximum force of below 0.0003 Hartree/Bohr in molecules and bulks, in most cases the RF method seems to be the most robust and efficient scheme, while the EF and BFGS methods also show a similar performance. The input files used for those calculations and the out files can be found in the directory 'work/geoopt_example/'.

It should be also noted that by these quasi Newton methods geometrical structures tend to be converged to a saddle point rather than a stationary minimum point. This is because the structure at which the quasi Newton method started to be employed does not reach at a flexion point. In such a case, the structure should be optimized well by the steepest decent method before moving to the quasi Newton method. The treatment can be easily done by only taking a larger value for 'MD.Opt.StartDIIS', or by restarting the calculation using a file '*.dat#', where '*' is 'System.Name' specified in your input file.

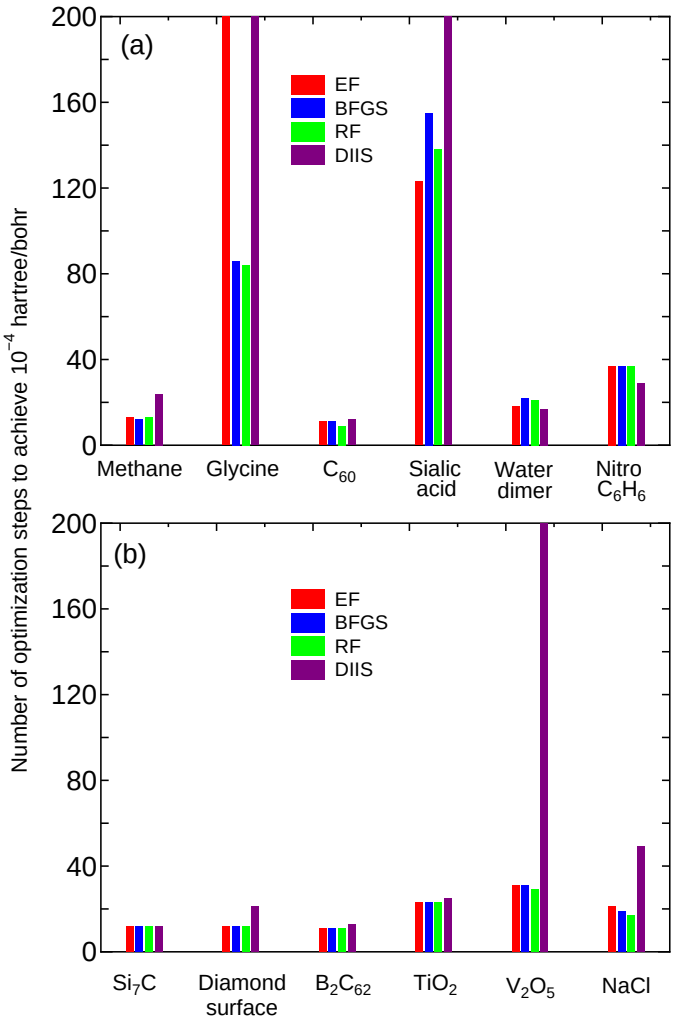

Figure 9: The number of optimization steps to achieve the maximum force of below 3×10^{-4} Hartree/Bohr for (a) molecular systems and (b) bulk systems using four kinds of optimization methods.

14.3 Constrained relaxation

It is possible to optimize geometrical structures with a constraint in which atoms can be fixed in the initial position. The constraint can be applied separately to the x-, y-, and z-coordinates to the initial atomic position in your input file by the following keyword 'MD.Fixed.XYZ':

```
<MD.Fixed.XYZ
   1  1 1 1
   2  1 0 0
 MD.Fixed.XYZ>
```

The example is for a system consisting of two atoms. If you have N atoms, then you have to provide N rows in this specification. The 1st column is the same sequential number to specify atom as in the specification of the keyword 'Atoms.SpeciesAndCoordinates'. The 2nd, 3rd, and 4th columns are

flags for the x-, y-, and z-coordinates, respectively. '1' means that the coordinate is fixed, and '0' relaxed. In the above example, the x-, y-, and z-coordinates of the atom '1' are fixed, and only the x-coordinate of the atom '2' is fixed. The default setting is that all the coordinates are relaxed. The fixing of atomic positions are valid for all the geometry optimizers and molecular dynamics schemes. The constrained relaxation may be useful for a refinement of the local structure in large-scale systems.

14.4 Restart of geometry optimization

If the first trial for geometry optimization does not reach a convergent result, one can restart the geometry optimization using an input file '*.dat#' which is generated at every geometry optimization step for the restart calculation with the final structure. In such a case, it is better to restart the optimization with the approximate Hessian matrix calculated in the first trial to accelerate the convergence. In OpenMX Ver. 3.7, the approximate Hessian matrix is also saved every geometry optimization step, and is reused when the restart is performed by '*.dat#'. Thus, even if the geometry optimization is intermittently repeated by subsequent job submission, the number of iterations for the geometry optimization step is the same as that in the single submission. The functionality may be useful when users optimize large-scale systems using computational systems in common use for which the wall time is set for each job.

15 Molecular dynamics

OpenMX Ver. 3.7 supports five molecular dynamics simulations: constant energy molecular dynamics (NVE), constant temperature molecular dynamics by a velocity scaling (NVT_VS), constant temperature molecular dynamics by a velocity scaling to be considered independently for every atoms (NVT_VS2), constant temperature molecular dynamics by the Nose-Hoover method (NVT_NH) and a multi-heat bath molecular dynamics (NVT_VS4).

15.1 NVE molecular dynamics

A constant energy molecular dynamics simulation is performed by the following keyword 'MD.Type':

```
MD.Type           NVE       # NOMD|Opt|NVE|NVT_VS|NVT_VS2|NVT_NH
```

Calculated quantities at every MD step are stored in an output file '*.ene', where * means 'System.Name'. Although you can find the details in 'iterout.c' in the directory 'source', several quantities are summarized for your convenience as follows:

```
 1:    MD step
 2:    MD time
14:    kinetic energy of nuclear motion, Ukc (Hartree)
15:    DFT total energy, Utot (Hartree)
16:    Utot + Ukc (Hartree)
17:    Fermi energy (Hartree)
```

which means that the first and second columns correspond to MD step and MD time, and so on.

15.2 NVT molecular dynamics by a velocity scaling

A velocity scaling scheme [17] is supported to perform NVT ensemble molecular dynamics simulation by the following keyword:

```
MD.Type           NVT_VS    # NOMD|Opt|NVE|NVT_VS|NVT_VS2|NVT_NH
```

Then, in this NVT molecular dynamics the temperature for nuclear motion can be controlled by

```
<MD.TempControl
  3
  100   2  1000.0  0.0
  400  10   700.0  0.4
  700  40   500.0  0.7
MD.TempControl>
```

The beginning of the description must be '<MD.TempControl', and the last of the description must be 'MD.TempControl>'. The first number '3' gives the number of the following lines to control the temperature. In this case you can see that there are three lines. Following the number '3', in the consecutive lines the first column means MD steps and the second column gives interval of MD steps that the velocity scaling is made. For the above example, a velocity scaling is performed at every two MD steps until 100 MD steps, at every 10 MD steps from 100 to 400 MD steps, and at every 40 MD steps from 400 to 700 MD steps. The third and fourth columns give a given temperature $T_{\rm give}$ (K)

and a scaling parameter α in the interval, while the temperature in the interval is given by a linear interpolation. In this velocity scaling, velocity is scaled by

$$s = \sqrt{\frac{T_{\rm given} + (T_{\rm calc} - T_{\rm given}) * \alpha}{T_{\rm calc}}}$$

$$\mathbf{v}_i' = \mathbf{v}_i \times s$$

where $T_{\rm given}$ and $T_{\rm calc}$ are a given and calculated temperatures, respectively. In 'NVT_VS' the temperature is calculated by using velocities of all the atoms. On the other hand, the *local* temperature is estimated by the velocity of each atom in 'NVT_VS2', and the velocity scaling is performed by the local temperature. After the final MD step given in the specification 'MD.TempControl', the NVT ensemble is switched to a NVE ensemble. Calculated quantities at every MD step are stored in an output file '*.ene', where '*' means 'System.Name'. Although you can find the details in 'iterout.c', several quantities are summarized for your convenience as follows:

```
 1:    MD step
 2:    MD time
14:    kinetic energy of nuclear motion, Ukc (Hartree)
15:    DFT total energy, Utot (Hartree)
16:    Utot + Ukc (Hartree)
17:    Fermi energy (Hartree)
18:    Given temperature for nuclear motion (K)
19:    Calculated temperature for nuclear motion (K)
22:    Nose-Hoover Hamiltonian (Hartree)
```

which means that the first and second columns correspond to MD step and MD time, and so on. As an example, we show a result for the velocity scaling MD of a glycine molecule in Fig. 10 (a). We see that the temperature in a molecule oscillates around the given temperature. Also for visualization of molecular dynamics, an output file '*.md' can be easily animated using free software xmakemol [91] and XCrySDen [61].

15.3 NVT molecular dynamics by the Nose-Hoover method

The Nose-Hoover molecular dynamics [18] is supported to perform NVT ensemble molecular dynamics simulations by the following keyword:

```
MD.Type          NVT_NH      # NOMD|Opt|NVE|NVT_VS|NVT_NH
```

Then, in this NVT molecular dynamics the temperature for nuclear motion can be controlled by

```
<MD.TempControl
  4
  1    1000.0
  100  1000.0
  400   700.0
  700   600.0
MD.TempControl>
```

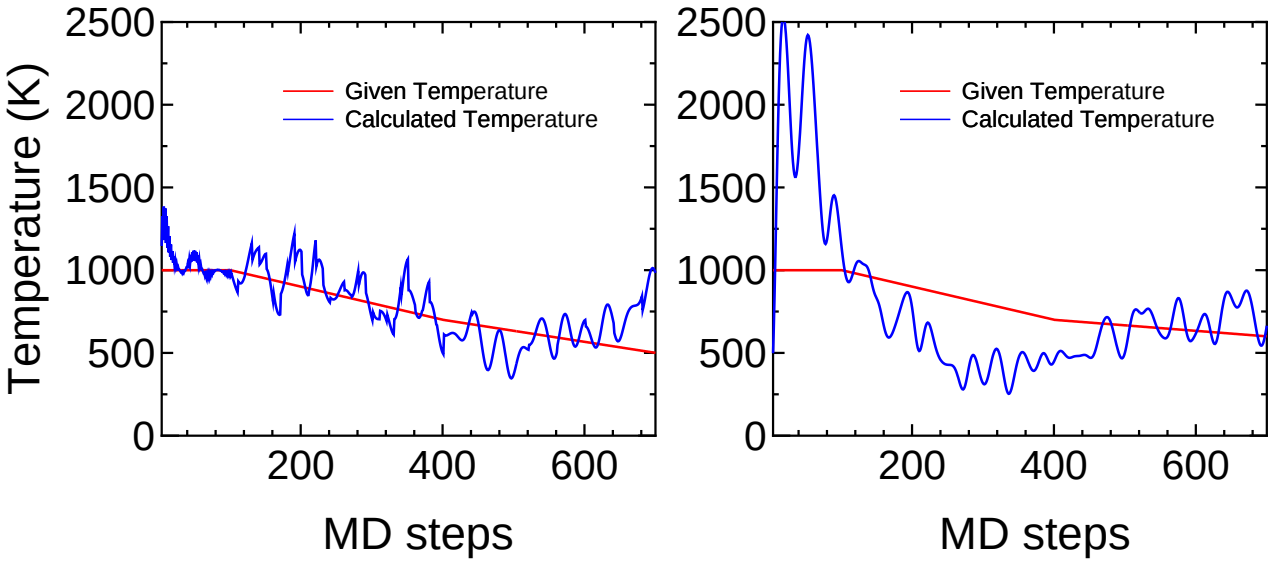

Figure 10: (a) Given and calculated temperatures of a glycine molecule as a function of MD steps in a velocity scaling NVT molecular dynamics. (b) Given and calculated temperatures of a glycine molecule as a function of MD steps in the Nose-Hoover NVT molecular dynamics. The input files are 'Gly_VS.dat' and 'Gly_NH.dat' in the directory 'work', respectively.

The beginning of the description must be '<MD.TempControl', and the last of the description must be 'MD.TempControl>'. The first number '4' gives the number of the following lines to control the temperature. In this case you can see that there are four lines. Following the number '4', in the consecutive lines the first and second columns give MD steps and a given temperature for nuclear motion. The temperature between the MD steps is given by linear interpolation. Although the same keyword 'MD.TempControl' as used in the velocity scaling MD is utilized in this specification, it is noted that the format is different from each other. In addition to the specification of 'MD.TempControl', you must specify a mass of heat bath by the following keyword:

```
NH.Mass.HeatBath          30.0      # default = 20.0
```

In this specification, we use the unified atomic mass unit that the principal isotope of carbon atom is 12.0. Calculated quantities at every MD step are stored in an output file '*.ene' as explained in 'NVT molecular dynamics by a velocity scaling'. As an example, we show a result for Nose-Hoover MD of a glycine molecule in Fig. 10 (b). We see that the temperature in the molecule oscillates around the given temperature. Also for visualization of molecular dynamics, an output file '*.md' can be easily animated using free software such xmakemol [91] and XCrySDen [61] as well as NVT_VS.

15.4 Multi-heat bath molecular dynamics

OpenMX Ver. 3.7 supports a multi-heat bath molecular dynamics simulation where temperature of each grouped atom is controlled with a heat-bath by a velocity scaling scheme [17]. The method is performed by the following keyword:

```
MD.Type           NVT_VS4
```

The number of groups is specified by

```
MD.num.AtomGroup    2
```

and the groups are defined by

```
<MD.AtomGroup
  1  1
  2  1
  3  1
  4  2
  5  2
MD.AtomGroup>
```

The beginning of the description must be '<MD.AtomGroup', and the last of the description must be 'MD.AtomGroup>'. The first column is a sequential serial number for identifying atoms. The second column is an identification number for each atom, representing the group to which the atom belongs. The identification number has to be specified from 1, and followed by 2, 3, $\cdots$. The above is an example where only five atoms are involved in the system and there are two groups. In Ver. 3.7, the profile of temperature for all the groups is controlled by the keyword 'MD.TempControl' as discussed in the subsection 'NVT molecular dynamics by a velocity scaling'. In the feature release, we will support a functionality that temperature is independently controlled for each group.

15.5 Constraint molecular dynamics

A constraint scheme is available in the molecular dynamics simulations in which atoms can be fixed in the initial position. The specification is the same as in the subsection 'Constrained relaxation'. See the subsection for the specification.

15.6 Initial velocity

For molecular dynamics simulations, it is possible to provide the initial velocity of each atom by the following keyword:

```
<MD.Init.Velocity
 1    3000.000  0.0  0.0
 2   -3000.000  0.0  0.0
MD.Init.Velocity>
```

The example is for a system consisting of two atoms. If you have N atoms, then you have to provide N rows in this specification. The 1st column is the same sequential number to specify atom as in the specification of the keyword 'Atoms.SpeciesAndCoordinates'. The 2nd, 3rd, and 4th columns are x-, y-, and z-components of the velocity of each atom, respectively. The unit of the velocity is m/s. The keyword 'MD.Init.Velocity' is compatible with the keyword 'MD.Fixed.XYZ'.

15.7 User definition of atomic mass

In molecular dynamics simulations, OpenMX uses the atomic mass defined in 'Set_Atom_Weight() of SetPara_DFT.c'. However, one can easily change the atomic mass by the keyword 'Definition.of.Atomic.Species'. In such a case, the atomic mass is defined by the fourth column as

```
<Definition.of.Atomic.Species
 H   H5.0-s1          H_PBE13      2.0
 C   C5.0-s1p1        C_PBE13     12.0
Definition.of.Atomic.Species>
```

If the fourth column is not given explicitly, then the default atomic mass will be used. This may be useful to investigate the effect of atomic mass in molecular dynamics, and also may allow us to use a larger time step by using especially the deuterium mass for hydrogen atom. For the definition of atomic mass, we use the unified atomic mass unit that the principal isotope of carbon atom is 12.0.

16 Visualization

The electron densities, molecular orbitals, and potentials are output to files in a Gaussian cube format. Figure 11 shows examples of isosurface maps visualized by XCrySDen [61]. These data are output in a form of the Gaussian cube. So, many softwares, such as Molekel [60] and XCrySDen [61], can be used for the visualization. One can find the details of output files in the cube format in the Section 'Output files'.

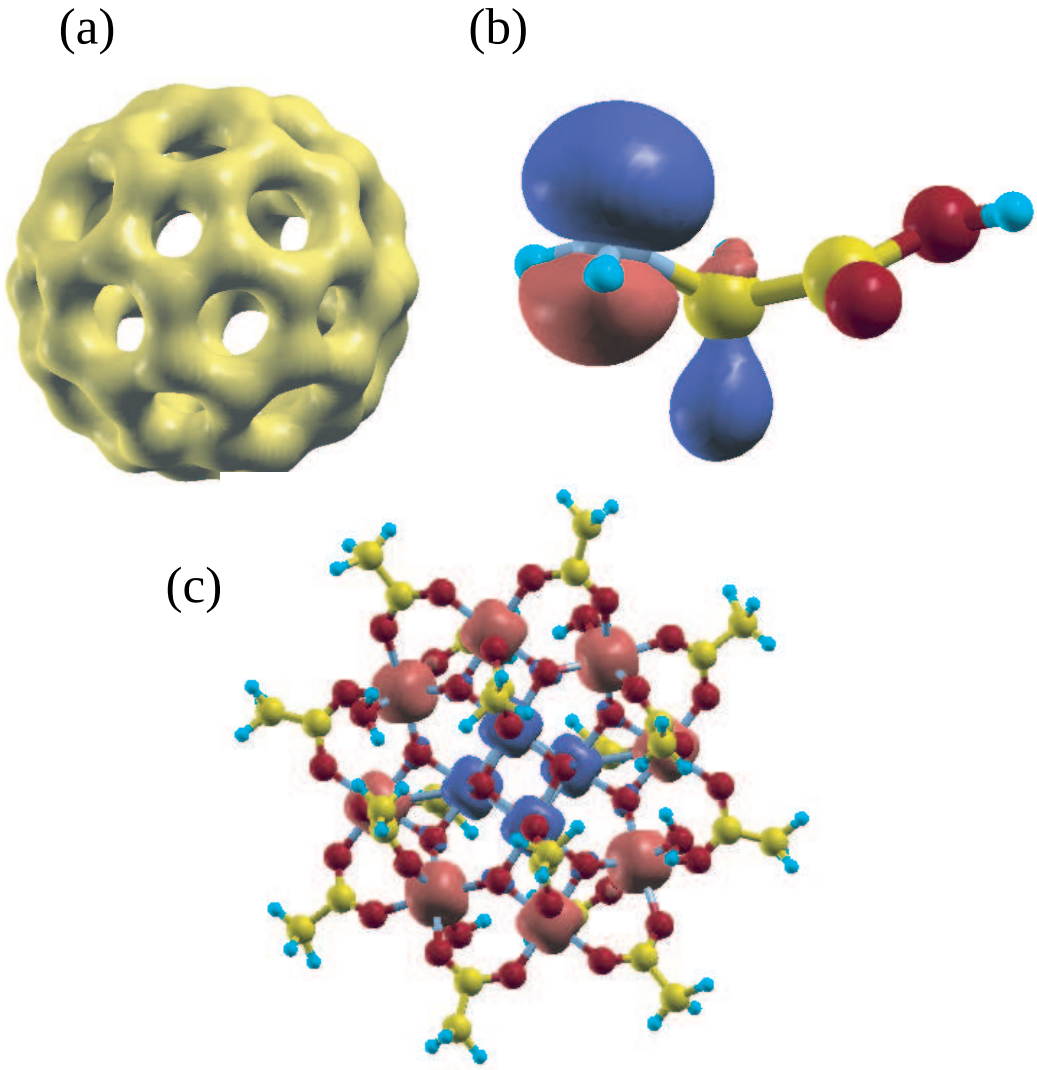

Figure 11: (a) Isosurface map of the total electron density of a C_{60} molecule where 0.13 was used as isovalue of total electron density. (b) Isosurface map of the highest occupied molecular orbital (HOMO) of a glycine molecule where |0.06| was used as isovalue of the molecular orbital. (b) Isosurface map of the spin electron density of a molecular magnet ($Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4$ [62]) where |0.02| was used as isovalue of the spin electron density.

17 Band dispersion

The band dispersion is calculated by the following two steps:

(1) SCF calculation

Let us illustrate the calculation of band dispersion using the carbon diamond. In a file 'Cdia.dat' of the directory 'work', the atomic coordinates, cell vectors, and 'scf.Kgrid' are given by

```
Atoms.Number         2
Atoms.SpeciesAndCoordinates.Unit   Ang # Ang|AU
<Atoms.SpeciesAndCoordinates
 1   C  0.000  0.000  0.000   2.0 2.0
 2   C  0.890  0.890  0.890   2.0 2.0
Atoms.SpeciesAndCoordinates>
Atoms.UnitVectors.Unit             Ang # Ang|AU
<Atoms.UnitVectors
  1.7800  1.7800  0.0000
  1.7800  0.0000  1.7800
  0.0000  1.7800  1.7800
Atoms.UnitVectors>

scf.Kgrid                  7 7 7       # means n1 x n2 x n3
```

The unit cell for the band dispersion and **k**-paths are given by

```
Band.dispersion             on        # on|off, default=off
<Band.KPath.UnitCell
 3.56  0.00  0.00
 0.00  3.56  0.00
 0.00  0.00  3.56
Band.KPath.UnitCell>
Band.Nkpath                  5
<Band.kpath
  15  0.0 0.0 0.0   1.0 0.0 0.0   g X
  15  1.0 0.0 0.0   1.0 0.5 0.0   X W
  15  1.0 0.5 0.0   0.5 0.5 0.5   W L
  15  0.5 0.5 0.5   0.0 0.0 0.0   L g
  15  0.0 0.0 0.0   1.0 0.0 0.0   g X
Band.kpath>
```

Then, we execute OpenMX as:

```
% ./openmx Cdia.dat
```

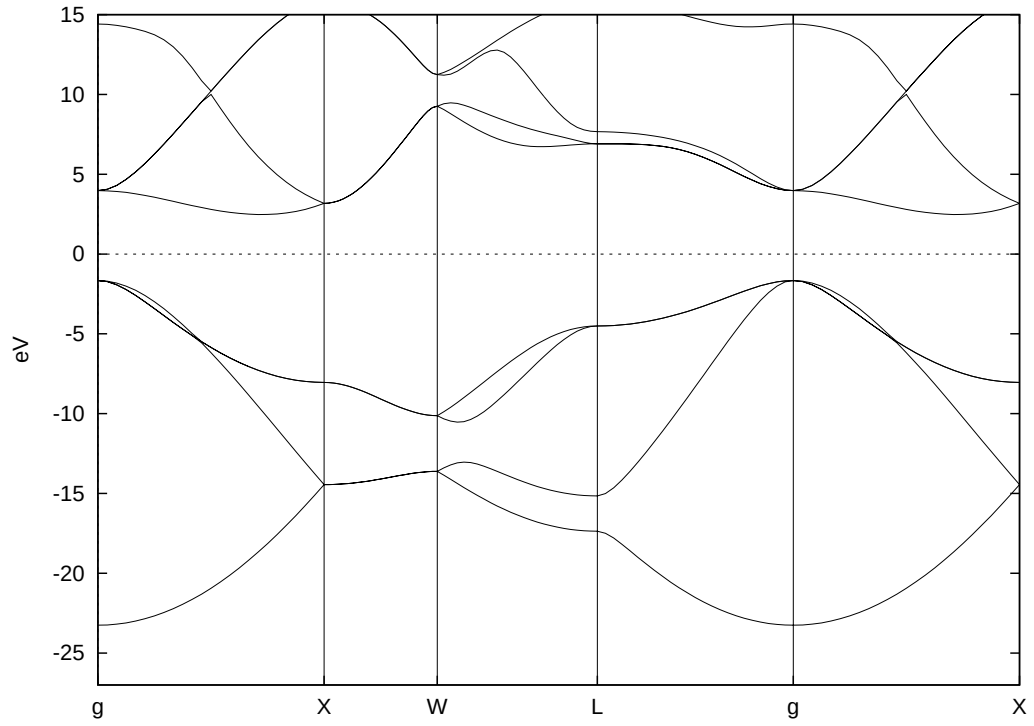

Figure 12: Band dispersion of carbon diamond. The input file is 'Cdia.dat' in the directory 'work'.

When the execution is completed normally, then you can find a file 'cdia.Band' in the directory 'work'. If 'Band.KPath.UnitCell' does not exist, the unit cell specified by the 'Atoms.UnitVectors' will be used.

(2) Converting of the data to a gnuplot form

There is a file 'bandgnu13.c' in the directory 'source'. Compile the file as follows:

```
% gcc bandgnu13.c -lm -o bandgnu13
```

When the compile is completed normally, then you can find an executable file 'bandgnu13' in the directory 'source'. Please copy the executable file to the directory 'work'. Using the executable file 'bandgnu13' a file 'cdia.Band' is converted in a gnuplot format as

```
% ./bandgnu13 cdia.Band
```

Then, two or three files 'cdia.GNUBAND' and 'cdia.BANDDAT1' ('cdia.BANDDAT2'), are generated. The file 'cdia.GNUBAND' is a script for gnuplot, and read the data files 'cdia.BANDDAT1' and 'cdia.BANDDAT2' for the up- and down-spin states, respectively. If spin-polarized calculations using 'LSDA-CA', 'LSDA-PW', or 'GGA-PBE' is employed in the SCF calculation, '*.BANDDAT2' for the down-spin state is generated in addition to '*.BANDDAT1'. The file 'cdia.GNUBAND' is plotted using gnuplot as follows:

```
% gnuplot cdia.GNUBAND
```

Figure 12 shows the band dispersion of carbon diamond generated by the above procedure, while the range of y-axis was changed in the file 'cdia.GNUBAND'. It is also noted that the chemical potential is automatically shifted to the origin of energy.

A problem in drawing of the band dispersion is how to choose a unit cell used in calculating of the band dispersion. Often, the unit cell used in calculating of the band dispersion is different from that used in the definition of the periodic system. In such a case, you need to define a unit cell used in calculating of the band dispersion by the keyword 'Band.KPath.UnitCell'. If you define 'Band.KPath.UnitCell', the reciprocal lattice vectors for the calculation of the band dispersion are calculated by the unit vectors specified in 'Band.KPath.UnitCell'. If you do not define 'Band.KPath.UnitCell', the reciprocal lattice vectors, which are calculated by the unit vectors specified in 'Atoms.UnitVectors', is employed for the calculation of the band dispersion. In case of fcc, bcc, base centered cubic, and trigonal cells, the reciprocal lattice vectors for the calculation of the band dispersion should be specified using the keyword 'Band.KPath.UnitCell' based on the consuetude in the band structure calculations.

18 Density of states

18.1 Conventional scheme

The density of states (DOS) is calculated by the following two steps:

(1) SCF calculation

Let us illustrate the calculation of DOS using the carbon diamond. In a file 'Cdia.dat' in the directory 'work', the keywords for the DOS calculation are set to

```
Dos.fileout                on
Dos.Erange             -25.0  20.0
Dos.Kgrid               12 12 12
```

In the specification of the keyword 'Dos.Erange', the first and second values are the lower and upper bounds of the energy range (eV) for the DOS calculation, respectively, where the origin (0.0) of energy corresponds to the chemical potential. Also, in the specification of the keyword 'Dos.Kgrid', a set of numbers (n1,n2,n3) is the number of grids to discretize the first Brillouin zone in the **k**-space, which is used in the DOS calculation. Then, we execute OpenMX by:

```
% ./openmx Cdia.dat
```

When the execution is completed normally, then you can find files 'cdia.Dos.val' and 'cdia.Dos.vec' in the directory 'work'. The eigenvalues and eigenvectors are stored in the files 'cdia.Dos.val' and 'cdia.Dos.vec' in a text and binary forms, respectively. The DOS calculation is supported even for the O(N) calculation, while a Gaussian broadening method is employed in this case.

(2) Calculation of the DOS

Let us compile a program package for calculating DOS. Move the directory 'source', and then compile as follows:

```
% make DosMain
```

When the compile is completed normally, then you can find an executable file 'DosMain' in the directory 'source'. Please copy the file 'DosMain' to the directory 'work', and then move to the directory 'work'. You can calculate DOS and projected DOS (PDOS) using the program 'DosMain' from two files 'cdia.Dos.val' and 'cdia.Dos.vec' as:

```
% ./DosMain cdia.Dos.val cdia.Dos.vec
```

Then, you are interactively asked from the program as follow:

```
% ./DosMain cdia.Dos.val cdia.Dos.vec
Max of Spe_Total_CNO = 8
```

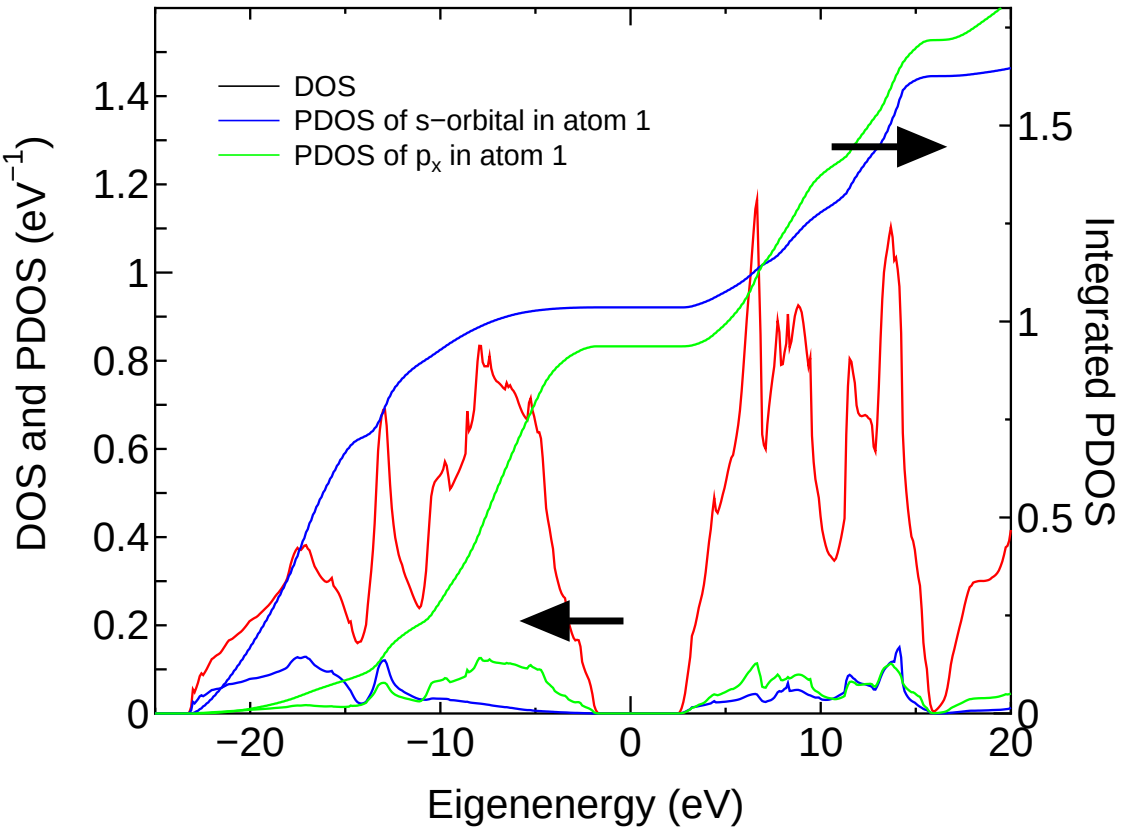

Figure 13: DOS and PDOS of the carbon diamond, and the integrated PDOS, where the Fermi level is set to zero. Since charge redistribution occurs among the s-, p-, and d-orbitals, the integrated PDOS of s- and p-orbitals at the Fermi level are not exactly 1. The calculation can be traced by using an input file 'Cdia.dat' in the directory 'work'.

```
1 1 101 102 103 101 102 103
<cdia.Dos.val>
<cdia>
Which method do you use?, Tetrahedron(1), Gaussian Broadeninig(2)
1
Do you want Dos(1) or PDos(2)?
2

Number of atoms=2
Which atoms for PDOS : (1,...,2), ex 1 2
1
pdos_n=1
1
<Spectra_Tetrahedron> start
Spe_Num_Relation 0 0 1
Spe_Num_Relation 0 1 1
Spe_Num_Relation 0 2 101
```

```
Spe_Num_Relation 0 3 102
Spe_Num_Relation 0 4 103
Spe_Num_Relation 0 5 101
Spe_Num_Relation 0 6 102
Spe_Num_Relation 0 7 103
make cdia.PDOS.Tetrahedron.atom1.s1
make cdia.PDOS.Tetrahedron.atom1.p1
make cdia.PDOS.Tetrahedron.atom1.p2
make cdia.PDOS.Tetrahedron.atom1.p3
make cdia.PDOS.Tetrahedron.atom1
```

The tetrahedron [48] and Gaussian broadening methods for evaluating DOS are available. Also, you can select DOS or PDOS. When you select the calculation of PDOS, then please select atoms for evaluating PDOS. In this case, each DOS projected on orbitals (s, px (p1), py (p2), pz (p3),..) in selected atoms are output in each file. In these files, the first and second columns are energy in eV and DOS (eV^{-1}) or PDOS (eV^{-1}), and the third column is the integrated DOS or PDOS. If a spin-polarized calculation using 'LSDA-CA', 'LSDA-PW', or 'GGA-PBE' is employed in the SCF calculation, the second and third columns in these files correspond to DOS or PDOS for up and down spin states, and the fourth and fifth columns are the corresponding integrated values. If you select the Gaussian broadening method, you are requested to set a parameter, value of Gaussian, a (eV), which determines the width of Gaussian defined by $\exp(-(E/a)^2)$. Figure 13 shows DOS and PDOS of carbon diamond.

18.2 For calculations with lots of k-points

Since the calculation of density of states (DOS) of a large-scale system with lots of k-points requires a considerable memory size, the post-processing code 'DosMain' for generating the partial and total DOS tends to suffer from a segmentation fault. For such a case, a Gaussian DOS scheme is available in which the partial DOS is calculated by the Gaussian broadening method in the OpenMX on-the fly calculation and the information of wave functions is not stored in the file '*.Dos.vec'. Since this scheme does not require a large sized memory, it can be used to calculate DOS of large-scale systems. Then, you can specify the following keywords in your input file.

```
DosGauss.fileout      on       # default=off, on|off
DosGauss.Num.Mesh    200       # default=200
DosGauss.Width       0.2       # default=0.2 (eV)
```

When you use the scheme, specify 'on' for the keyword 'DosGauss.fileout'. And the keyword 'DosGauss.Num.Mesh' gives the number of partitioning for the energy range specified by the keyword 'Dos.Erange'. The keyword 'DosGauss.Width' gives the width, a, of the Gaussian $\exp(-(E/a)^2)$. The keyword 'DosGauss.fileout' and the keyword 'Dos.fileout' are mutually exclusive. Therefore, when you use the scheme the keyword, 'Dos.fileout' must be 'off' as follows:

```
Dos.fileout          off       # on|off, default=off
```

Also, the following two keywords are valid for both the keywords 'Dos.fileout' and 'DosGauss.file'.

```
Dos.Erange       -20.0  20.0   # default=-20 20
Dos.Kgrid           5 5 5      # default=Kgrid1 Kgrid2 Kgrid3
```

It should be noted that the keyword 'DosGauss.fileout' generates only the Gaussian broadening DOS, which means that DOS by the tetrahedron method cannot be calculated by the keyword 'DosGauss.fileout'. After the OpenMX calculation with these keywords, the procedure for DosMain is the same as in the conventional scheme.

19 Orbital optimization

The radial function of basis orbitals can be variationally optimized using the orbital optimization method [28]. As an illustration of the orbital optimization, let us explain it using a methane molecule of which input file is 'Methane_OO.dat'. In the orbital optimization method the optimized orbitals are expressed by the linear combination of primitive orbitals, and obtained by variationally optimizing the contraction coefficients. The number of the primitive and optimized orbitals in the optimization are specified by

```
<Definition.of.Atomic.Species
  H   H5.0-s4>1            H_CA13
  C   C5.0-s4>1p4>1        C_CA13
Definition.of.Atomic.Species>
```

For 'H' one optimized radial function for the s-orbital is obtained from the linear combination of four primitive radial functions. Similarly, one optimized radial function for the s-(p-)orbital is obtained from the linear combination of four primitive radial functions for 'C'. In addition, the following keywords are set in the input file as follows:

```
orbitalOpt.Method          species     # Off|Species|Atoms
orbitalOpt.Opt.Method        EF        # DIIS|EF
orbitalOpt.SD.step        0.001        # default=0.001
orbitalOpt.HistoryPulay     30         # default=15
orbitalOpt.StartPulay       10         # default=1
orbitalOpt.scf.maxIter      60         # default=40
orbitalOpt.Opt.maxIter     140         # default=100
orbitalOpt.per.MDIter       20         # default=1000000
orbitalOpt.criterion      1.0e-4       # default=1.0e-4

CntOrb.fileout               on        # on|off, default=off
Num.CntOrb.Atoms             2         # default=1
<Atoms.Cont.Orbitals
 1
 2
Atoms.Cont.Orbitals>
```

Then, we execute OpenMX as:

```
% ./openmx Methane_OO.dat
```

When the execution is completed normally, you can find the history of orbital optimization in the file 'met_oo.out' as:

```
*************************************************************
*************************************************************
         History of orbital optimization   MD= 1
*********     Gradient Norm ((Hartree/borh)^2)     ********
```

```
              Required criterion=  0.000100000000
*********************************************************

   iter=   1  Gradient Norm=  0.057098961101  Uele= -3.217161102876
   iter=   2  Gradient Norm=  0.044668461503  Uele= -3.220120116009
   iter=   3  Gradient Norm=  0.034308306321  Uele= -3.223123238394
   iter=   4  Gradient Norm=  0.025847573248  Uele= -3.226177980300
   iter=   5  Gradient Norm=  0.019106400842  Uele= -3.229294858054
   iter=   6  Gradient Norm=  0.013893824906  Uele= -3.232489198284
   iter=   7  Gradient Norm=  0.010499500005  Uele= -3.235304178159
   iter=   8  Gradient Norm=  0.008362635043  Uele= -3.237652870812
   iter=   9  Gradient Norm=  0.006959703539  Uele= -3.239618540761
   iter=  10  Gradient Norm=  0.005994816379  Uele= -3.241268535418
   iter=  11  Gradient Norm=  0.005298095979  Uele= -3.242657118263
   iter=  12  Gradient Norm=  0.003059655878  Uele= -3.250892948269
   iter=  13  Gradient Norm=  0.001390201488  Uele= -3.255123241210
   iter=  14  Gradient Norm=  0.000780925380  Uele= -3.255179362845
   iter=  15  Gradient Norm=  0.000726631072  Uele= -3.255263012792
   iter=  16  Gradient Norm=  0.000390930576  Uele= -3.250873416989
   iter=  17  Gradient Norm=  0.000280785975  Uele= -3.250333677139
   iter=  18  Gradient Norm=  0.000200668585  Uele= -3.252345643243
   iter=  19  Gradient Norm=  0.000240367596  Uele= -3.254238199726
   iter=  20  Gradient Norm=  0.000081974594  Uele= -3.258146794679
```

In most cases, 20-50 iterative steps are enough to achieve a sufficient convergence. The comparison between the primitive basis orbitals and the optimized orbitals in the total energy is given by

```
Primitive basis orbitals
   Utot  =      -7.992569945749 (Hartree)

Optimized orbitals by the orbital optimization
   Utot  =      -8.133746986502 (Hartree)
```

We see that the small but accurate basis set orbitals can be generated by the orbital optimization. In Fig. 14 we show the convergence properties of total energies for molecules and bulks as a function of the number of unoptimized and optimized orbitals, implying that a remarkable convergent results are obtained using the optimized orbitals for all the systems. In this illustration of a methane molecule, the optimized radial orbitals are output to files 'C_1.pao' and 'H_2.pao'. These output files 'C_1.pao' and 'H_2.pao' could be an input data for pseudo-atomic orbitals as is. This means that it is possible to perform a pre-optimization of basis orbitals for systems you are interested in. The pre-optimization could be performed for smaller but chemically similar systems.

The following two options are available for the keyword 'orbitalOpt.Method': 'atoms' in which basis obitals on each atom are fully optimized, 'species' in which basis obitals on each species are optimized.

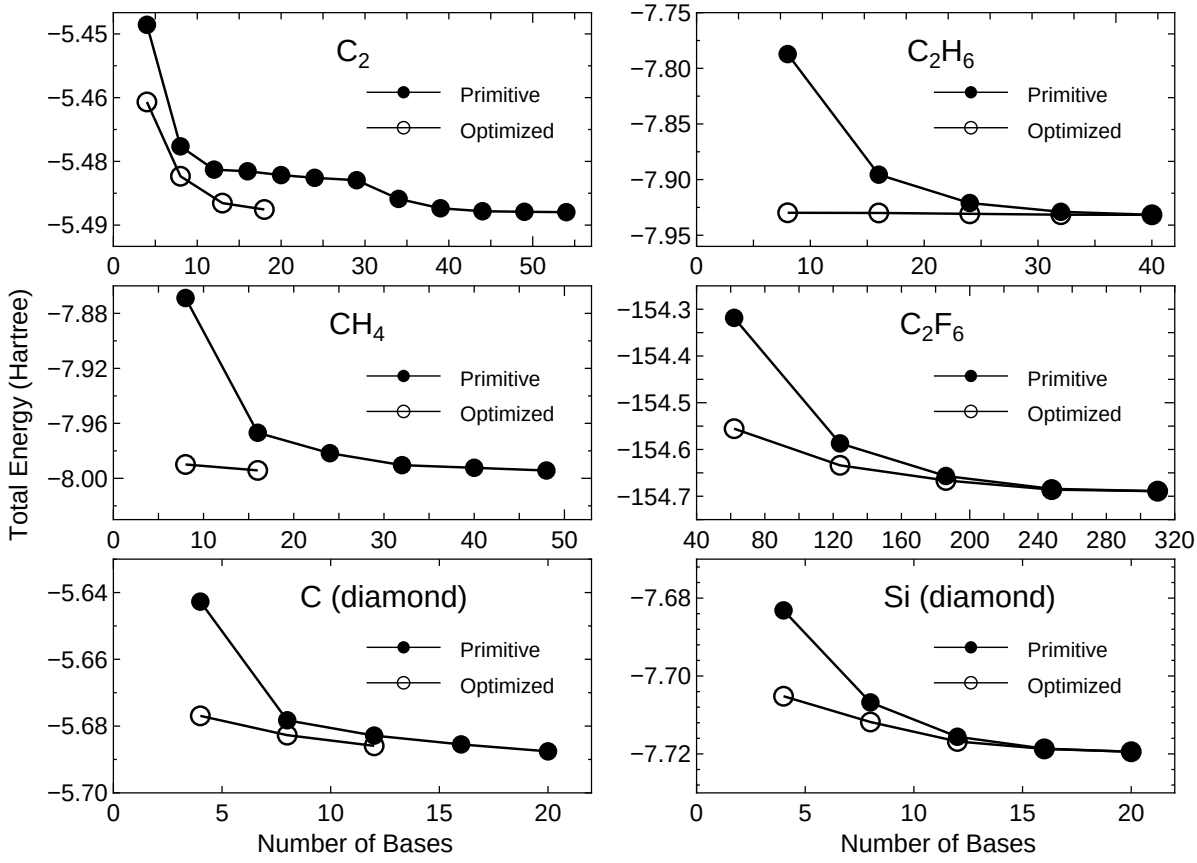

Figure 14: The total energy for a carbon dimer C_2, a methane molecule CH_4, carbon and silicon in the diamond structure, a ethane molecule C_2H_6, and a hexafluoro ethane molecule C_2F_6 as a function of the number of primitive and optimized orbitals. The total energy and the number of orbitals are defined as those per atom for C_2, carbon and silicon in the diamond, and as those per molecule for CH_4, C_2H_6, and C_2F_6.

- atoms

  The radial functions of basis orbitals are optimized with a constraint that the radial wave function R is independent of the magnetic quantum number, which guarantees the rotational invariance of the total energy. However, the optimized orbital on all the atoms can be different from eath other.

- species

  Basis orbitals in atoms with the same species name, that you define in 'Definition.of.Atomic.Species', are optimized as the same orbitals. If you want to assign the same orbitals to atoms with almost the same chemical environment, and optimize these orbitals, this scheme could be quite convenient. As well as 'atoms', the optimized radial functions are independent of the magnetic quantum number, which guarantees the rotational invariance of the total energy.

Although the same information is available in the section 'Input file', for convenience the details of the other keywords are listed below:

orbitalOpt.scf.maxIter
The maximum number of SCF iterations in the orbital optimization is specified by the keyword 'orbitalOpt.scf.maxIter'.

orbitalOpt.Opt.maxIter
The maximum number of iterations for the orbital optimization is specified by the keyword 'orbitalOpt.Opt.maxIter'. The iteration loop for the orbital optimization is terminated at the number specified by 'orbitalOpt.Opt.maxIter' even when a convergence criterion is not satisfied.

orbitalOpt.Opt.Method
Two schemes for the optimization of orbitals are available: 'EF' which is an eigenvector following method, 'DIIS' which is the direct inversion method in iterative subspace. The algorithms are basically same as for the geometry optimization. Either 'EF' or 'DIIS' is chosen by the keyword, 'orbitalOpt.Opt.Method'.

orbitalOpt.StartPulay
The quasi Newton method, 'EF' and 'DIIS' starts from the optimization step specified by the keyword 'orbitalOpt.StartPulay'.

orbitalOpt.HistoryPulay
The keyword 'orbitalOpt.HistoryPulay' specifies the number of previous steps to estimate the next input contraction coefficients used in the quasi Newton method, 'EF' and 'DIIS'.

orbitalOpt.SD.step
Steps before moving the quasi Newton method, 'EF' and 'DIIS' is performed by the steepest decent method. The prefactor used in the steepest decent method is specified by the keyword 'orbitalOpt.SD.step'. In most cases, orbitalOpt.SD.step of 0.001 can be a good prefactor.

orbitalOpt.criterion
The keyword 'orbitalOpt.criterion' specifies a convergence criterion ((Hartree/borh)^2) for the orbital optimization. The iterations loop is finished when a condition, Norm of derivatives<orbitalOpt.criterion, is satisfied.

CntOrb.fileout
If you want to output the optimized radial orbitals to files, then the keyword 'CntOrb.fileout' must be ON.

Num.CntOrb.Atoms
The keyword 'Num.CntOrb.Atoms' gives the number of atoms whose optimized radial orbitals are output to files.

Atoms.Cont.Orbitals
The keyword 'Atoms.Cont.Orbitals' specifies the atom number, which was given by the first column in the specification of the keyword 'Atoms.SpeciesAndCoordinates' for the output of optimized orbitals as follows:

```
<Atoms.Cont.Orbitals
 1
 2
```

```
Atoms.Cont.Orbitals>
```

The beginning of the description must be '<Atoms.Cont.Orbitals', and the last of the description must be 'Atoms.Cont.Orbitals>'. The number of lines should be consistent with the number specified in the keyword 'Atoms.Cont.Orbitals'. For example, the name of files are 'C_1.pao' and 'H_2.pao', where the symbol corresponds to that given by the first column in the specification of the keyword 'Definition.of.Atomic.Species' and the number after the symbol means that of the first column in the specification of the keyword 'Atoms.SpeciesAndCoordinates'. These output files 'C_1.pao' and 'H_2.pao', can be an input data for pseudo-atomic orbitals as is.

20 Order(N) method

The computational effort of the conventional diagonalization scheme scales as the third power of the number of basis orbitals, which means that the part could be a bottleneck when large-scale systems are calculated. On the other hand, the O(N) methods can solve the eigenvalue problem in O(N) operation in exchange for accuracy. Thus, O(N) methods could be efficient for large-scale systems, while a careful consideration is always required for the accuracy. In OpenMX Ver. 3.7, two O(N) methods are available: a divide-conquer (DC) method [37] and a Krylov subspace method [30]. In the following subsections each O(N) method is illustrated by examples.

20.1 Divide-conquer method

The DC method is a robust scheme and can be applicable to a wide variety of materials with a reasonable degree of accuracy and efficiency, while this scheme is suitable especially for covalent systems. In this subsection, the O(N) calculation using the DC method is illustrated. In an input file 'DIA8_DC.dat' which can be found in the directory 'work', please specify DC for the keyword 'scf.EigenvalueSolver'.

```
scf.EigenvalueSolver    DC
```

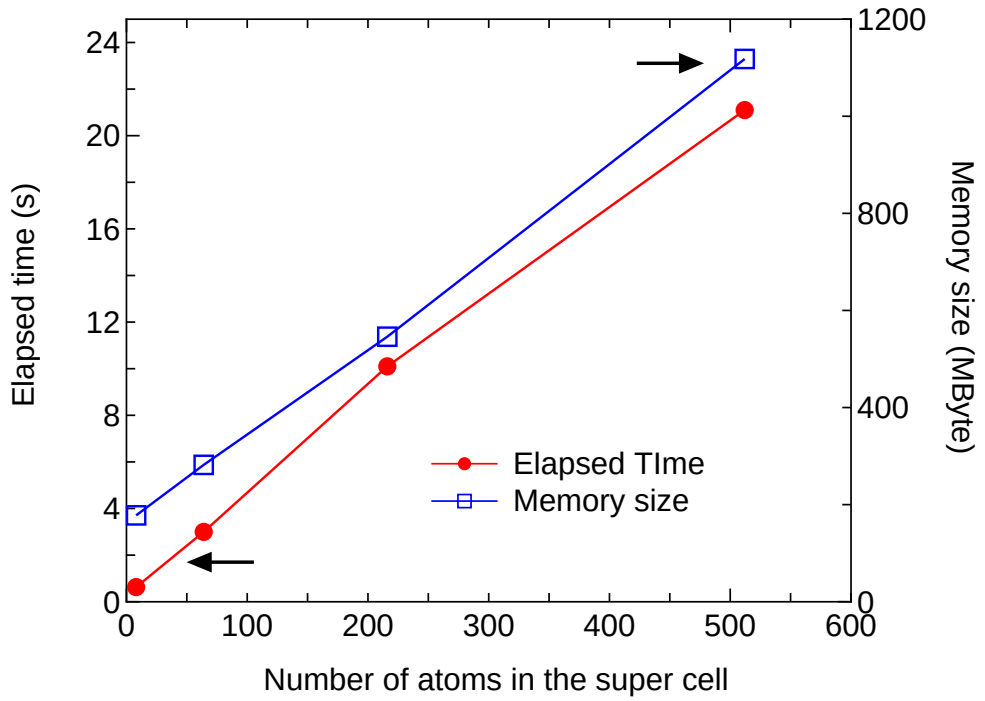

Figure 15: Elapsed time of the diagonalization part per SCF step and computational memory size per MPI process as a function of carbon atoms in the diamond supercell, where 16 processes were used in the MPI parallel calculations. C5.0-s1p1 was used as basis functions. For the DC method, orderN.HoppingRanges=6.0 (Å) is used. A Xeon machine (2.6 GHz) was used to measure the elapsed time. The input files are 'DIA8_DC.dat', 'DIA64_DC.dat', 'DIA216_DC.dat', and 'DIA512_DC.dat' in the directory 'work'.

Table 2: Total energy and computational time per MD step of a C_{60} molecule and small peptide molecules (valorphin [63]) and DNA consisting of cytosines and guanines calculated by the conventional diagonalization and the O(N) DC method, where a minimal basis set was used. In this Table, numbers in the parenthesis after DC means 'orderN.HoppingRanges' used in the DC calculation. The computational times were measured using an Opteron PC cluster (48 cpus × 2.4 GHz). The input files are 'C60_DC.dat', 'Valorphin_DC.dat', 'CG15c_DC.dat' in the directory 'work'.

	Total energy (Hartree)	Computational time (s)
C_{60}		
(60 atoms, 240 orbitals)		
Conventional	-343.89680	36
DC (7.0, 2)	-343.89555	37
Valorphin		
(125 atoms, 317 orbitals)		
Conventional	-555.28953	81
DC (6.5, 2)	-555.29019	76
DNA		
(650 atoms, 1880 orbitals)		
Conventional	-4090.95463	576
DC (6.3, 2)	-4090.95092	415

Then, one can execute OpenMX by:

```
% ./openmx DIA8_DC.dat
```

The input file is for an O(N) calculation (1 MD step) of the diamond including 8 carbon atoms. The computational time is 120 seconds using a Xeon machine (2.6 GHz). Figure 15 shows the computational time and memory size to calculate a MD step of the carbon diamond as a function of number of atoms in the supercell. In fact, we see that the computational time and memory size are almost proportional to the number of atoms. The accuracy and efficiency of the DC method are controlled by a single parameter: 'orderN.HoppingRanges'.

- orderN.HoppingRanges

  The keyword 'orderN.HoppingRanges' defines the radius of a sphere which is centered on each atom. The physically truncated cluster for each atom is constructed by picking up atoms inside the sphere with the radius in the DC and O(N) Krylov subspace methods.

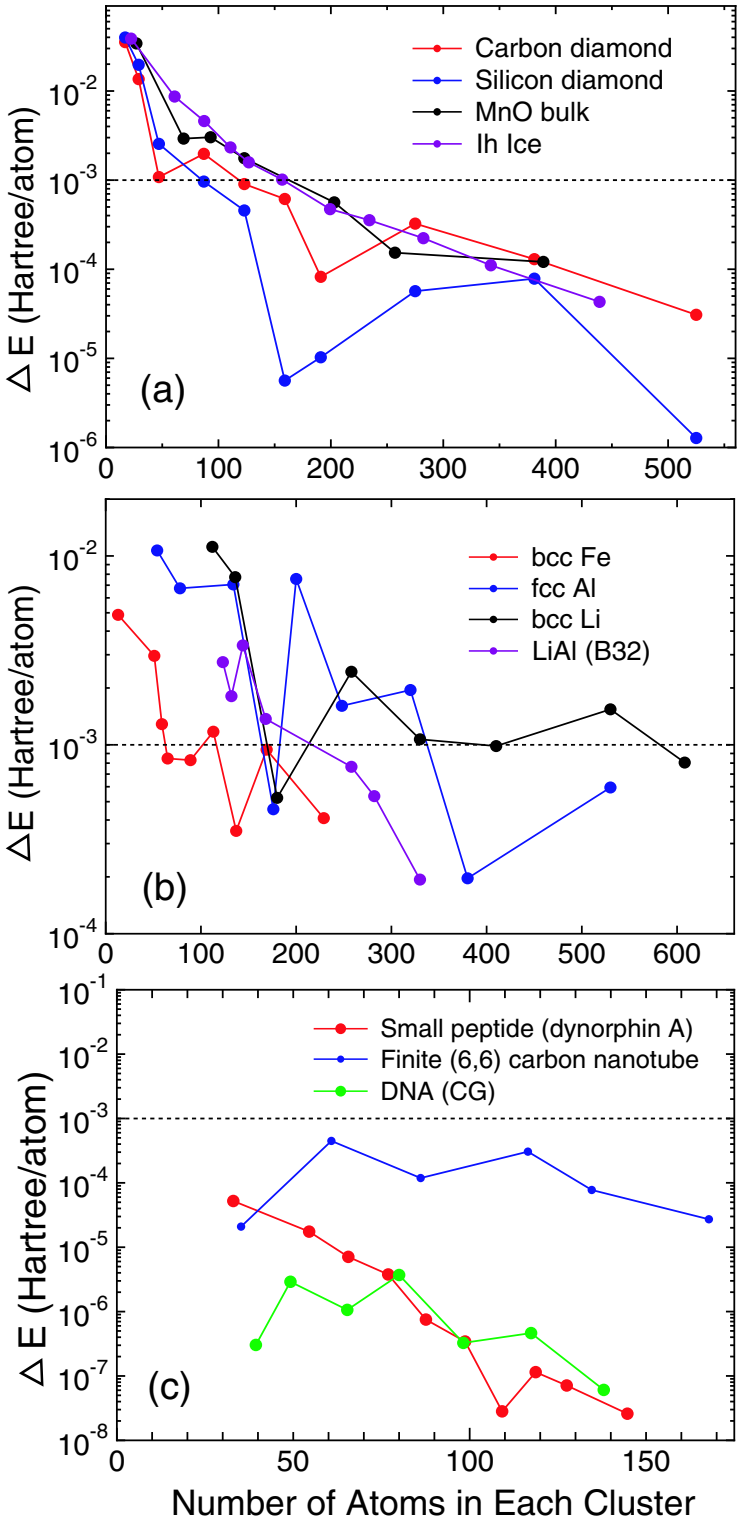

Figure 16: Error in the total energy of (a) bulks with a finite gap, (b) metals, and (c) molecular systems calculated by the divide-conquer (DC) method as a function of the number of atoms in each cluster. The dotted horizontal line indicates 'milli-Hartree' accuracy.

If the number of atoms in the systems is N, N small eigenvalue problems for the N physically truncated clusters are solved, and then the total density of states (DOS) is constructed as the sum of the projected DOS of each physically truncated cluster. Although the appropriate value for 'orderN.HoppingRanges' depends on systems, for molecular systems the following values are recommended as a trade-off between the computational accuracy and efficiency:

```
orderN.HoppingRanges      6.0 - 7.0
```

Table 2 shows the comparison in the total energy between the exact diagonalization and the DC method for a C_{60} molecule and small peptide molecules (valorphin [63]), and DNA consisting of cytosines and guanines. We find that errors in the total energy calculated by the DC method are about a few mHartree in the system size. Also, it can be estimated that the DC method is faster than the conventional diagonalization when the number of atoms is larger than 500 atoms, while the crossing point between the conventional diagonalization and the DC method with respect to computational time depends on systems and the number of processors in the parallel calculation.

To see an overall tendency in the convergence properties of total energy with respect to the size of truncated cluster, the error in the total energy, compared to the exact diagonalization, is shown as a function of the number of atoms in each cluster for (a) bulks with a finite gap, (b) metals, and (c) molecular systems in Fig. 16. We see that the error decreases almost exponentially for the bulks with a finite gap and molecular systems, while the convergence speed is slower for metals.

20.2 Krylov subspace method

The DC method is robust and accurate for a wide variety of systems. However, the size of truncated clusters to obtain an accurate result tends to be large for metallic systems as shown in Fig. 16. A way of reducing the computational efforts is to map the original vector space defined by the truncated cluster into a Krylov subspace of which dimension is smaller than that of the original space [30]. The Krylov subspace method is available by

```
scf.EigenvalueSolver       Krylov
```

Basically, the accuracy and efficiency are controlled by the following two keywords:

```
orderN.HoppingRanges         6.0
orderN.KrylovH.order         400
```

The keyword 'orderN.HoppingRanges' defines the radius of a sphere centered on each atom in the same sense as that in the DC method. The dimension of the Krylov subspace of Hamiltonian in each truncated cluster is given by 'orderN.KrylovH.order'. Moreover, the Krylov subspace method can be precisely tuned by the following keywords:

- orderN.Exact.Inverse.S on| off, default=on

  In case of 'orderN.Exact.Inverse.S=on', the inverse of overlap matrix for each truncated cluster is exactly evaluated. Otherwise, see the next keyword 'orderN.KrylovS.order'.

- orderN.KrylovS.order 1200, default=orderN.KrylovH.order×4

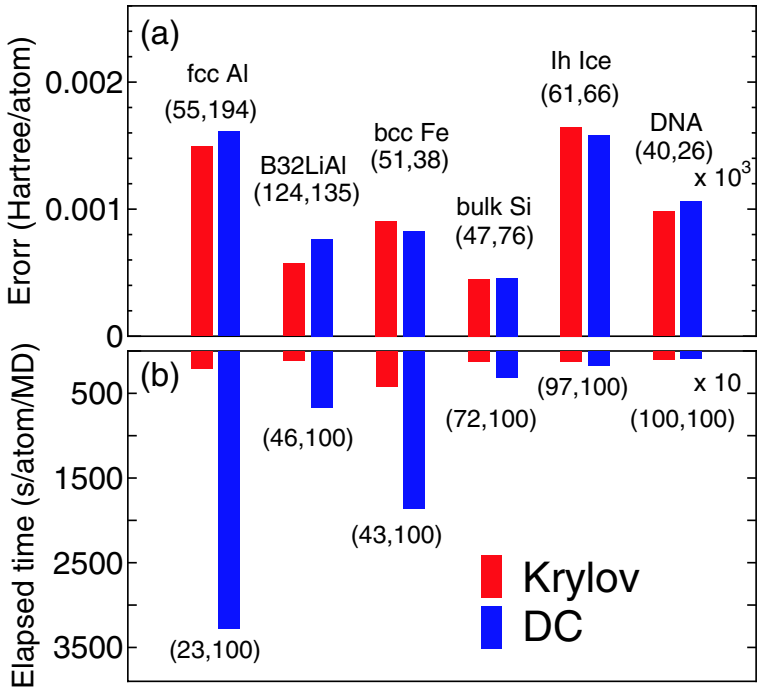

Figure 17: (a) absolute error, with respect to the band calculations, in the total energy (Hartree/atom) calculated by the Krylov subspace and DC methods for metals and finite gap systems, (b) computational time (s/atom/MD). For a substantial comparison, the calculations were performed using a single Xeon processor. The set of numbers in the parenthesis of (a) means the average number of atoms in the core and buffer regions. The set of numbers in the parenthesis of (b) means the percentage of the dimension of the subspaces relative to the total number of basis functions in the truncated cluster, respectively.

In case of 'orderN.Exact.Inverse.S=off', the inverse is approximated by a Krylov subspace method for the inverse, where the dimension of the Krylov subspace of overlap matrix in each truncated cluster is given by the keyword 'orderN.KrylovS.order'.

- orderN.Recalc.Buffer on| off, default=on

  In case of 'orderN.Recalc.Buffer=on', the buffer matrix is recalculated at every SCF step. Otherwise, the buffer matrix is calculated at the first SCF step, and fixed at the subsequent SCF steps.

- orderN.Expand.Core on| off, default=on

  In case of 'orderN.Expand.Core=on', the core region is defined by atoms within a sphere with radius of $1.2 \times r_{\rm min}$, where $r_{\rm min}$ is the distance between the central atom and the nearest atom. The core region defines a set of vectors used for the first step in the generation of the Krylov subspace for each truncated cluster. In case of 'orderN.Expand.Core=off', the central atom is considered as the core region. The default is 'on'.

It is better to switch on 'orderN.Exact.Inverse.S' and 'orderN.Expand.Core' as the covalency increases, while the opposite could becomes better in simple metallic systems. In Fig. 17 the absolute error in the

total energy calculated by the Krylov and DC methods are shown for a wide variety of materials. It is found that in comparison with the DC method, the Krylov subspace method is more efficient especially for metallic systems, and that the efficiency become comparable as the covalency and ionicity in the electronic structure increase.

It is also noted that the O(N) Krylov subspace method is well parallelized to realize large-scale calculations. The most efficient parallelization for the O(N) Krylov subspace method can be realized by using the same number of MPI processes as that of atoms together with OpenMP threads. Figure 18 shows that a system consisting of a hundred thousand atoms can be treated on a massively parallel computer [31, 32], where the diamond structure consisting of 131072 carbon atoms is considered as a benchmark system.

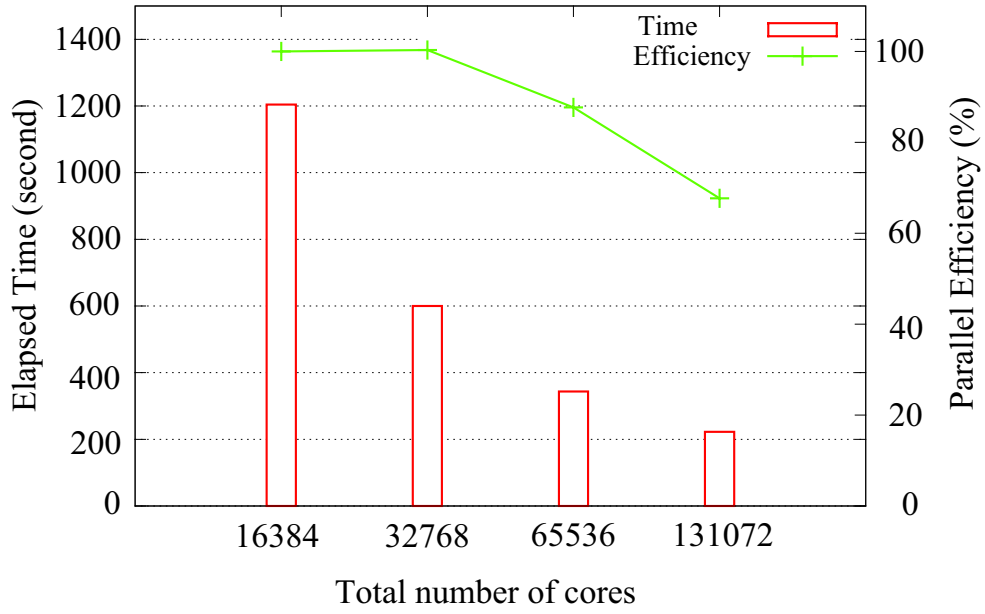

Figure 18: Parallel efficiency of the O(N) Krylov subspace method in the hybrid parallelization on the K-computer, where eight threads were used for all the cases. The diamond structure consisting of 131072 carbon atoms was considered as a benchmark system.

20.3 User definition of FNAN+SNAN

In all the O(N) methods supported by OpenMX Ver. 3.7, neighboring atoms in each truncated cluster are classified into two categories: *first* and *second* neighboring atoms. If the sum, $r_0 + r_{\rm N}$, of a cutoff radius, r_0, of basis functions allocated to the central atom and that, $r_{\rm N}$, of a neighboring atom is smaller than the distance between the two atoms, then the neighboring atom is regarded as a first neighboring atom, and the other atoms, which does not satisfy the criterion, in the truncated cluster are called the second neighboring atom. The second neighboring atoms are determined by a keyword 'orderN.HoppingRanges'. The numbers of the first and second neighboring atoms determined by the keyword are shown in the standard output as *FNAN* and *SNAN*, respectively. In addition to the use of the keyword 'orderN.HoppingRanges' for determining FNAN and SNAN, one can directory control the number, FNAN+SNAN, by the following keyword:

```
<orderN.FNAN+SNAN
  1  60
  2  65
  3  60
  4  50
  ..
  .
orderN.FNAN+SNAN>
```

In this specification, the number of row should be equivalent to that of atoms. The first column is a serial number corresponding to the serial number defined in the keyword 'Atoms.SpeciesAndCoordinates', and the second column is the number of FNAN+SNAN. Then, the first and second neighboring atoms in each truncated cluster are determined by taking account of the distance between the central atom and neighboring atoms so that the number of FNAN+SNAN can be equivalent to the value provided by the second column. FNAN+SNAN may largely change when unit vectors are changed, leading to sudden change of the total energy as a function of lattice constant. The user definition of FNAN+SNAN is useful to avoid such a case.

21 MPI parallelization

For large-scale calculations, parallel execution by MPI is supported for parallel machines with distributed memories.

21.1 O(N) calculation

When the O(N) method is employed, it is expected that one can obtain a good parallel efficiency because of the inherent algorithm. A typical MPI execution is as follows:

```
% mpirun -np 4 openmx DIA512_DC.dat > dia512_dc.std &
```

The input file 'DIA512_DC.dat' found in the directory 'work' is for the SCF calculation (1 MD) of the diamond including 512 carbon atoms using the divide-conquer (DC) method. The speed-up ratio in comparison of the elapsed time per MD step is shown in Fig. 19 (a) as a function of the number of processes on a CRAY-XC30 (2.6 GHz/Xeon processors). We see that the parallel efficiency decreases as the number of processors increase, and the speed-up ratio at 128 CPUs is about 84. The decreasing efficiency is due to the decrease of the number of atoms allocated to one processor. So, the weight of other unparallelized parts such as disk I/O becomes significant. Moreover, it should be noted that the efficiency is significantly reduced in non-uniform systems in terms of atomic species and geometrical structure due to disruption of the road balance, while an algorithm is implemented to avoid the disruption. See also the subsection 'Krylov subspace method' for further information on parallelization.

21.2 Cluster calculation

In the cluster calculation, a double parallelization is made for two loops: spin multiplicity and eigenstates, where the spin multiplicity is one for the spin-unpolarized and non-collinear calculation, and two for the spin-polarized calculation, respectively. The priority of parallelization is in order of spin multiplicity and eigenstates. OpenMX Ver. 3.7 employs ELPA [26] to solve the eigenvalue problem in the cluster calculation, which is a highly parallelized eigevalue solver. Figure 19 (b) shows the speed-up ratio as a function of processors in the elapsed time for a spin-polarized calculation of a single molecular magnet consisting of 148 atoms. The input file 'Mn12.dat' is found in the directory 'work'. It is found that the speed-up ratio is 11 and 17 using 32 and 64 processes, respectively.

21.3 Band calculation

In the band calculation, a triple parallelization is made for three loops: spin multiplicity, **k**-points, and eigenstates, where the spin multiplicity is one for the spin-unpolarized and non-collinear calculations, and two for the spin-polarized calculation, respectively. The priority of parallelization is in order of spin multiplicity, **k**-points, and eigenstates. In addition, when the number of processes used in the parallelization exceeds (spin multiplicity)×(the number of k-points), OpenMX uses an efficient way in which finding the Fermi level and calculating the density matrix are performed by just one diagonalization at each **k**-point. For the other cases, twice diagonalizations are performed at each **k**-point for saving the size of used memory in which the second diagonalization is performed to calculate

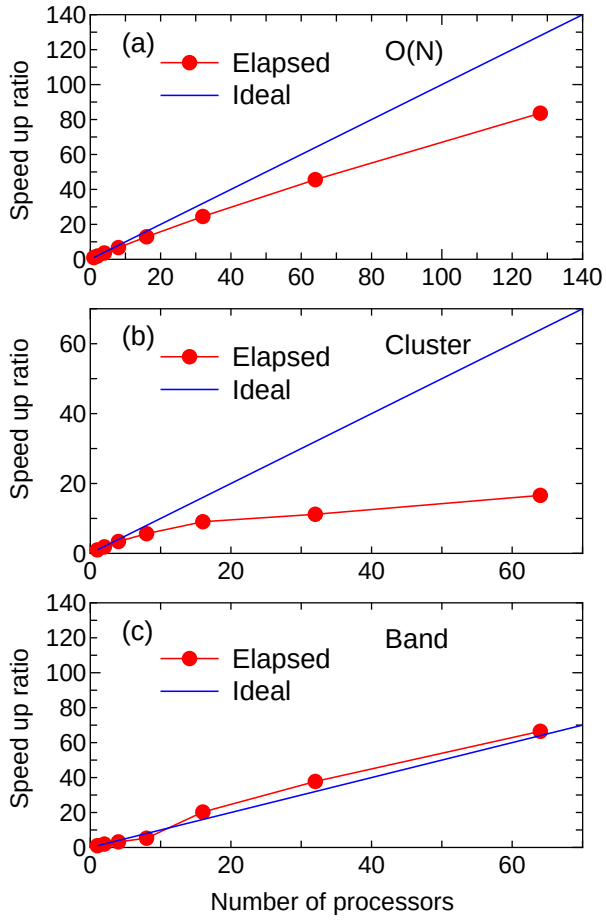

Figure 19: Speed-up ratio of the elapsed time per MD step in parallel calculations using MPI on a CRAY-XC30 (2.6 GHz Xeon processors) (a) for the carbon diamond including 512 atoms in the supercell by the DC method, (b) for a single molecular magnet consisting of 148 atoms by the cluster method, and (c) for the carbon diamond including 64 atoms in the super cell by the band method with 3×3×3 k-points. For comparison, a line which corresponds to the ideal speed-up ratio is also shown.

the density matrix after finding the Fermi level. In Fig. 19 (c) we see a good speed-up ratio as a function of processes in the elapsed time for a spin-unpolarized calculation of carbon diamond consisting of 64 carbon atoms with 3×3×3 k-points. The input file 'DIA64_Band.dat' is found in the directory 'work'. In this case the spin multiplicity is one, and the number of k-points used for the actual calculation is (3*3*3-1)/2+1=14, since the **k**-points in the half Brillouin zone is taken into account for the collinear calculation, and the Γ-point is included when all the numbers of **k**-points for **a**-, **b**-, and **c**-axes are odd. So it is found that the speed-up ratio exceeds the ideal one in the range of processes over 14, which means the algorithm in the parallelization is changed to the efficient scheme. As well as the cluster calculation, OpenMX Ver. 3.7 employs ELPA [26] to solve the eigenvalue problem in the band calculation, which is a highly parallelized eigevalue solver.

21.4 Fully three dimensional parallelization

OpenMX Ver. 3.7 supports a fully three dimensional parallelization for data distribution, while up to and including Ver. 3.6, the parallelization is made by a simple one-dimensional domain decomposition for **a**-axis of the unit cell for data distribution. Thus, users do not need to care about how unit cells are specified to achieve good road balancing. In OpenMX Ver. 3.7, a nearly equivalent parallel efficiency will be obtained without depending on choice of the unit cell vectors.

21.5 Maximum number of processors

Up to and including Ver. 3.6, the number of MPI processes that users can utilize for the parallel calculations is limited up to the number of atoms in the system. OpenMX Ver. 3.7 does no have the limitation. Even if the number of MPI processes exceeds the number of atoms, the MPI parallelization is efficiently performed. The functionality may be useful especially for a calculation where the number of **k**-points is much larger than the number of atoms in the system.

22 OpenMP/MPI hybrid parallelization

The OpenMP/MPI hybrid parallel execution can be performed by

```
% mpirun -np 32 openmx DIA512-1.dat -nt 4 > dia512-1.std &
```

where '-nt' means the number of threads in each process managed by MPI. If '-nt' is not specified, then the number of threads is set to 1, which corresponds to the flat MPI parallelization. Since the parallelization of OpenMX Ver. 3.7 is largely changed from OpenMX Ver. 3.6, we do not have enough data to validate the hybrid parallelization compared to the flat MPI with respect to efficiency of computation and memory usage. However, our preliminary benchmark calculations imply that the hybrid parallelization seems to be efficient as for memory usage, while the computational efficiency seems to be comparable to each other.

23 Large-scale calculations

23.1 Conventional scheme

Using the conventional diagonalization method, OpenMX Ver. 3.7 is capable of performing geometry optimization for systems consisting of 1000 atoms if several hundreds processor cores are available. To demonstrate the capability, one can perform 'runtestL2' as follows:

```
% mpirun -np 128 openmx -runtestL2 -nt 4
```

Then, OpenMX will run with 7 test files, and compare calculated results with the reference results which are stored in 'work/large2_example'. The following is a result of 'runtestL2' performed using 128 MPI processes and 2 OpenMP threads on CRAY-XC30.

1	large2_example/C1000.dat	Elapsed time(s)= 1731.83	diff Utot= 0.000000002838	diff Force= 0.000000007504
2	large2_example/Fe1000.dat	Elapsed time(s)=21731.24	diff Utot= 0.000000010856	diff Force= 0.000000000580
3	large2_example/GRA1024.dat	Elapsed time(s)= 2245.67	diff Utot= 0.000000002291	diff Force= 0.000000015333
4	large2_example/Ih-Ice1200.dat	Elapsed time(s)= 952.84	diff Utot= 0.000000000031	diff Force= 0.000000000213
5	large2_example/Pt500.dat	Elapsed time(s)= 6831.16	diff Utot= 0.000000002285	diff Force= 0.000000004010
6	large2_example/R-TiO2-1050.dat	Elapsed time(s)= 2259.97	diff Utot= 0.000000000106	diff Force= 0.000000001249
7	large2_example/Si1000.dat	Elapsed time(s)= 1655.25	diff Utot= 0.000000001615	diff Force= 0.000000005764

Total elapsed time (s) 37407.95

The quality of all the calculations is at a level of production run where double valence plus a single polarization functions are allocated to each atom as basis functions. Except for 'Pt500.dat', all the systems include more than 1000 atoms, where the last number of the file name implies the number of atoms for each system, and the elapsed time implies that geometry optimization for systems consisting of 1000 atoms is possible if several hundreds processor cores are available. The input files used for the calculations and the output files are found in the directory 'work/large2_example'. The following information is compiled from the output files.

No.	Input file	SCF steps	Elapsed time(s/SCF/spin)	Dimension
1	large2_example/C1000.dat	44	35	13000
2	large2_example/Fe1000.dat	384	30	13000
3	large2_example/GRA1024.dat	54	35	13312
4	large2_example/Ih-Ice1200.dat	41	18	9200
5	large2_example/Pt500.dat	171	35	12500
6	large2_example/R-TiO2-1050.dat	35	57	15750
7	large2_example/Si1000.dat	48	34	13000

The dimension of the Kohn-Sham Hamiltonian is of the order of 10000, and the elapsed time per SCF step is around 40 seconds for all the systems, implying that the difference in the total elapsed time mainly comes from the difference in the SCF iterations to achieve the SCF convergence of 10e-10 (Hartree) for the band energy.

23.2 Combination of the O(N) and conventional schemes

Although the O(N) methods can treat large-scale systems consisting of more than 1000 atoms, a serious problem is that information about wave functions is lost in the O(N) methods implemented in OpenMX. A simple way of obtaining wave functions and the corresponding eigenvalues for the large-scale systems is firstly to employ the O(N) methods to obtain a self-consistent charge density,

and then is to just once diagonalize using the conventional diagonalization method under the self-consistent charge density to obtain full wave functions. As an illustration of this procedure, we show a large-scale calculation of a multiply connected carbon nanotube (MCCN) consisting of 564 carbon atoms. First, the SCF calculation of a MCCN was performed using the O(N) Krylov subspace method and 16 CPU cores of a 2.6 GHz Xeon, where C5.0-s2p1 (basis function), 130 Ryd (scf.energycutoff), 1.0e-7 (scf.criterion), 6.5 Å (orderN.HoppingRanges), 'orderN.KrylovH.order=400', and RMM-DIISK (mixing scheme) were used. The input file is 'MCCN.dat' in the directory 'work'. Figure 20 shows the norm of residual charge density in Fourier space as a function of SCF steps. We see that 56 SCF steps is enough to obtain convergent charge density for the system, where the computational time was about seven minutes. After that, the following keywords were set in

```
scf.maxIter                1
scf.EigenvalueSolver     Band
scf.Kgrid               1 1 1
scf.restart                on
MO.fileout                 on
num.HOMOs                   2
num.LUMOs                   2
MO.Nkpoint                  1
<MO.kpoint
  0.0  0.0  0.0
MO.kpoint>
```

Then we calculated the same system in order to obtain wave functions using 16 CPU cores of a 2.6 GHz Xeon machine, where the computational time was about 2 minutes. Figure 21 shows isosurface maps of the HOMO and LUMO (Γ-point) of MCCN calculated by the above procedure. Although the difference between the O(N) method and the conventional diagonalization scheme in the computational time is not significant in this example, the procedure will be useful for larger system including more than several thousands atoms.

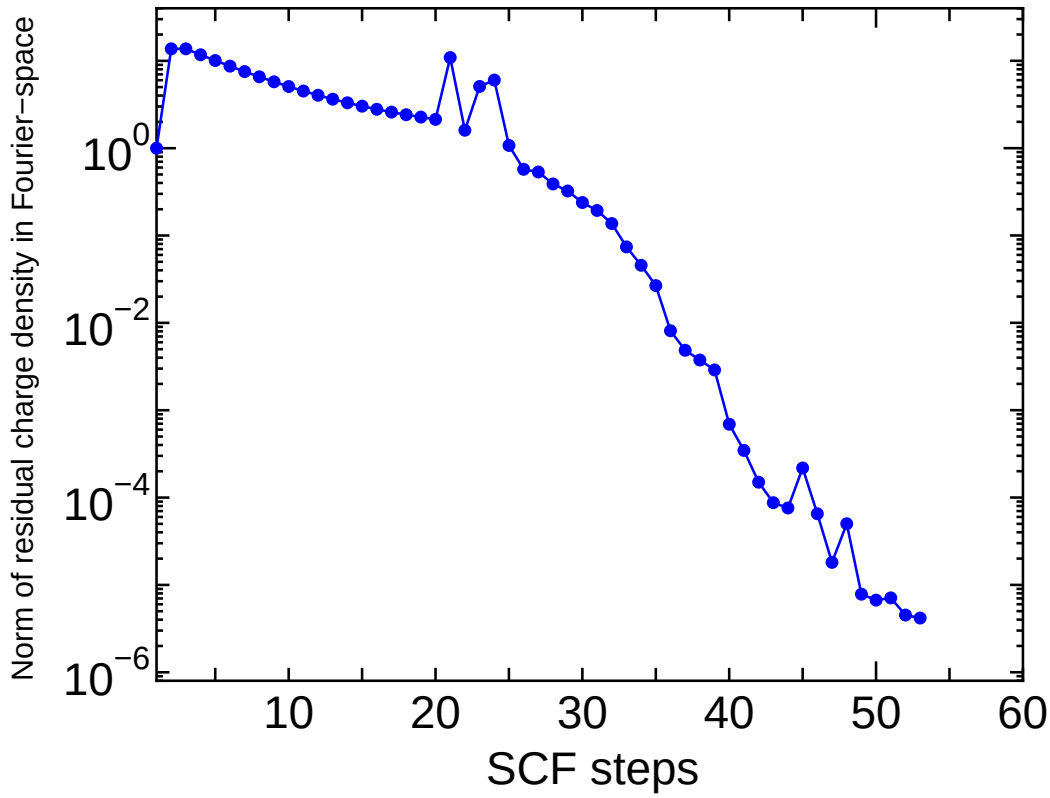

Figure 20: Norm of residual charge density in Fourier space as a function of SCF steps for a multiply connected carbon nanotube (MCCN) consisting of 564 carbon atoms. The input file is 'MCCN.dat' in the directory 'work'.

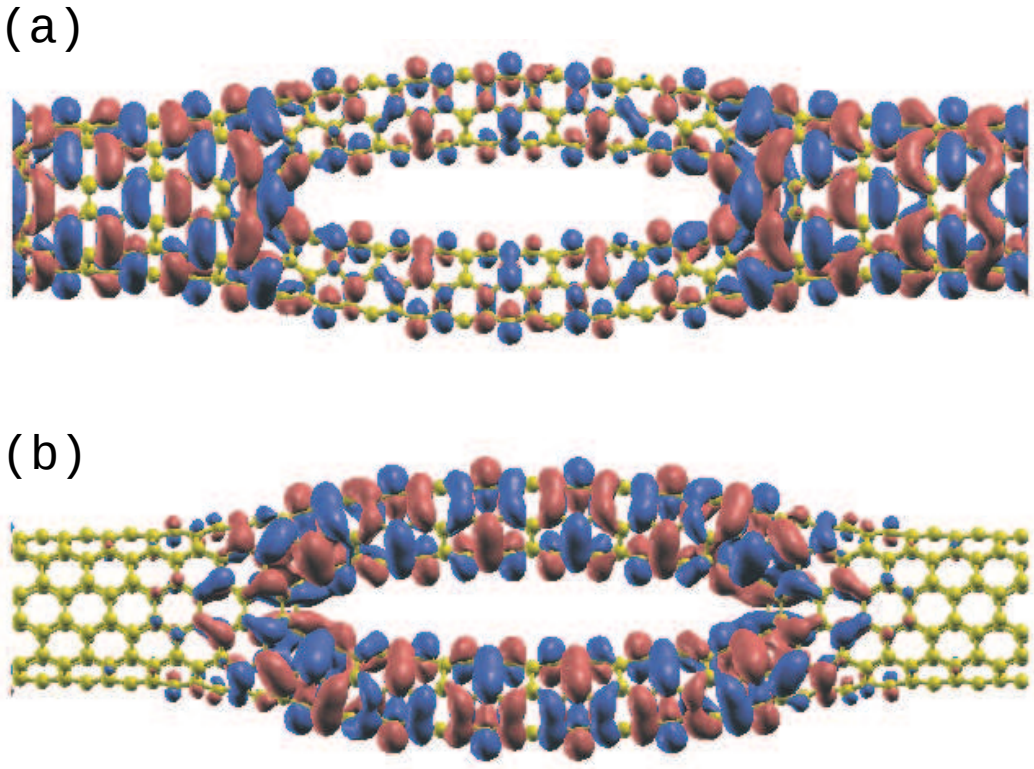

Figure 21: Isosurface map of (a) the highest occupied molecular orbital (HOMO) and (b) the lowest unoccupied molecular orbital (LUMO) of a multiply connected carbon nanotube (MCCN) consisting of 564 carbon atoms, where |0.005| was used as an isovalue of the molecular orbital.

24 Electric field

It is possible to apply a uniform external electric field given by a sawtooth waveform during the SCF calculation and the geometry optimization. For example, when an electric field of 1.0 GV/m (10^9 V/m) is applied along the **a**-axis, please specify the keyword 'scf.Electric.Field' in your input file as follows:

```
scf.Electric.Field   1.0 0.0 0.0   # default=0.0 0.0 0.0 (GV/m)
```

The sign of electric field is taken as that applied to electrons. If the uniform external electric field is applied to a periodic bulk system without vacuum region, discontinuities of the potential are introduced, which may cause numerical instability. On the other hand, for molecular systems, the discontinuities are located in the vacuum region, indicating that numerical instability may not be induced.

As an illustration of the electric field, changes of total charge in a nitrobenzene molecule induced by the electric field are shown in Fig. 22. We can see that a large charge transfer takes place among oxygens in -NO_2, para-carbon atom, and para-hydrogen atom. The input file is 'Nitro_Benzene.dat' in the directory 'work'. See also Section 'Analysis of difference in two Gaussian cube files' as for the difference charge maps shown in Fig. 22.

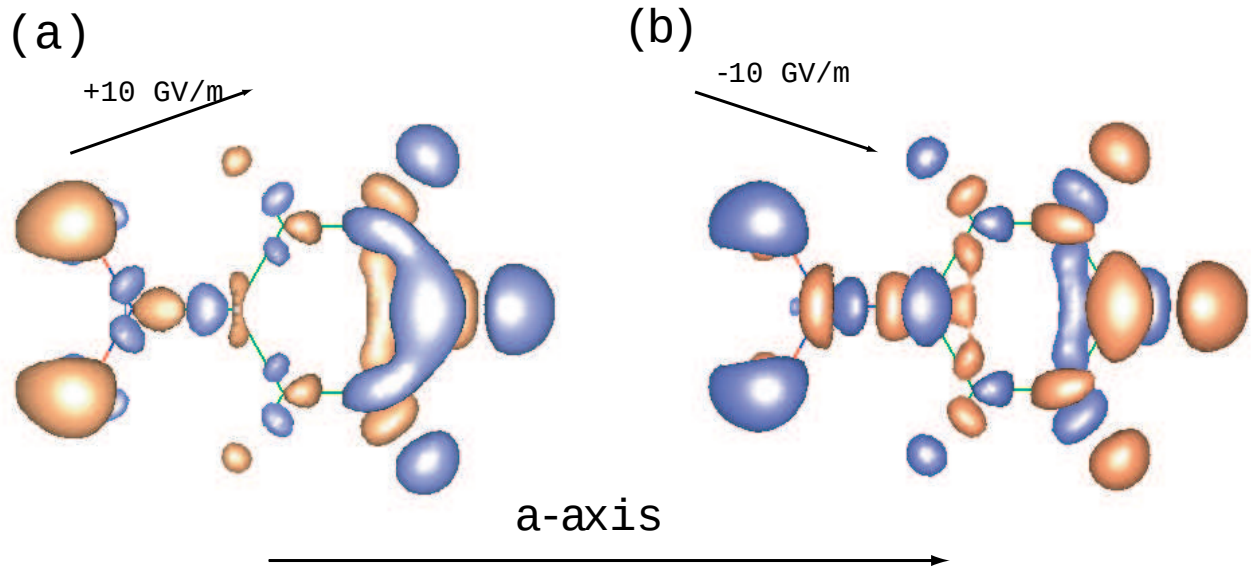

Figure 22: Difference in the total charge density of a nitrobenzene molecule between the zero-bias voltage and (a) 10 GV/m, and (b) -10 GV/m of applied bias along the **a**-axis, where orange and blue colors mean the increase and decrease of charge density. Tilted arrows depict the slope of applied electric fields. The input file is 'Nitro_Benzene.dat' in the directory 'work'.

25 Charge doping

The following keyword is available for both the electron and hole dopings.

```
scf.system.charge      1.0      # default=0.0
```

The plus and minus signs correspond to hole and electron dopings, respectively. A partial charge doping is also possible. The excess charge given by the keyword 'scf.system.charge' is compensated by a uniform background opposite charge, since FFT is used to solve Poisson's equation in OpenMX. Therefore, if you compare the total energy between different charged states, a careful treatment is required, because additional electrostatic interactions induced by the background charge are included in the total energy. As an example, we show spin densities of hole doped, neutral, and electron doped (5,5) carbon nanotubes with a finite length of 14 Å in Fig. 23. The neutral and electron doped nanotubes possess the total spin moment of 1.0 and 2.2, while the total spin moment almost disappears in the hole doped nanotube. We can see that the spin polarization takes place at the edges of the neutral and electron doped nanotubes due to dangling bonds of edge regions.

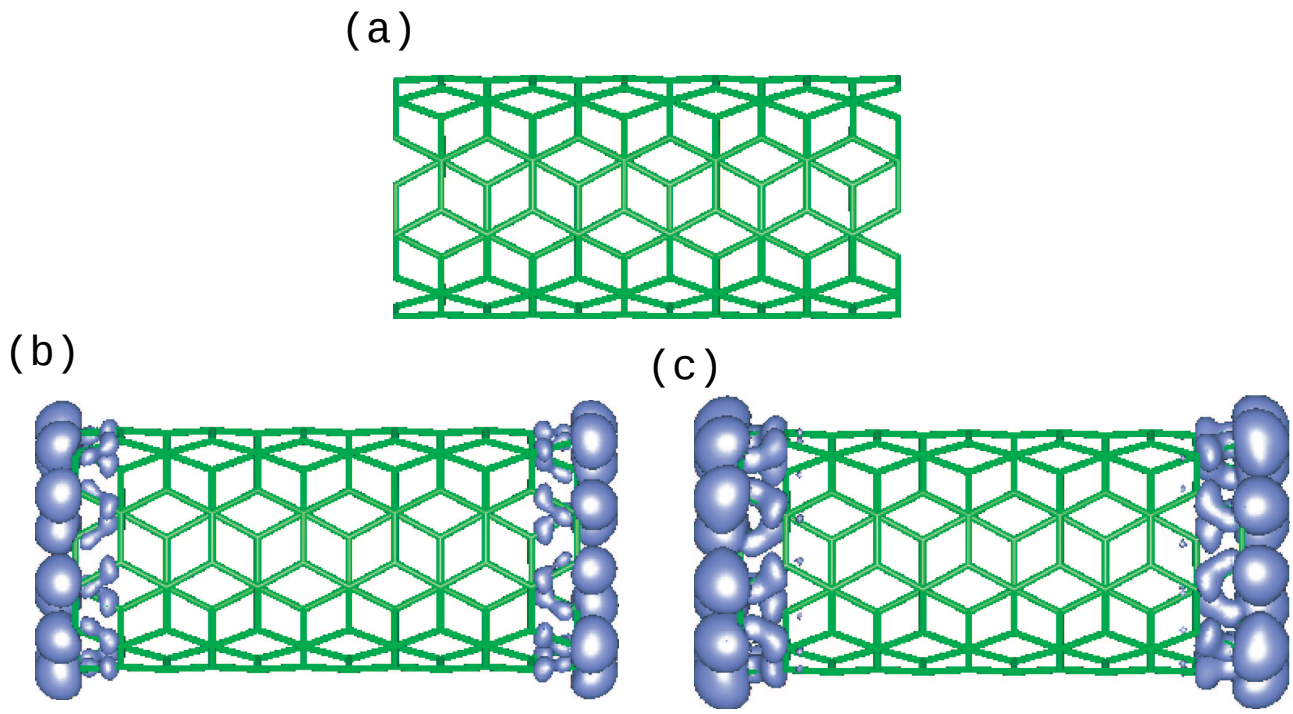

Figure 23: Spin densities of (a) four hole doped, (b) neutral, and (c) four electron doped (5,5) carbon nanotubes with a finite length of 14 Å. The input file is 'Doped_NT.dat' in the directory 'work'.

26 Virtual atom with fractional nuclear charge

It is possible to treat a virtual atom with fractional nuclear charge by using a pseudopotential with the corresponding fractional nuclear charge. The pseudopotential for the virtual atom can be generated by ADPACK. The relevant keywords in ADPACK are given by

```
AtomSpecies             6.2
total.electron          6.2
valence.electron        4.2
<occupied.electrons
 1    2.0
 2    2.0   2.2
occupied.electrons>
```

The above example is for a virtual atom on the way of carbon and nitrogen atoms. Also, it is noted that basis functions for the pseudopotential of the virtual atom must be generated for the virtual atom with the same fractional nuclear charge, since the atomic charge density stored in *.pao is used to make the neutral atom potential.

As an illustration, the DOS of $C_{7.8}N_{0.2}$ calculated using the method is shown in Fig. 24. The input file is 'DIA8-VA.dat' which can be found in the directory, work. In the calculation, one of eight carbon atoms in the unit cell was replaced by a virtual atom with an effective nuclear charge of 4.2, which corresponds to a stoichiometric compound of $C_{7.8}N_{0.2}$.

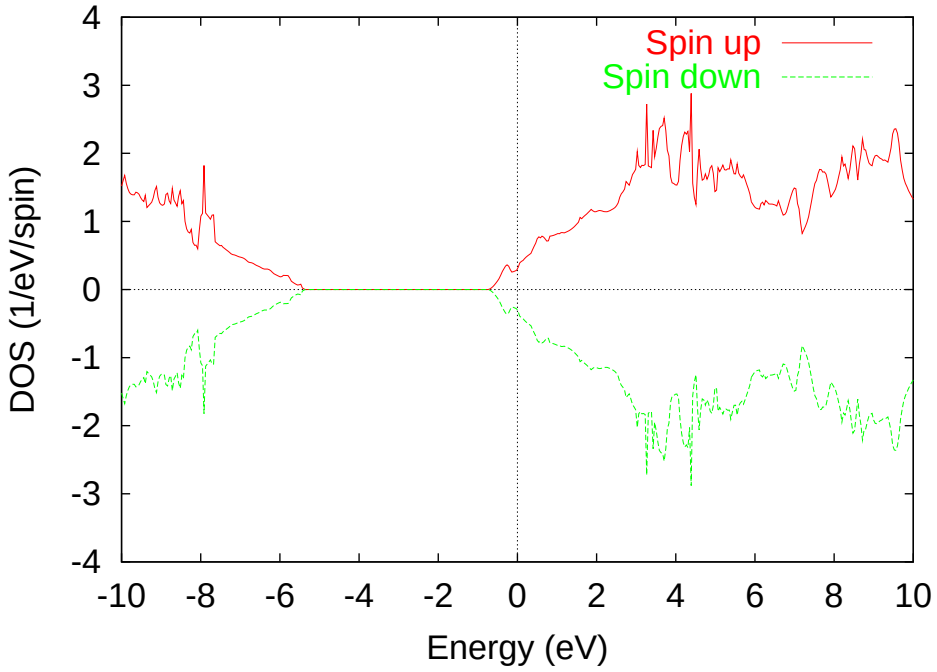

Figure 24: Density of states (DOS) of $C_{7.8}N_{0.2}$ calculated with a pseudopotential of the virtual atom. The input file used for the calculation is 'DIA8-VA.dat' which can be found in the directory 'work'.

27 LCAO coefficients

It is possible to analyze LCAO coefficients in both the cluster and band calculations. In the cluster calculation, if a keyword 'level.of.fileout'' is set in 2, the LCAO coefficients are added into a file '*.out'. As an example, LCAO coefficients of 'Methane.dat' discussed in the Section 'Test calculation' are shown below:

```
************************************************************
************************************************************
  Eigenvalues (Hartree) and Eigenvectors for SCF KS-eq.
************************************************************
************************************************************

   Chemical Potential (Hartree) =   0.00000000000000
   HOMO =  4

   LCAO coefficients for up (U) and down (D) spins


                          1 (U)     2 (U)     3 (U)     4 (U)     5 (U)     6 (U)
                        -0.69899  -0.41525  -0.41525  -0.41524   0.21215   0.21215

   1   C 0 s             0.69137  -0.00000   0.00000   0.00000   0.00000   0.00000
         0 px            0.00000  -0.10055   0.63544   0.00033  -0.68649  -1.00467
         0 py            0.00000   0.00028  -0.00029   0.64331   0.00000  -0.00001
         0 pz           -0.00000   0.63544   0.10055  -0.00023  -1.00467   0.68649
   2   H 0 s             0.12870   0.05604  -0.35474  -0.25425  -0.59781  -0.87489
   3   H 0 s             0.12870  -0.35475  -0.05627   0.25420  -0.87488   0.59781
   4   H 0 s             0.12870   0.35497   0.05604   0.25393   0.87488  -0.59781
   5   H 0 s             0.12870  -0.05626   0.35497  -0.25388   0.59781   0.87488

                          7 (U)     8 (U)
                        0.21223   0.24739

   1   C 0 s             0.00000   1.90847
         0 px            0.00000   0.00000
         0 py           -1.21683  -0.00000
         0 pz           -0.00000   0.00000
   2   H 0 s            -0.74926  -0.76083
   ......
   ....
```

In bulk calculations, if a keyword 'MO.fileout' is set in ON, LCAO coefficients at k-points which are specified by the keyword 'MO.kpoint' are output into a file '*.out'. For cluster calculations, 'level.of.fileout' should be 2 in order to output LCAO coefficients. But, for band calculations, the relevant keyword is 'MO.fileout' rather than 'level.of.fileout'.

28 Charge analysis

Although it is a somewhat ambiguous issue to assign effective charge to each atom, OpenMX provides three schemes, Mulliken charge analysis, Voronoi charge analysis, and electro static potential (ESP) fitting method, to analyze the charge state of each atom.

28.1 Mulliken charge

The Mulliken charges are output in '*.out' by default as shown in Section 'Test calculation'. In addition to the Mulliken charge projected to each atom, you can also find a decomposed Mulliken charge to each orbital in '*.out'. The result stored in '*.out' for a methane molecule is as follows:

```
Decomposed Mulliken populations

  1    C          Up spin      Down spin     Sum           Diff
          multiple
s           0    0.598003833  0.598003833   1.196007667   0.000000000
 sum over m      0.598003833  0.598003833   1.196007667   0.000000000
 sum over m+mul  0.598003833  0.598003833   1.196007667   0.000000000
px          0    0.588514081  0.588514081   1.177028163   0.000000000
py          0    0.588703212  0.588703212   1.177406424   0.000000000
pz          0    0.588514081  0.588514081   1.177028162   0.000000000
 sum over m      1.765731375  1.765731375   3.531462749   0.000000000
 sum over m+mul  1.765731375  1.765731375   3.531462749   0.000000000

  2    H          Up spin      Down spin     Sum           Diff
          multiple
s           0    0.409066346  0.409066346   0.818132693   0.000000000
 sum over m      0.409066346  0.409066346   0.818132693   0.000000000
 sum over m+mul  0.409066346  0.409066346   0.818132693   0.000000000

  3    H          Up spin      Down spin     Sum           Diff
          multiple
s           0    0.409065912  0.409065912   0.818131824   0.000000000
 sum over m      0.409065912  0.409065912   0.818131824   0.000000000
 sum over m+mul  0.409065912  0.409065912   0.818131824   0.000000000

 .......
 ....
```

As you can see, the Mulliken charges are decomposed for all the orbitals. There are two kind of summations in this decomposition. One of summations is 'sum over m' which means a summation over magnetic quantum number for each multiple orbital. The second summation is 'sum over m+mul' which means a summation over both magnetic quantum number and orbital multiplicity, where "multiple" means a number to specify a radial wave function. Therefore, Mulliken charges are decomposed to contributions of all the orbitals.

28.2 Voronoi charge

Voronoi charge of each atom is calculated by integrating electron and spin densities in a Voronoi polyhedron. The Voronoi polyhedron is constructed from smeared surfaces which are defined by a Fuzzy cell partitioning method [49]. It should be noted that this Voronoi analysis gives often overestimated or underestimated charge, since Voronoi polyhedron is determined by only the structure without taking account of atomic radius. If you want to calculate Voronoi charge, specify the following keyword 'Voronoi.charge' in your input file:

```
Voronoi.charge      on       # on|off, default = off
```

In case of a methane molecule, the following Voronoi charges are output to '*.out'.

```
***********************************************************
***********************************************************
                    Voronoi charges
***********************************************************
***********************************************************

  Sum of Voronoi charges for up    =  3.999999031463
  Sum of Voronoi charges for down  =  3.999999031463
  Sum of Voronoi charges for total =  7.999998062926

  Total spin S by Voronoi charges  =  0.000000000000

                    Up spin      Down spin     Sum          Diff
      Atom=   1   1.137912511  1.137912511   2.275825021   0.000000000
      Atom=   2   0.715521700  0.715521700   1.431043399   0.000000000
      Atom=   3   0.715521486  0.715521486   1.431042973   0.000000000
      Atom=   4   0.715521776  0.715521776   1.431043552   0.000000000
      Atom=   5   0.715521559  0.715521559   1.431043118   0.000000000
```

Clearly, we see that carbon atom (Atom=1) and hydrogen atoms (Atom=2-5) tend to possess less charge and much charge, respectively, from a chemical sense. However, the Voronoi analysis could be a useful and complementary information for a bulk system with a closed pack structure.

28.3 Electro-static potential fitting

For small molecular systems, the electro-static potential (ESP) fitting method [65, 66, 67] is useful to determine an effective charge of each atom, while the ESP fitting method cannot be applied for large molecules and bulk systems, since there are not enough sampling points for atoms far from surface areas in the ESP fitting method. In the ESP fitting method an effective point net charge on each atom is determined by a least square method with constraints so that the sum of the electro-static potential by effective point charges can reproduce electro-static potential calculated by the DFT calculation as much as possible. The ESP fitting charge is calculated by the following two steps:

(1) SCF calculation

After finishing a usual SCF calculation, you have two output files:

```
*.out
*.vhart.cube
```

There is no additional keyword to generate the two files which are default output files by the SCF calculation, while the keyword 'level.of.stdout' should be 1 or 2.

(2) ESP fitting charge

Let us compile a program code for calculating the ESP fitting charge. Move the directory 'source' and then compile as follows:

```
% make esp
```

When the compilation is completed normally, then you can find an executable file 'esp' in the directory 'work'. The ESP fitting charge can be calculated from two files '*.out' and '*.vhart.cube' using the program 'esp'. For example, you can calculate them for a methane molecule shown in the Section 'Input file' as follows:

```
% ./esp met -c 0 -s 1.4 2.0
```

Then, it is enough to specify the file name without the file extension, however, two files 'met.out' and 'met.vhart.cube' must exist in the directory 'work'. The options '-c' and '-s' are key parameters to specify a constraint and scale factors. You can find the following statement in the header part of a source code 'esp.c':

```
-c      constraint parameter
        '-c 0' means charge conservation
        '-c 1' means charge and dipole moment conservation
-s      scale factors for vdw radius
        '-s 1.4 2.0' means that 1.4 and 2.0 are 1st and 2nd scale factors
```

In the ESP fitting method, we support two constraints, charge conservation and, charge and dipole moment conservation. Although the latter can reproduce charge and dipole moment calculated by the DFT calculation, it seems that the introduction of the dipole moment conservation gives often physically unacceptable point charges especially for a relatively large molecule. Thus, we would like to recommend the former constraint. The sampling points are given by the grids in real space between two shells of the first and second scale factors times van der Waals radii [68]. In the above example, 1.4 and 2.0 correspond to the first and second scale factors. The calculated result appears in the standard output (your display) as follows:

```
 % ./esp met -c 0 -s 1.4 2.0

*********************************************************************
*********************************************************************
 esp: effective charges by a ESP fitting method
 Copyright (C), 2004, Taisuke Ozaki
 This is free software, and you are welcome to
 redistribute it under the constitution of the GNU-GPL.
*********************************************************************
*********************************************************************

Constraint: charge
Scale factors for vdw radius    1.40000    2.00000
Number of grids in a van der Waals shell = 28464
Volume per grid =    0.0235870615 (Bohr^3)
Success

  Atom=   1  Fitting Effective Charge= -0.93558216739
  Atom=   2  Fitting Effective Charge=  0.23389552572
  Atom=   3  Fitting Effective Charge=  0.23389569182
  Atom=   4  Fitting Effective Charge=  0.23389535126
  Atom=   5  Fitting Effective Charge=  0.23389559858

  Magnitude of dipole moment    0.0000015089 (Debye)
  Component x y z     0.0000003114   -0.0000002455   -0.0000014558
RMS between the given ESP and fitting charges (Hartree/Bohr^3)= 0.096515449505
```

29 Non-collinear DFT

A fully unconstrained non-collinear density functional theory (DFT) is supported including the spin-orbit coupling (SOC) [6, 7, 8, 9, 13]. When the non-collinear DFT is performed, the following option for the keyword 'scf.SpinPolarization' is available.

```
scf.SpinPolarization        NC        # On|Off|NC
```

If the option 'NC' is specified, wave functions are expressed by a two component spinor. An initial spin orientation of each site is given by

```
<Atoms.SpeciesAndCoordinates           # Unit=Ang
  1  Mn    0.00000   0.00000   0.00000   8.0  5.0  45.0 0.0 45.0 0.0  1 on
  2  O     1.70000   0.00000   0.00000   3.0  3.0  45.0 0.0 45.0 0.0  1 on
Atoms.SpeciesAndCoordinates>


 1:    sequential serial number
 2:    species name
 3:    x-coordinate
 4:    y-coordinate
 5:    z-coordinate
 6:    initial occupation for up spin
 7:    initial occupation for down spin
 8:    Euler angle, theta, of the magnetic field for spin magnetic moment
 9:    Euler angle, phi, of the magnetic field for spin magnetic moment
       Also, the 8th and 9th are used to generate the initial non-collinear
       spin charge distribution
10:    the Euler angle, theta, of the magnetic field for orbital magnetic moment
11:    the Euler angle, phi, of the magnetic field for orbital magnetic moment
12:    switch for the constraint schemes specified by the keywords
       'scf.Constraint.NC.Spin', 'scf.NC.Zeeman.Orbital' and 'scf.NC.Zeeman.Orbital'.
       '1' means that the constraint is applied, and '0' no constraint.
13:    switch for enhancement of orbital polarization in the LDA+U method,
       'on' means that the enhancement is made, 'off' no enhancement.
```

The initial Euler angles, θ and ϕ, for orientation of the spin and orbital magnetic moment are given by the 8th and 9th columns, and 10th and 11th columns, respectively. The 12th column is a switch for a constraint scheme that a constraint (penalty or Zeeman) functional to the spin and orbital orientation is added on each site, where '1' means that the constraint functional is added, and '0' means no constraint. For the details of the constraint DFT for the spin orientation, see the Section 'Constraint DFT for non-collinear spin orientation'. The final 13th column is a switch for enhancement of orbital polarization in the LDA+U method, 'on' means that the enhancement is made, 'off' no enhancement. Figure 25 shows the spin orientation in a MnO molecule calculated by the non-collinear DFT. You can follow the calculation using an input file 'Mol_MnO_NC.dat' in the directory 'work'. To visualize the spin orientation in real space, two files are generated:

```
*.nc.xsf
*.ncsden.xsf
```

where * means 'System.Name' you specified. Two files '*.nc.xsf' and '*.ncsden.xsf' store a projected spin orientation to each atom by Mulliken analysis and the spin orientation on real space grids in a vector file format (XSF) supported by XCrySDen. Both the files can be visualized using 'Display→ Forces' in XCrySDen as shown in Fig. 25.

The spin moment and Euler angles of each atom, which are calculated by Mulliken analysis, are found in the file '*.out' as follows:

```
************************************************************
************************************************************
                  Mulliken populations
************************************************************
************************************************************

  Total spin moment (muB)   4.998503442   Angles (Deg) 44.991211196   0.000000000

                Up       Down       Sum       Diff        theta       phi
 1   Mn    9.59803   4.76902   14.36705   4.82901    44.99208    0.00000
 2    O    3.40122   3.23173    6.63295   0.16949    44.96650   -0.00000
```

Also it should be noted that it is difficult to achieve a self consistent field in the non-collinear DFT more than the collinear DFT calculation, since there are many minima, having almost comparable energy, in the spin orientation space, while the constraint DFT is useful for such a case.

In the non-collinear DFT, the inclusion of spin-orbit coupling is supported, while it is not supported for the collinear DFT. See also the Section 'Relativistic effects' for the issue.

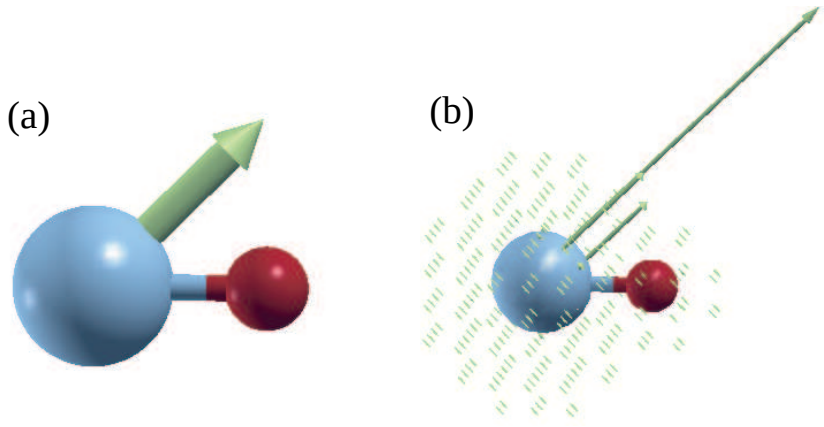

Figure 25: Spin orientation in (a) a projected form on each atom and (b) a real space representation of a MnO molecule calculated by the non-collinear DFT. The figures were visualized by 'Display→ Forces' in XCrySDen. The input file is 'Mol_MnO_NC.dat' in the directory 'work'.

30 Relativistic effects

Relativistic effects can be incorporated by fully relativistic and scalar relativistic pseudopotentials. In the fully relativistic treatment, the spin-orbit coupling is included in addition to kinematic relativistic effects (Darwin and mass velocity terms). On the other hand, the spin-orbit coupling is averaged in the scalar relativistic treatment. Although the scalar relativistic treatment can be incorporated in both the collinear and non-collinear DFT calculations, the fully relativistic treatment is supported for only the non-collinear DFT in OpenMX.

30.1 Fully relativistic

The fully relativistic effects including the spin-orbit coupling within the pseudopotential scheme can be included in the non-collinear DFT calculations [10, 19, 13], while the inclusion of the spin-orbit coupling is not supported in the collinear DFT calculation. The inclusion of fully relativistic effects is made by the following two steps:

(1) Making of j-dependent pseudopotentials

First, you are requested to generate j-dependent pseudopotentials using ADPACK. For your convenience, the j-dependent pseudopotentials are available for many elements in the database Ver. 2013 [89]. The details how to make the j-dependent pseudopotential are found in the manual of ADPACK.

(2) SCF calculation

If you specify j-dependent pseudopotentials in the specification of '<Definition.of.Atomic.Species', it is possible to include spin-orbit coupling by the following keyword 'scf.SpinOrbit.Coupling':

```
scf.SpinOrbit.Coupling      on          # On|Off, default=off
```

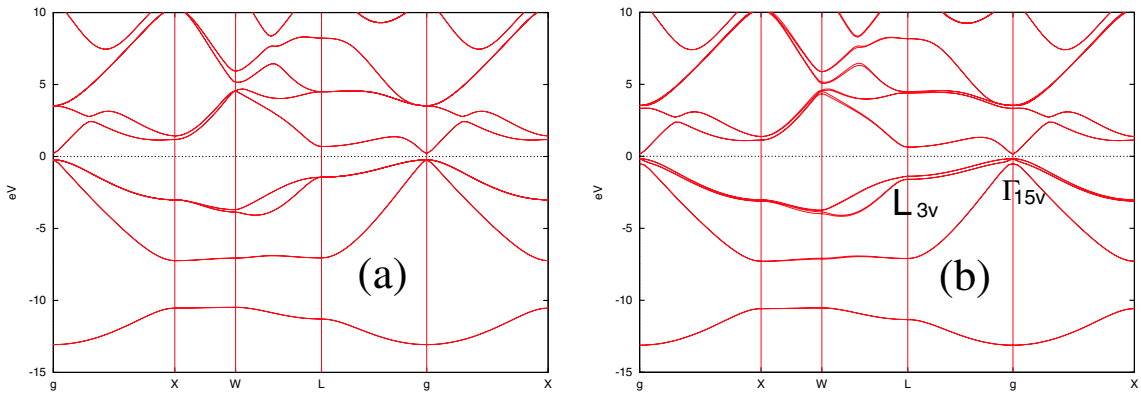

Figure 26: Band structures of a bulk GaAs calculated by the non-collinear DFT (a) without and (b) with the spin-orbit coupling. In these calculations, Ga7.0-s2p2d2 and As7.0-s2p2d2 were used as a basis set, and Ga_CA13.vps and As_CA13.vps were used for pseudopotentials, which are stored in the database Ver. 2013. For the exchange-correlation terms, LDA was used. We used 12× 12× 12 and 140 (Ryd) for scf.Kgrid and scf.energycutoff, respectively. Also the experimental value (5.65Å) was used for the lattice constant. The input file is 'GaAs.dat' in the directory 'work'.

Table 3: Calculated spin-orbit splittings (eV) at the Γ_{15v} and the L_{3v} of a bulk GaAs. The other theoretical values (LMTO: Ref. [69], PP: Ref. [70]) and experimental value (Ref.[71]) are also shown for comparison. The calculation conditions are given in the caption of Fig. 26 and the input file is 'GaAs.dat' in the directory 'work'.

Level	OpenMX	LMTO	PP	Expt.
Γ_{15v}	0.344	0.351	0.35	0.34
L_{3v}	0.213	0.213	0.22	

Then, the spin-orbit coupling can be self-consistently incorporated within the pseudopotential scheme rather than a perturbation scheme. Due to the spin-orbit coupling, α and β spin components in the two component spinor can directly interact. In order to determine the absolute spin orientation in the non-collinear DFT calculations, you have to include the spin-orbit coupling, otherwise the spin orientation is not uniquely determined in real space. As an illustration of spin-orbit splitting, we show band structures of a bulk GaAs calculated by the non-collinear DFT without and with spin-orbit coupling in Fig. 26, where the input file is 'GaAs.dat' in the directory 'work'. In Fig. 26(b) we can see that there are spin-orbit splittings in the band dispersion, while no spin-orbit splitting is observed in Fig. 26(a). The spin-orbit splittings at two **k**-points, Γ and L, are listed together with the other calculations and experimental values in Table 3. We see a good agreement in this table.

30.2 Scalar relativistic treatment

A simple way to incorporate a scalar relativistic treatment is to use scalar relativistic pseudopotentials which can be generated by ADPACK. The another way is to use fully relativistic j-dependent pseudopotentials and to switch off the keyword 'scf.SpinOrbit.Coupling' as follows:

```
scf.SpinOrbit.Coupling      off         # On|Off, default=off
```

Then, the j-dependent pseudopotentials are automatically averaged with a weight of j-degeneracy when they are read by OpenMX, which corresponds to scalar relativistic pseudopotentials. So, once j-dependent pseudopotentials are generated, you can utilize the pseudopotentials for both the fully and scalar relativistic treatments. Thus, we recommend that you make a fully relativistic j-dependent pseudopotential rather than a scalar relativistic pseudopotential, when relativistic effects are taken into account. In fact, the calculation in Fig. 26(a) was performed using the same pseudopotential as in Fig. 26(b) with 'scf.SpinOrbit.Coupling=off'.

31 Orbital magnetic moment

The orbital magnetic moment at each atomic site is calculated as default in the non-collinear DFT. Since the orbital magnetic moment appears as a manifestation of spin-orbit coupling (SOC), the calculated values become finite when the SOC is included [74, 75]. As an example, a non-collinear LDA+U (U=5 eV) calculation of iron monoxide bulk is illustrated using an input file 'FeO_NC.dat' in the directory 'work'. As for the LDA+U calculation, see the Section 'LDA+U'. The calculated orbital and spin magnetic moments at the Fe site are listed in Table 4. Also, you can find the orientation of the (decomposed) orbital moment in '*.out', where '*' means 'System.Name' as follows:

```
***********************************************************
***********************************************************
                    Orbital moments
***********************************************************
***********************************************************

  Total Orbital Moment (muB)   0.000001885   Angles  (Deg) 126.954120326  185.681623854

        Orbital moment (muB)   theta (Deg)  phi (Deg)
   1   Fe   0.76440           131.30039   51.57082
   2   Fe   0.76440            48.69972  231.57071
   3    O   0.00000            40.68612  210.48405
   4    O   0.00000            48.18387  222.72367


 Decomposed Orbital Moments

   1   Fe         Orbital Moment(muB)    Angles (Deg)
          multiple
s           0    0.000000000           90.0000    0.0000
 sum over m      0.000000000           90.0000    0.0000
s           1    0.000000000           90.0000    0.0000
 sum over m      0.000000000           90.0000    0.0000
px          0    0.000055764           42.7669  270.0000
py          0    0.000046795           28.9750  180.0000
pz          0    0.000044132           90.0000  239.0920
 sum over m      0.000120390           47.1503  239.0920
px          1    0.001838092           10.8128  -90.0000
py          1    0.001809013            3.5933  180.0000
pz          1    0.000362989           90.0000  251.7994
 sum over m      0.003683170           11.3678  251.7994
d3z^2-r^2   0    0.043435663           90.0000  224.2874
dx^2-y^2    0    0.066105902           24.3591  229.7056
dxy         0    0.361874370           80.4206   50.6465
dxz         0    0.397108491          144.2572  -12.7324
```

```
dyz          0    0.427070801          138.9995  100.0151
 sum over m       0.776513038          132.4577   51.6984
d3z^2-r^2    1    0.000144144           90.0000  196.4795
dx^2-y^2     1    0.000270422           31.2673  224.0799
dxy          1    0.003006770           85.5910   50.2117
dxz          1    0.002952926          139.3539   -4.1301
dyz          1    0.003222374          134.0513   95.9246
 sum over m       0.006795789          126.2536   52.1993
f5z^2-3r^2   0    0.001903274           90.0000   33.4663
f5xz^2-xr^2  0    0.005186342           14.5594  118.0868
f5yz^2-yr^2  0    0.005258572           17.3323  -35.0807
fzx^2-zy^2   0    0.005477755           29.3372  224.9067
fxyz         0    0.004851020           10.1407  249.0607
fx^3-3*xy^2  0    0.002029489           84.1842  -81.2087
f3yx^2-y^3   0    0.001611593           82.6686  176.3172
 sum over m       0.020307129            9.9551  249.3739
.....
...
```

As shown in Table 4, OpenMX gives a good agreement for both the spin and orbital magnetic moments of a series of 3*d*-transition metal oxides with other calculation results. However, it is noted that the absolute value of orbital magnetic moment seems to be significantly influenced by calculation conditions such as basis functions and on-site 'U' in the LDA+U method, while the spin magnetic moment is relatively insensitive to the calculation conditions, and that a rather rich basis set including polarization functions will be needed for convergent calculations of the orbital magnetic moment.

Table 4: Spin magnetic moment $M_s(\mu_B)$ and orbital magnetic moment $M_o(\mu_B)$ of transition metal oxides, MO (M=Mn, Fe, Co, Ni). In the LDA+U scheme [16], for the first d-orbital of M, the effective U of 3.0 (eV) for Mn, 5.0 (eV) for Fe, Co for 7.0 (eV), and Ni for 7.0 (eV) were used. For the others zero. The local spin moment was calculated by the Voronoi decomposition discussed in the Section 'Voronoi charge' rather than Mulliken charge, since the Mulliken analysis tends to give a larger spin moment in the use of multiple basis functions. The input files are 'MnO_NC.dat', 'FeO_NC.dat', 'CoO_NC.dat', and 'NiO_NC.dat' in the directory 'work'. The other theoretical value [50] and experimental value [50] are also shown for comparison.

	M_s		M_o		
Compound	OpenMX	Other calc.	OpenMX	Other calc.	Expt. in total
MnO	4.519	4.49	0.004	0.00	4.79,4.58
FeO	3.653	3.54	0.764	1.01	3.32
CoO	2.714	2.53	1.269	1.19	3.35,3.8
NiO	1.687	1.53	0.247	0.27	1.77,1.64,1.90

32 LDA+U

LDA+U methods with different definitions of the occupation number operator [16] are available for both the collinear and non-collinear calculations by the following keyword 'scf.Hubbard.U':

```
scf.Hubbard.U              on       # On|Off, default=off
```

It is noted that the *LDA*+U methods can be applied to not only LDA but also GGA. The occupation number operator is specified by the following keyword 'scf.Hubbard.Occupation':

```
scf.Hubbard.Occupation     dual     # onsite|full|dual, default=dual
```

Among three occupation number operators, only the *dual* operator satisfies a sum rule that the trace of occupation number matrix gives the total number of electrons which is the most primitive conserved quantity in a Hubbard model. For the details of the operators *onsite*, *full*, and *dual*, see Ref. [16]. The effective U-value in eV on each orbital of species defined by

```
<Definition.of.Atomic.Species
 Ni  Ni6.0S-s2p2d2     Ni_CA13S
 O   O5.0-s2p2d1       O_CA13
Definition.of.Atomic.Species>
```

is specified by

```
<Hubbard.U.values                  #  eV
 Ni  1s 0.0 2s 0.0 1p 0.0 2p 0.0 1d 4.0 2d 0.0
 O   1s 0.0 2s 0.0 1p 0.0 2p 0.0 1d 0.0
Hubbard.U.values>
```

The beginning of the description must be '<Hubbard.U.values', and the last of the description must be 'Hubbard.U.values>'. For all the basis orbitals, you have to give an effective U-value in eV in the above format. The '1s' and '2s' mean the first and second s-orbital, and the number behind '1s' is the effective U-value for the first s-orbital. The same rule is applied to p- and d-orbitals. As an example of the LDA+U calculation, the density of states for a nickel monoxide bulk is shown for cases with an effective U-value of 0 and 4 (eV) for d-orbitals of Ni in Fig. 27, where the input file is 'Crys-NiO.dat' in the directory 'work'. We see that the gap increases due to the introduction of a Hubbard term on the d-orbitals. The occupation number for each orbital is output to the file '*.out' in the same form as that of decomposed Mulliken populations which starts from the title 'Occupation Number in LDA+U' as follows:

```
***********************************************************
***********************************************************
       Occupation Number in LDA+U and Constraint DFT

    Eigenvalues and eigenvectors for a matrix consisting
           of occupation numbers on each site
***********************************************************
***********************************************************
```

```
  1   Ni

   spin= 0

Sum =  8.591857905308

                 1       2       3       4       5       6       7       8
Individual    -0.0024  0.0026  0.0026  0.0038  0.0051  0.0051  0.0888  0.0950

s          0   0.1671  0.0005 -0.0006  0.0040  0.0000  0.0005 -0.0124  0.0000
s          1  -0.9856 -0.0030  0.0039 -0.0227 -0.0000 -0.0072  0.0066  0.0000
px         0   0.0010  0.0004  0.0011 -0.0131  0.0004  0.0001 -0.0261 -0.0291
py         0   0.0010  0.0006 -0.0008 -0.0130  0.0000  0.0009 -0.0271 -0.0000
pz         0   0.0010 -0.0012 -0.0001 -0.0131 -0.0004  0.0001 -0.0261  0.0291
px         1   0.0067  0.0023  0.0066 -0.0792 -0.0161  0.0123  0.5594  0.7062
py         1   0.0068  0.0041 -0.0053 -0.0801 -0.0000 -0.0162  0.5797  0.0002
pz         1   0.0067 -0.0070 -0.0005 -0.0792  0.0161  0.0123  0.5594 -0.7063
d3z^2-r^2  0   0.0002 -0.0781 -0.0105  0.0002  0.0023  0.0014  0.0002  0.0108
dx^2-y^2   0   0.0004 -0.0105  0.0781  0.0004 -0.0013  0.0024  0.0003 -0.0062
dxy        0   0.0004 -0.0009 -0.0002  0.0246 -0.0421 -0.0251  0.0794 -0.0050
dxz        0  -0.0001  0.0008 -0.0010  0.0269  0.0000  0.0478  0.0795  0.0000
dyz        0   0.0004  0.0004  0.0008  0.0246  0.0420 -0.0251  0.0794  0.0050
d3z^2-r^2  1  -0.0023  0.9875  0.1327 -0.0033 -0.0262 -0.0159 -0.0001 -0.0069
dx^2-y^2   1  -0.0040  0.1326 -0.9875 -0.0056  0.0151 -0.0275 -0.0002  0.0040
dxy        1   0.0091  0.0233  0.0052 -0.5578  0.7055  0.4249 -0.0749  0.0157
dxz        1   0.0189 -0.0180  0.0233 -0.5964 -0.0003 -0.7958 -0.0748 -0.0000
dyz        1   0.0091 -0.0110 -0.0212 -0.5578 -0.7052  0.4255 -0.0749 -0.0157

                 9      10      11      12      13      14      15      16
Individual    0.0952  0.2456  0.9902  0.9974  0.9975  1.0060  1.0060  1.0137

s          0   0.0002  0.9859 -0.0036 -0.0001  0.0000 -0.0000  0.0000 -0.0000
.....
...
```

The eigenvalues of the occupation number matrix of each atomic site correspond to the occupation number to each local state given by the eigenvector. The LDA+U functional possesses multiple minima in the degree of freedom of the orbital occupation, leading to that the SCF calculation tends to be trapped to some local minimum. To find the ground state with an orbital polarization, a way of enhancing explicitly the orbital polarization is available by the following switch :

```
 For collinear cases

 <Atoms.SpeciesAndCoordinates           # Unit=AU
```

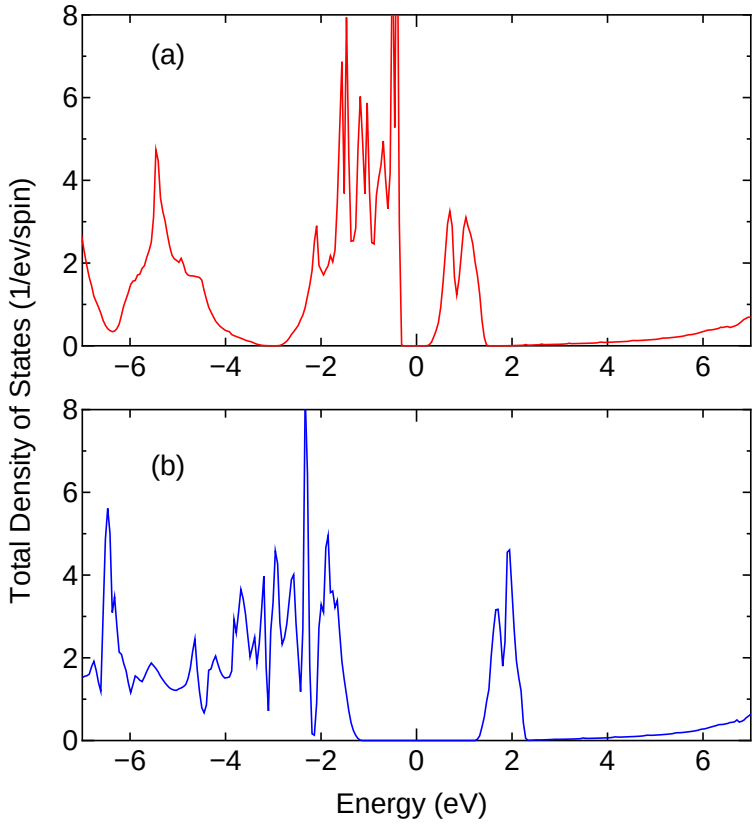

Figure 27: The total density of states for up-spin in NiO bulk calculated with (a) U=0 (eV) and (b) U=4 (eV) in the LDA+U method. The input file is 'Crys-NiO.dat' in the directory 'work'.

```
 1  Ni   0.0       0.0       0.0       10.0  6.0  on
 2  Ni   3.94955   3.94955   0.0        6.0 10.0  on
 3   O   3.94955   0.0       0.0        3.0  3.0  on
 4   O   3.94955   3.94955   3.94955    3.0  3.0  on
Atoms.SpeciesAndCoordinates>

For non-collinear cases

<Atoms.SpeciesAndCoordinates            # Unit=AU
 1  Ni   0.0       0.0       0.0       10.0  6.0  40.0 10.0 0 on
 2  Ni   3.94955   3.94955   0.0        6.0 10.0  40.0 10.0 0 on
 3   O   3.94955   0.0       0.0        3.0  3.0  10.0 40.0 0 on
 4   O   3.94955   3.94955   3.94955    3.0  3.0  10.0 40.0 0 on
Atoms.SpeciesAndCoordinates>
```

The specification of each column can be found in the section 'Non-collinear DFT'. Since the enhancement treatment for the orbital polarization is performed on each atom, you have to set the switch for all the atoms in the specification of atomic coordinates as given above. The enhancement for the atoms switched on is applied during the first few self-consistent (SC) steps, then no more enhancement

are required during the subsequent SC steps. It is also emphasized that the enhancement does not always give the ground state, and that it can work badly in some case. See Ref. [16] for the details.

33 Constraint DFT for non-collinear spin orientation

To calculate an electronic structure with an arbitrary spin orientation in the non-collinear DFT, OpenMX Ver. 3.7 provides a constraint functional which gives a penalty unless the difference between the calculated spin orientation and the initial one is zero [11]. The constraint DFT for the non-collinear spin orientation is available by the following keywords:

```
scf.Constraint.NC.Spin       on      # on|off, default=off
scf.Constraint.NC.Spin.v     0.5     # default=0.0(eV)
```

You can switch on the keyword 'scf.Constraint.NC.Spin' and give a magnitude by 'scf.Constraint.NC.Spin.v' which determines the strength of constraint, when the constraint for the spin orientation is introduced. The constraint is applied on each atom by specifying a switch as follows:

```
<Atoms.SpeciesAndCoordinates
   1    Cr    0.00000    0.00000    0.00000  7.0  5.0 -20.0 0.0  1   off
   2    Cr    0.00000    2.00000    0.00000  7.0  5.0  20.0 0.0  1   off
Atoms.SpeciesAndCoordinates>
```

The '1' in the 10th column means that the constraint is applied, and '0' no constraint. The method constrains only the spin orientation. Therefore, the magnitude of spin can vary. Also the constraint scheme is compatible with the LDA+U calculation explained in the Section 'LDA+U'. As an illustration of this method, the dependence of the total energy and magnetic moment in a chromium dimer on the relative angle between two local spins is shown in Fig. 28. You can trace the calculation using an input file 'Cr2_CNC.dat' in the directory 'work'.

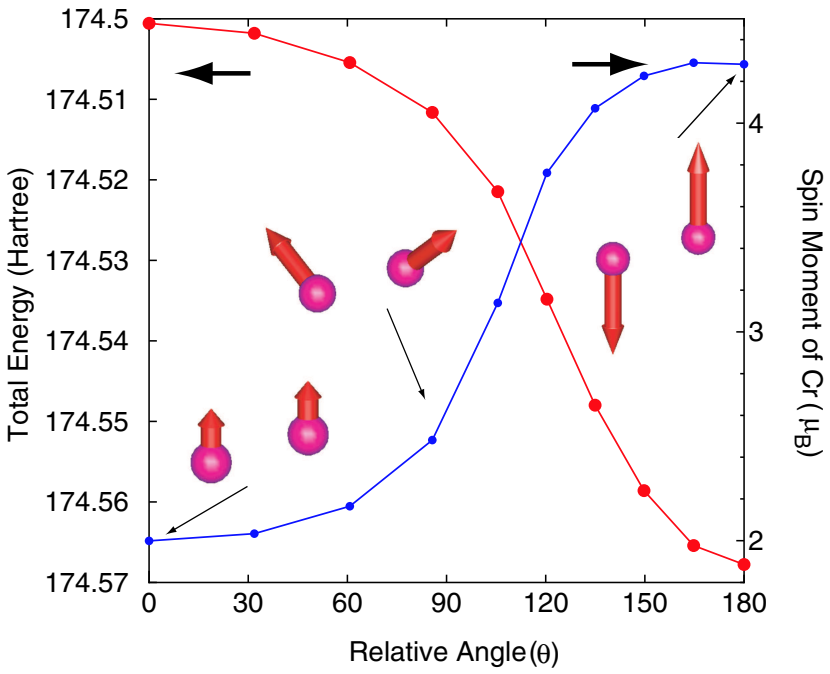

Figure 28: Total energy and magnetic moment of Cr atom for a chromium dimer of which bond length is 2.0 Å. The input file is 'Cr2_CNC.dat' in the directory 'work'.

34 Zeeman terms

It is possible to apply Zeeman terms to spin and orbital magnetic moments.

34.1 Zeeman term for spin magnetic moment

The Zeeman term for spin magnetic moment is available as an interaction with a uniform magnetic field by the following keywords:

```
scf.NC.Zeeman.Spin            on        # on|off, default=off
scf.NC.Mag.Field.Spin        100.0      # default=0.0(Tesla)
```

When you include the Zeeman term for spin magnetic moment, switch on the keyword 'scf.NC.Zeeman.Spin'. The magnitude of the uniform magnetic field can be specified by the keyword 'scf.NC.Mag.Field.Spin' in units of Tesla. Moreover, we extend the scheme as a constraint scheme in which the direction of the magnetic field can be different from each atomic site atom by atom. Then, the direction of magnetic field for spin magnetic moment can be controlled, for example, by the keyword 'Atoms.SpeciesAndCoordinates':

```
<Atoms.SpeciesAndCoordinates
 1  Sc  0.000  0.000  0.000   6.6 4.4  10.0 50.0  160.0 20.0  1  on
 2  Sc  2.000  0.000  0.000   6.6 4.4  80.0 50.0  160.0 20.0  1  on
Atoms.SpeciesAndCoordinates>
```

The 8th and 9th columns give the Euler angles, θ and ϕ, in order to specify the magnetic field for spin magnetic moment. The 12th column is a switch to the constraint. '1' means that the constraint is applied, and '0' no constraint. Since for each atomic site a different direction of the magnetic field can be applied, this scheme provides a way of studying non-collinear spin configuration. It is noted that the keyword 'scf.NC.Zeeman.Spin' and the keyword 'scf.Constraint.NC.Spin' are mutually exclusive. Therefore, when 'scf.NC.Zeeman.Spin' is 'on', the keyword 'scf.Constraint.NC.Spin' must be switched off as follows:

```
scf.Constraint.NC.Spin        off       # on|off, default=off
```

Although the Zeeman term and the constraint scheme for spin orientation can be regarded as ways for controlling the spin orientation, it is noted that the magnitude of spin magnetic moment by the Zeeman term tends to be enhanced unlike the constraint scheme.

34.2 Zeeman term for orbital magnetic moment

The Zeeman term for orbital magnetic moment is available as an interaction with a uniform magnetic field by the following keywords:

```
scf.NC.Zeeman.Orbital         on        # on|off, default=off
scf.NC.Mag.Field.Orbital     100.0      # default=0.0(Tesla)
```

When you include the Zeeman term for orbital magnetic moment, switch on the keyword 'scf.NC.Zeeman.Orbital'. The magnitude of the uniform magnetic field can be specified by the keyword 'scf.NC.Mag.Field.Orbital' in units of Tesla. Moreover, we extend the scheme as a constraint scheme in which the direction of the magnetic field can be different from each atomic site atom by atom. Then, the direction of magnetic field for orbital magnetic moment can be controlled, for example, by the keyword 'Atoms.SpeciesAndCoordinates':

```
<Atoms.SpeciesAndCoordinates
 1  Sc  0.000  0.000  0.000   6.6 4.4  10.0 50.0  160.0 20.0  1  on
 2  Sc  2.000  0.000  0.000   6.6 4.4  80.0 50.0  160.0 20.0  1  on
Atoms.SpeciesAndCoordinates>
```

The 10th and 11th columns give the Euler angles, theta and phi, in order to specify the magnetic field for orbital magnetic moment. The 12th column is a switch to the constraint. '1' means that the constraint is applied, and '0' no constraint. Since for each atomic site a different direction of the magnetic field can be applied, this scheme provides a way of studying non-collinear orbital configuration. Also, it is noted that the direction of magnetic field for orbital magnetic moment can be different from that for spin moment.

35 Macroscopic polarization by Berry's phase

The macroscopic electric polarization of a bulk system can be calculated based on the Berry phase formalism [12]. As an example, let us illustrate a calculation of a Born effective charge of Na in a NaCl bulk via the macroscopic polarization.

(1) SCF calculation

First, perform a conventional SCF calculation using an input file 'NaCl.dat' in the directory 'work'. Then, the following keyword 'HS.fileout' should be switched on

```
HS.fileout              on     # on|off, default=off
```

When the calculation is completed normally, then you can find an output file 'nacl.scfout' in the directory 'work'.

(2) Calculation of macroscopic polarization

The macroscopic polarization is calculated by a post-processing code 'polB' of which input data is 'nacl.scfout'. In the directory 'source', compile as follows:

```
% make polB
```

When the compile is completed normally, then you can find an executable file 'polB' in the directory 'work'. Then, move to the directory 'work', and perform as follows:

```
 % polB nacl.scfout
or
 % polB nacl.scfout < in > out
```

In the latter case, the file 'in' contains the following ingredients:

```
9 9 9
1 1 1
```

In the former case, you will be interactively asked from the program as follows:

```
*****************************************************************
*****************************************************************
 polB:
 code for calculating the electric polarization of bulk systems
 Copyright (C), 2006-2007, Fumiyuki Ishii and Taisuke Ozaki
 This is free software, and you are welcome to
 redistribute it under the constitution of the GNU-GPL.
*****************************************************************
*****************************************************************

Read the scfout file (nacl.scfout)
 Previous eigenvalue solver = Band
```

```
 atomnum                    = 2
 ChemP                      = -0.156250000000 (Hartree)
 E_Temp                     = 300.000000000000 (K)
 Total_SpinS                =  0.000000000000 (K)
 Spin treatment             = collinear spin-unpolarized

 r-space primitive vector (Bohr)
  tv1=  0.000000   5.319579   5.319579
  tv2=  5.319579   0.000000   5.319579
  tv3=  5.319579   5.319579   0.000000
 k-space primitive vector (Bohr^-1)
  rtv1= -0.590572   0.590572   0.590572
  rtv2=  0.590572  -0.590572   0.590572
  rtv3=  0.590572   0.590572  -0.590572

  Cell_Volume=301.065992 (Bohr^3)

 Specify the number of grids to discretize reciprocal a-, b-, and c-vectors
 (e.g 2 4 3)
   k1    0.00000    0.11111    0.22222    0.33333    0.44444  ...
   k2    0.00000    0.11111    0.22222    0.33333    0.44444  ...
   k3    0.00000    0.11111    0.22222    0.33333    0.44444  ...

 Specify the direction of polarization as reciprocal a-, b-, and c-vectors
 (e.g 0 0 1 ) 1 1 1
```

Then, the calculation will start like this:

```
calculating the polarization along the a-axis ....
The number of strings for Berry phase : AB mesh=81

  calculating the polarization along the a-axis ....   1/  82
  calculating the polarization along the a-axis ....   2/  82
  .....
  ...

*********************************************************
              Electric dipole  (Debye) : Berry phase
*********************************************************

 Absolute dipole moment      163.93373639

               Background        Core              Electron          Total

 Dx           -0.00000000       94.64718996       -0.00000338       94.64718658
```

```
 Dy          -0.00000000       94.64718996       -0.00000283       94.64718713
 Dz          -0.00000000       94.64718996       -0.00000317       94.64718679


************************************************************
             Electric polarization (muC/cm^2) : Berry phase
************************************************************

              Background        Core              Electron          Total

 Px          -0.00000000      707.66166752       -0.00002529      707.66164223
 Py          -0.00000000      707.66166752       -0.00002118      707.66164633
 Pz          -0.00000000      707.66166752       -0.00002371      707.66164381


Elapsed time = 77.772559 (s) for myid=  0
```

Since the Born effective charge $Z^*_{\alpha\beta}$ is defined by a tensor:

$$Z^*_{\alpha\beta} = \frac{V_c}{|e|}\frac{\Delta P_\alpha}{\Delta u_\beta}$$

where V_c is the volume of the unit cell, e the elementary charge, Δu_β displacement along β-coordinate, ΔP_α the change of macroscopic polarization along α-coordinate, therefore we will perform the above procedures (1) and (2) at least two or three times by varying the x, y, or z-coordinate of Na atom. Then, for example, we have along x-coordinates

```
Px = 94.39497736 (Debye/unit cell) at x= -0.05 (Ang)
Px = 94.64718658 (Debye/unit cell) at x=  0.0  (Ang)
Px = 94.89939513 (Debye/unit cell) at x=  0.05 (Ang)
```

Thus,

$$\begin{aligned} Z^*_{xx} &= \frac{(94.89939513 - 94.39497736)/(2.54174776)}{0.1/0.529177} \\ &= 1.050 \end{aligned}$$

Table 5: Calculated Born effective charge of Na in a NaCl bulk. The input file is 'NaCl.dat' in the directory 'work'. Another theoretical value (FD: Ref. [72]) and experimental value (Ref. [73]) are also shown for comparison.

	OpenMX	FD	Expt.
Z^*	1.05	1.09	1.12

Note that in the NaCl bulk the off-diagonal terms in the tensor of Born charge are zero, and $Z^*_{xx} = Z^*_{yy} = Z^*_{zz}$. In Table 5 we see that the calculated value is in good agreement with the other calculation [72] and an experimental result [73]. The calculation of macroscopic polarization is supported for both the collinear and non-collinear DFT. It is also noted that the code 'polB' has been parallelized for large-scale systems where the number of processors can exceed the number of atoms in the system.

36 Exchange coupling parameter

To analyze an effective interaction between spins located on two atomic sites, an exchange coupling parameter between two localized spins can be evaluated based on Green's function method [14, 15]. In OpenMX Ver. 3.7 the evaluation is supported for only the collinear calculations of cluster and bulk systems. Also the MPI parallelization of 'jx' is supported only when the eigenvalue solver is 'band', while the parallelization is not supported for 'cluster'. If you want to calculate the exchange coupling parameter between two spins which are localized to different atomic sites, you can calculate it by the following two steps:

(1) SCF calculation

First, you would perform a collinear DFT calculation using an input file 'Fe2.dat' in the directory 'work' as an example. Then, you have to set the following keyword 'HS.fileout' as follows:

```
HS.fileout                    on       # on|off, default=off
```

When the execution is completed normally, then you can find a file 'fe2.scfout' in the directory 'work'.

(2) Calculation of exchange coupling parameter

Let us compile a program code for calculating the exchange coupling parameter. Move the directory 'source' and then compile as follows:

```
% make jx
```

When the compile is completed normally, then you can find an executable file 'jx' in the directory 'work'. The exchange coupling parameter can be calculated from the file '*.scfout' using the program 'jx' as follows:

```
% ./jx fe2.scfout
```

where an iron dimer is considered as an example. Then, you are interactively asked from the program as follow:

```
*******************************************************************
*******************************************************************
 jx: code for calculating an effective exchange coupling constant J
 Copyright (C), 2003, Myung Joon Han, Jaejun Yu, and Taisuke Ozaki
 This is free software, and you are welcome to
 redistribute it under the constitution of the GNU-GPL.
*******************************************************************
*******************************************************************

Read the scfout file (fe2.scfout)
 Previous eigenvalue solver = Cluster
 atomnum                    = 2
```

```
 ChemP                        = -0.108015991530 (Hartree)
 E_Temp                       = 600.000000000000 (K)

Evaluation of J based on cluster calculation
 Diagonalize the overlap matrix
 Diagonalize the Hamiltonian for spin= 0
 Diagonalize the Hamiltonian for spin= 1

 Specify two atoms (e.g 1 2, quit: 0 0)  1 2
 J_ij between 1th atom and 2th atom is 848.136902053845 cm^{-1}
 Specify two atoms (e.g 1 2, quit: 0 0)  2 1
 J_ij between 2th atom and 1th atom is 848.136902053844 cm^{-1}
 Specify two atoms (e.g 1 2, quit: 0 0)  0 0
```

Please specify two atoms you want to calculate the exchange coupling parameter until typing '0 0'.

37 Optical conductivity

The functionality suffers from some program bugs. The revised code will be released in future.

The optical conductivity can be evaluated within linear response theory [51]. OpenMX Ver. 3.7 supports the calculation for only the collinear cluster calculation. If you want to calculate the optical conductivity of molecular systems, you can calculate it by the following two steps:

(1) SCF calculation

First, you would perform a collinear cluster calculation using an input file *Methane_OC.dat* in the directory 'work' as an example. Then, you have to set the following two keywords 'Dos.fileout' and 'OpticalConductivity.fileout' as follows:

```
Dos.fileout                    on    # on|off, default=off
OpticalConductivity.fileout    on    # on|off, default=off
```

When the execution is completed normally, then you can find files, *.optical and *.Dos.val, in the directory 'work'.

(2) Calculation of optical conductivity

Let us make a program code for calculating the optical conductivity. Move the directory 'source' and then compile as follows:

```
% make OpticalConductivityMain
```

When the compile is completed normally, then you can find a executable file 'OpticalConductivityMain' in the directory 'work'. The optical conductivity can be calculated from the files '*.optical' and '*.Dos.val' using the program 'OpticalConductivityMain' as follows:

```
% ./OpticalConductivityMain met.optical met.Dos.val met.optout
```

where a methane molecule is considered as an example. Then, you are interactively asked from the program as follow:

```
 # freqmax=100.000000
 # gaussian=0.036749
 freqmax (Hartree)=? 3
 freq mech=? 1000
```

In the output file 'met.optout' the second, third, and fourth columns correspond to the frequency (Hartree) and optical conductivity (arbitrary unit) for up- and down-spins, respectively.

38 Electric transport calculations

38.1 General

Electronic transport properties of molecules, nano-wires, and bulks such as superlattice structures can be calculated based on a non-equilibrium Green function (NEGF) method within the collinear and non-collinear DFT methods. The features and capabilities are listed below:

- SCF calculation of system with two leads under zero and finite bias voltage
- SCF calculation under gate bias voltage
- Compatible with the LDA+U method
- Spin-dependent transmission and current
- **k**-resolved transmission and current along perpendicular to the current axis
- Calculation of current-voltage curve
- Accurate and efficient contour integration scheme
- Interpolation of the effect by the bias voltage
- Quick calculation for periodic systems under zero bias

The details of the implementation can be found in Ref. [54]. First the usage of the functionalities for the collinear case is explained in the following subsections. After then, the non-collinear case will be discussed.

System we consider

In the current implementation of OpenMX Ver. 3.7, a system shown in Fig. 29(a) is treated by the NEGF method. The system consists of a central region connected with infinite left and right leads, and the two dimensional periodicity spreads over the **bc**-plane. Considering the two dimensional periodicity, the system can be cast into a one-dimensional problem depending on the Bloch wave vector **k** shown in Fig. 29(b). Also, the Green function of the region $C(\equiv L_0|C_0|R_0)$ is self-consistently determined in order to take account of relaxation of electronic structure around the interface between the central region C_0 and the region $L_0(R_0)$. It should be noted that the electronic transport is assumed to be along the **a**-axis in the current implementation. Thus, users have to keep in mind the specification when the geometrical structure is constructed. See also the subsection 'Step 1: The calculations for leads'.

Computational flow

The NEGF calculation is performed by the following three steps:

Step 1 → Step 2 → Step 3

Each step consists of

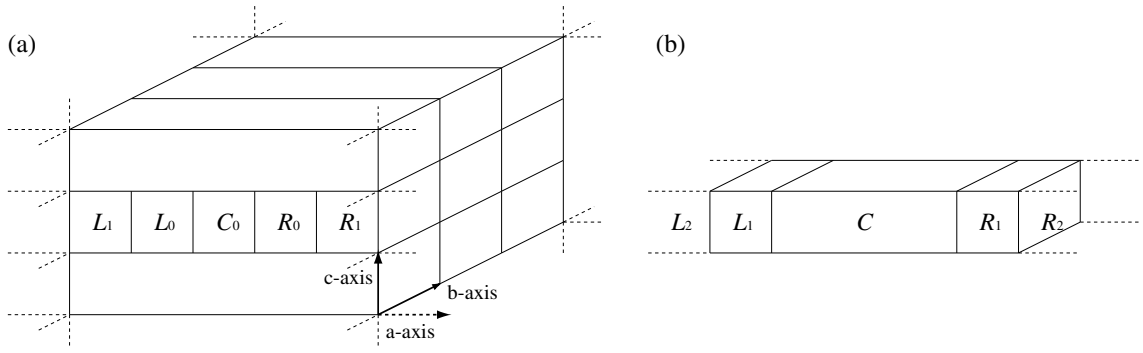

Figure 29: (a) Configuration of the system, treated by the NEGF method, with infinite left and right leads along the **a**-axis under a two dimensional periodic boundary condition on the **bc**-plane. (b) One dimensional system compacted from the configuration of (a) by considering the periodicity on the **bc**-plane, where the region C is an extended central region consisting of C_0, L_0, and R_0.

- **Step 1**

  The band structure calculations are performed for the left and right leads using a program code 'openmx'. The calculated results will be used to represent the Hamiltonian of the leads in the NEGF calculation of the step 2.

- **Step 2**

  The NEGF calculation is performed for the structure shown in Fig. 29 under zero or a finite bias voltage using a program code 'openmx', where the result in the step 1 is used for the construction of the leads.

- **Step 3**

  By making use of the result of the step 2, the transmission and current are calculated by a program code 'TranMain'.

An example: carbon chain

As a first trial, let us illustrate the three steps by employing a carbon chain. Before going to the illustration, a code 'TranMain' used in the step 3 has to be compiled in the directory 'source' as follows:

```
% make TranMain
```

If the compilation is successful, you will find the executable file 'TranMain', and may copy it your work directory, possibly 'work'. Then, you can proceed the following three calculations:

Step 1

```
%./openmx Lead-Chain.dat | tee lead-chain.std
```

A file 'negf-chain.hks' is generated by the step 1.

Step 2

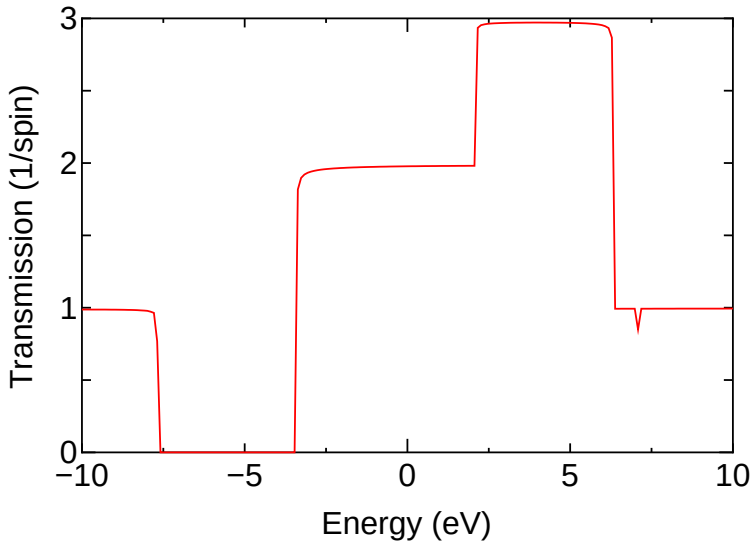

Figure 30: Transmission of a carbon chain as a function of energy. The origin of energy is set to the chemical potential of the left lead.

```
%./openmx NEGF-Chain.dat | tee negf-chain.std
```

A file 'negf-chain.tranb' is generated by the step 2.

Step 3

```
%./TranMain NEGF-Chain.dat
```

'negf-chain.tran0_0', 'negf-chain.current', and 'negf-chain.conductance' are generated by the step 3.

The calculations can be traced by using the input files stored in a directory of 'work/negf_example'. By plotting the sixth column in 'negf-chain.tran0_0' as a function of the fourth column, you can see a transmission curve as shown in Fig. 30.

38.2 Step 1: The calculations for leads

The calculation of the step 1 is the conventional band structure calculation to construct information of the lead except for adding the following two keywords 'NEGF.output_hks' and 'NEGF.filename.hks':

```
NEGF.output_hks     on
NEGF.filename.hks   lead-chain.hks
```

The calculated results such as Hamiltonian matrix elements, charge distribution, and difference Hartree potential are stored in a file specified by the keyword 'NEGF.filename.hks'. In this case, a file 'lead-chain.hks' is generated. The file '*.hks' is used in the calculation of the step 2. Since the electronic transport is assumed to be along the **a**-axis in the current implementation, you have to set the **a**-axis for the direction of electronic transport in the band structure calculation. However, you do not need rotate your structure. All you have to do is to change the specification of the lattice vectors. For example, if you want to specify a vector (0.0, 0.0, 10.0) as the **a**-axis in the following lattice vectors:

```
<Atoms.UnitVectors
  3.0  0.0  0.0
  0.0  3.0  0.0
  0.0  0.0 10.0
Atoms.UnitVectors>
```

you only have to specify as follows:

```
<Atoms.UnitVectors
  0.0  0.0 10.0
  3.0  0.0  0.0
  0.0  3.0  0.0
Atoms.UnitVectors>
```

Then, the direction of (0.0, 0.0, 10.0) becomes the direction of electronic transport. As shown in the above example, when you change the order of the lattice vectors, please make sure that the keyword 'scf.Kgrid' has to be changed as well.

In the calculation of the step 2, the semi-infiniteness of the leads is taken into account by using the surface Green function which allows us to treat the semi-infiniteness without introducing any discretization. Thus, it would be better to use a large number of **k**-points along the **a**-axis to keep the consistency between the steps 1 and 2 with respect to treatment of the semi-infiniteness of the **a**-axis. Also it is noted that the number of **k**-points for the **bc**-plane should be consistent in the steps 1 and 2.

38.3 Step 2: The NEGF calculation

A. Setting up Lead|Device|Lead

You can set up the regions L_0, C_0, and R_0 in the structural configuration shown in Fig. 29 in the following way:

The geometrical structure of the central region C_0 is specified by the following keywords 'Atoms.Number' and 'Atoms.SpeciesAndCoordinates':

```
Atoms.Number        18
<Atoms.SpeciesAndCoordinates
  1  C  3.000  0.000  0.000  2.0 2.0
   .....
 18  C 28.500  0.000  0.000  2.0 2.0
Atoms.SpeciesAndCoordinates>
```

The geometrical structure of the left lead region L_0 is specified by the following keywords 'LeftLeadAtoms.Number' and 'LeftLeadAtoms.SpeciesAndCoordinates':

```
LeftLeadAtoms.Number         3
<LeftLeadAtoms.SpeciesAndCoordinates
  1  C -1.500  0.000  0.000  2.0 2.0
  2  C  0.000  0.000  0.000  2.0 2.0
```

```
  3  C  1.500  0.000  0.000  2.0 2.0
LeftLeadAtoms.SpeciesAndCoordinates>
```

The geometrical structure of the right lead region R_0 is specified by the following keywords 'RightLeadAtoms.Number' and 'RightLeadAtoms.SpeciesAndCoordinates'

```
RightLeadAtoms.Number        3
<RightLeadAtoms.SpeciesAndCoordinates
  1  C 30.000  0.000  0.000  2.0 2.0
  2  C 31.500  0.000  0.000  2.0 2.0
  3  C 33.000  0.000  0.000  2.0 2.0
RightLeadAtoms.SpeciesAndCoordinates>
```

This is the case of carbon chain which is demonstrated in the previous subsection. The central region C_0 is formed by 18 carbon atoms, and the left and right regions L_0 and R_0 contains three carbon atoms, respectively, where every bond length is 1.5 Å. Following the geometrical specification of device and leads, OpenMX will construct an extended central region $C(\equiv L_0|C_0|R_0)$ as shown in Fig. 29. The Green function for the extended central region C is self-consistently determined in order to take account of relaxation of electronic structure around the interface between the central region C_0 and the region $L_0(R_0)$. In addition, we impose two conditions so that the central Green function can be calculated in the NEGF method [54]:

1. The localized basis orbitals ϕ in the region C_0 overlap with those in the regions L_0 and R_0, but do not overlap with those in the regions L_1 and R_1.

2. The localized basis orbitals ϕ in the L_i (R_i) region has no overlap with basis orbitals in the cells beyond the nearest neighboring cells L_{i-1} (R_{i-1}) and L_{i+1} (R_{i+1}).

In our implementation the basis functions are strictly localized in real space because of the generation of basis orbitals by a confinement scheme [28, 29]. Therefore, once the localized basis orbitals with specific cutoff radii are chosen for each region, the two conditions can be always satisfied by just adjusting the size of the unit cells for L_i and R_i.

Although the specification of unit cells for the regions L_0, C_0, and R_0 is not required, it should be noted that some periodicity is implicitly assumed. The construction of infinite leads is made by employing the unit cells used in the band structure calculations by the step 1, and the informations are stored in a file '*.hks'. Also, due to the structural configuration shown in Fig. 29, the unit vectors on the **bc**-plane for the left and right leads should be consistent. Thus, the unit vector on the **bc**-plane for the extended central region C is implicitly assumed to be same as that of the leads. Within the structural limitation, you can set up the structural configuration.

The unit in the specification of the geometrical structure can be given by

```
Atoms.SpeciesAndCoordinates.Unit   Ang # Ang|AU
```

In the NEGF calculation, either 'Ang' or 'AU' for 'Atoms.SpeciesAndCoordinates.Unit' is supported, but 'FRAC' is not.

How OpenMX analyzes the geometrical structure can be confirmed by the standard output as shown below:

```
<TRAN_Calc_GridBound>

*******************************************************
The extended cell consists of Left0-Center-Right0.
The cells of left and right reads are connected as.
...|Left2|Left1|Left0-Center-Right0|Right1|Right2...

Each atom in the extended cell is assigned as follows:
where '12' and '2' mean that they are in 'Left0', and
'12' has overlap with atoms in the Left1,
and '13' and '3' mean that they are in 'Right0', and
'13' has overlap with atoms in the 'Right1', and also
'1' means atom in the 'Center'.
*******************************************************

Atom1  = 12 Atom2  =  2 Atom3  =  1 Atom4  =  1 Atom5  =  1 Atom6  =  1 Atom7  =  1
Atom8  =  1 Atom9  =  1 Atom10 =  1 Atom11 =  1 Atom12 =  1 Atom13 =  1 Atom14 =  1
Atom15 =  1 Atom16 =  1 Atom17 =  1 Atom18 =  1 Atom19 =  1 Atom20 =  1 Atom21 =  3
Atom22 = 13
```

The atoms in the extended cell consisting of $L_0|C_0|R_0$ are assigned by the numbers, where '12' and '2' mean that they are in L_0, and '12' has overlap with atoms in L_1, and '13' and '3' mean that they are in R_0, and '13' has overlap with atoms in R_1, and also '1' means atom in C_0. By checking the analysis you may confirm whether the structure is properly constructed or not.

B. Keywords

The NEGF calculation of the step 2 is performed by the keyword 'scf.EigenvalueSolver'

```
scf.EigenvalueSolver       NEGF
```

For the NEGF calculation the following keywords are newly added.

```
NEGF.filename.hks.l     lead-chain.hks
NEGF.filename.hks.r     lead-chain.hks

NEGF.Num.Poles             100       # defalut=150
NEGF.scf.Kgrid             1 1       # defalut=1 1

NEGF.bias.voltage          0.0       # default=0.0 (eV)
NEGF.bias.neq.im.energy    0.01      # default=0.01 (eV)
NEGF.bias.neq.energy.step  0.02      # default=0.02 (eV)
```

An explanation for each keyword is given below.

```
NEGF.filename.hks.l     lead-chain.hks
NEGF.filename.hks.r     lead-chain.hks
```

The files containing information of leads are specified by the above two keywords, where 'NEGF.filename.hks.l' and 'NEGF.filename.hks.r' are for the left and right leads, respectively.

```
NEGF.Num.Poles              100       # defalut=150
```

The equilibrium density matrix is evaluated by a contour integration method [54, 55]. The number of poles used in the method is specified by the keyword 'NEGF.Num.Poles'.

```
NEGF.scf.Kgrid              1 1       # defalut=1 1
```

The numbers of **k**-points to discretize the reciprocal vectors $\tilde{\mathbf{b}}$ and $\tilde{\mathbf{c}}$ are specified by the keyword 'NEGF.scf.Kgrid'. Since no periodicity is assumed along the **a**-axis, you do not need to specify that for the **a**-axis.

```
NEGF.scf.Iter.Band           6        # defalut=6
```

It would be better to use the conventional diagonalization method for a few SCF steps in the initial SCF iterations by assuming a periodicity along the **a**-axis as well as **b**- and **c**-axes. The procedure is effective to avoid an erratic charge distribution which is a serious problem in the self-consistent NEGF method. The number of first SCF steps for which the conventional diagonalization method is applied is controlled by the keyword 'NEGF.scf.Iter.Band'. Up to and including the SCF steps specified by 'NEGF.scf.Iter.Band', the conventional diagonalization method is used and then onward, the solver is switched from the conventional method to the NEGF method. The default is 6.

```
NEGF.bias.voltage           0.0       # default=0.0 (eV)
```

The source-drain bias voltage applied to the left and right leads is specified by the keyword 'NEGF.bias.voltage' in units of eV, corresponding to Volt. Noting that only the difference between applied bias voltages has physical meaning, you only have to give a single value as the source-drain bias voltage.

```
NEGF.bias.neq.im.energy    0.01       # default=0.01 (eV)
NEGF.bias.neq.energy.step  0.02       # default=0.02 (eV)
```

When a finite source-drain bias voltage is applied, a part of the density matrix is contributed by the non-equilibrium Green function. Since the non-equilibrium Green function is not analytic in general in the complex plane, the contour integration method used for the equilibrium Green function cannot be applied. Thus, in the current implementation the non-equilibrium Green function is evaluated on the real axis with a small imaginary part using a simple rectangular quadrature scheme. Then, the imaginary part is given by the keyword 'NEGF.bias.neq.im.energy' and the step width is given by the keyword 'NEGF.bias.neq.energy.step' in units of eV. In most cases, the default values are sufficient, while the detailed analysis of the convergence property can be found in Ref. [54]. How many energy points on the real axis are used for the evaluation of the non-equilibrium Green function can be confirmed in the standard output and the file '*.out'. In case of 'NEGF-Chain.dat', if the bias voltage of 0.5 V is applied, you will see in the standard output that the energy points of 120 are allocated for the calculation as follows:

```
Intrinsic chemical potential (eV) of the leads
  Left lead:  -7.752843837400
  Right lead: -7.752843837400
  add voltage =  0.0000 (eV) to the  left lead: new ChemP (eV):  -7.7528
  add voltage =  0.5000 (eV) to the right lead: new ChemP (eV):  -7.2528

Parameters for the integration of the non-equilibrium part
  lower bound:           -8.706843837400 (eV)
  upper bound:           -6.298843837400 (eV)
  energy step:            0.020000000000 (eV)
  number of steps:           120
```

The total number of energy points where the Green function is evaluated is given by the sum of the number of poles and the number of energy points on the real axis determined by the two keywords 'NEGF.bias.neq.im.energy' and 'NEGF.bias.neq.energy.step', and you should notice that the computational time is proportional to the total number of energy points.

```
NEGF.Poisson.Solver       FD     # FD|FFT, default=FD
```

In the NEGF method, the electrostatic potential is calculated by either a finite difference plus two dimensional FFT (FD) [54] or three dimensional FFT (FFT) [56]. The choice of the Poisson solver is specified by the keyword 'NEGF.Poisson.Solver'. Both the methods provide similar electrostatic potentials for non-polar systems, while the difference can be large for polar systems. The former is a proper choice in a sense that the eletrostatic potential at the boundaries between the leads and the central region should be the same as that in the calculations of the step 1 for the leads, while the SCF convergence seems to be rather easily obtained by the latter. The default is FD.

C. SCF criterion

In the NEGF method, the SCF criterion given by the keyword 'scf.criterion' is applied to the residual norm between the input and output charge densities 'NormRD', while in the other cases 'dUele' is monitored. See also the keyword 'NEGF.scf.Iter.Band'.

D. Gate bias voltage

In our implementation, the gate voltage $V_{\rm g}(x)$ is treated by adding an electric potential defined by

$$V_{\rm g}(x) = V_{\rm g}^{(0)} \exp\left[-\left(\frac{x - x_{\rm c}}{d}\right)^8\right],$$

where $V_{\rm g}^{(0)}$ is a constant value corresponding to the gate voltage, and is specified by the keyword 'NEGF.gate.voltage' as follows:

```
NEGF.gate.voltage   1.0    # default=0.0 (in eV)
```

x_c the center of the region C_0, and d the length of the unit vector along **a**-axis for the region C_0. Due to the form of the equation, the applied gate voltage affects mainly the region C_0 in the central region C. The electric potential may resemble the potential produced by the image charges [57].

E. Density of States (DOS)

In the NEGF calculation, the density of states can be calculated by setting the following keywords:

```
Dos.fileout                  on              # on|off, default=off
NEGF.Dos.energyrange     -15.0 25.0 5.0e-3   #default=-10.0 10.0 5.0e-3 (eV)
NEGF.Dos.energy.div         200              # default=200
NEGF.Dos.Kgrid              1 1              # default=1 1
```

When you want to calculate DOS, the keyword 'Dos.fileout' should be set to 'on' as usual. Also, the energy range where DOS is calculated is given by the keyword 'NEGF.Dos.energyrange', where the first and second numbers correspond to the lower and upper bounds, and the third number is an imaginary number used for smearing out DOS. The energy range specified by 'NEGF.Dos.energyrange' is divided by the number specified by the keyword 'NEGF.Dos.energy.div'. The numbers of **k**-points to discretize the reciprocal vectors $\tilde{\mathbf{b}}$ and $\tilde{\mathbf{c}}$ are specified by the keyword 'NEGF.Dos.Kgrid'. The set of numbers given by 'NEGF.Dos.Kgrid' tends to be larger than that by 'NEGF.scf.Kgrid' because of computational efficiency. After the NEGF calculation with these parameters, you will find two files '*.Dos.val' and '*.Dos.vec', and can analyze those by the same procedure as usual. Also, it should be noted that the origin of energy is set to the chemical potential of the **left** lead.

38.4 Step 3: The transmission and current

After the calculations of the steps 2 and 3, you can proceed calculations of transmission and current by adding the following keywords to the input file used in the calculation of the step 2:

```
NEGF.tran.energyrange -10 10 1.0e-3  # default=-10.0 10.0 1.0e-3 (eV)
NEGF.tran.energydiv        200       # default=200
NEGF.tran.Kgrid            1 1       # default= 1 1
```

The energy range where the transmission is calculated is given by the keyword 'NEGF.tran.energyrange', where the first and second numbers correspond to the lower and upper bounds, and the third number is an imaginary number used for smearing out the transmission. The energy range specified by 'NEGF.tran.energyrange' is divided by the number specified by the keyword 'NEGF.tran.energydiv'. The numbers of **k**-points to discretize the reciprocal vectors $\tilde{\mathbf{b}}$ and $\tilde{\mathbf{c}}$ are specified by the keyword 'NEGF.tran.Kgrid'. The set of numbers given by 'NEGF.tran.Kgrid' can be different and tends to be larger than that by 'NEGF.scf.Kgrid' because of computational efficiency.

The calculations of the transmission and current are performed by a program code 'TranMain', which can be compiled in the directory 'source' as follows:

```
% make TranMain
```

If the compilation is successful, you will find the executable file 'TranMain', and may copy it your work directory, possibly 'work'. Using the code 'TranMain' you can perform the calculation of the step 3, for example, as follows:

```
%./TranMain NEGF-Chain.dat

*******************************************************
*******************************************************
 Welcome to TranMain
 This is a post-processing code of OpenMX to calculate
 electronic transmission and current.
 Copyright (C), 2002-2013, H.Kino and T.Ozaki
 TranMain comes with ABSOLUTELY NO WARRANTY.
 This is free software, and you are welcome to
 redistribute it under the constitution of the GNU-GPL.
*******************************************************
*******************************************************


Chemical potentials used in the SCF calculation
  Left lead:  -7.752843837400 (eV)
  Right lead: -7.752843837400 (eV)
NEGF.current.energy.step 1.0000e-02 seems to be large for the calculation ....
The recommended Tran.current.energy.step is 0.0000e+00 (eV).

Parameters for the calculation of the current
  lower bound:    -7.752843837400 (eV)
  upper bound:    -7.752843837400 (eV)
  energy step:     0.010000000000 (eV)
  imginary energy  0.001000000000 (eV)
  number of steps:   0

  calculating...

  myid0= 0 i2= 0 i3= 0  k2=  0.0000 k3= -0.0000

Transmission:  files

  ./negf-chain.tran0_0

Current:  file

  ./negf-chain.current


Conductance:  file

  ./negf-chain.conductance
```

After the calculation, in this case you will obtain three files 'negf-chain.tran0_0', 'negf-chain.current', and 'negf-chain.conductance':

- *.tran#_%

  The file stores transmissions for up- and down-spin states. The fourth column is the energy relative to the chemical potential of the **left** lead, and the sixth and eighth columns are transmission for up- and down-spin states, respectively. When you employ a lot of **k**-points which is given by 'NEGF.tran.Kgrid', a file with a different set of '#' and '%' in the file extension is generated for each **k**-point. The correspondence between the numbers and the **k**-points can be found in the file.

- *.current

  The file stores **k**-resolved currents and its average for up- and down-spin states in units of ampere.

- *.conductance

  The file stores **k**-resolved conductance at 0 K and its average for up- and down-spin states in units of quantum conductance ($G_0 \equiv \frac{e^2}{h}$). Thus, the conductance G is proportional to the transmission T at the chemical potential of the **left** lead, μ_L, as follows:

$$G = \frac{e^2}{h} T(\mu_L)$$

As an example, the **k**-resolved transmission drawn by using the file '*.conductance' is shown in Fig. 31.

38.5 Periodic system under zero bias

When the transmission of a system with the periodicity along the **a**-axis as well as the periodicity of the **bc**-plane is evaluated under zero bias voltage, it can be easily obtained by making use of the Hamiltonian calculated by the conventional band structure calculation without employing the Green function method. This scheme enables us to explore transport properties for a wide variety of possible geometric and magnetic structures with a low computational cost, and thereby can be very useful for many materials such as superlattice structures. The calculation is performed by adding a keyword 'NEGF.Output.for.TranMain':

```
NEGF.Output.for.TranMain    on
```

in the band structure calculation of the step 1. Then, after the calculation of the step 1, you will obtain a file '*.tranb' which can be used in the calculation of the step 3, which means that you can skip the calculation of the step 2.

38.6 Interpolation of the effect by the bias voltage

Since for large-scale systems it is very time-consuming to perform the SCF calculation at each bias voltage, an interpolation scheme is available to reduce the computational cost in the calculations by the NEGF method. The interpolation scheme is performed in the following way: (i) the SCF calculations are performed for a few bias voltages which are selected in the regime of the bias voltage of interest. (ii) when the transmission and current are calculated, linear interpolation is made for the Hamiltonian

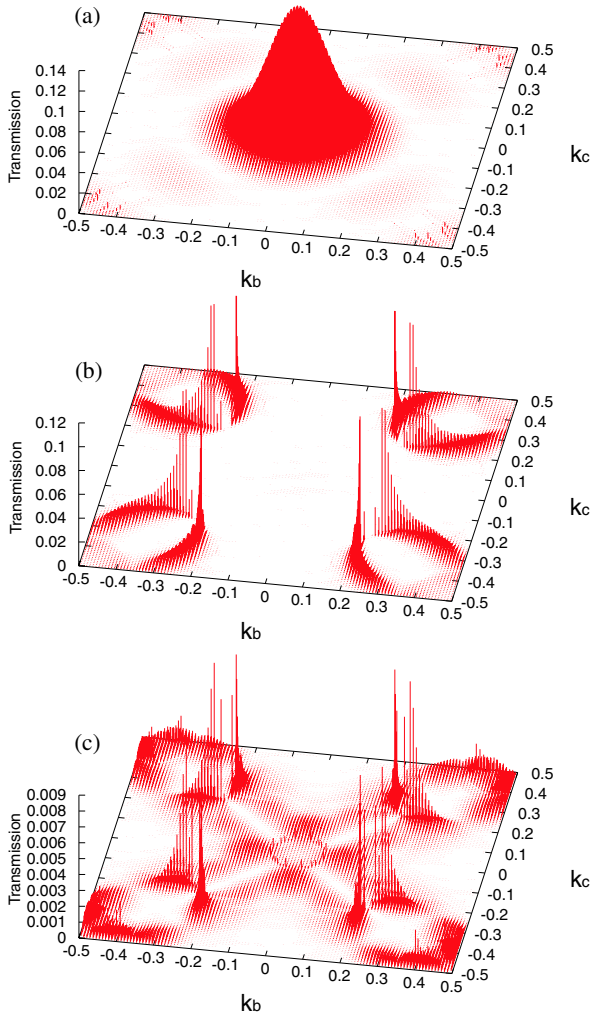

Figure 31: **k**-resolved Transmission at the chemical potential for (a) the majority spin state of the parallel configuration, (b) the minority spin state of the parallel configuration, and (c) a spin state of the antiparallel configuration of Fe|MgO|Fe, respectively. For the calculations **k**-points of 120×120 were used.

block elements, $H^{(\mathbf{k})}_{\sigma,C}$ and $H^{(\mathbf{k})}_{\sigma,R}$, of the central scattering region and the right lead, and the chemical potential, μ_R, of the right lead by

$$\begin{aligned} H^{(\mathbf{k})}_{\sigma,C} &= \lambda H^{(\mathbf{k},1)}_{\sigma,C} + (1-\lambda) H^{(\mathbf{k},2)}_{\sigma,C}, \\ H^{(\mathbf{k})}_{\sigma,R} &= \lambda H^{(\mathbf{k},1)}_{\sigma,R} + (1-\lambda) H^{(\mathbf{k},2)}_{\sigma,R}, \\ \mu_R &= \lambda \mu^{(1)}_R + (1-\lambda)\mu^{(2)}_R, \end{aligned}$$

where the indices 1 and 2 in the superscript mean that the quantities are calculated or used at the corresponding bias voltages where the SCF calculations are performed beforehand. In general, λ should range from 0 to 1 for the moderate interpolation.

In the calculation of the step 3, the interpolation is made by adding the following keywords in the input file:

```
NEGF.tran.interpolate          on                # default=off, on|off
NEGF.tran.interpolate.file1   c1-negf-0.5.tranb
```

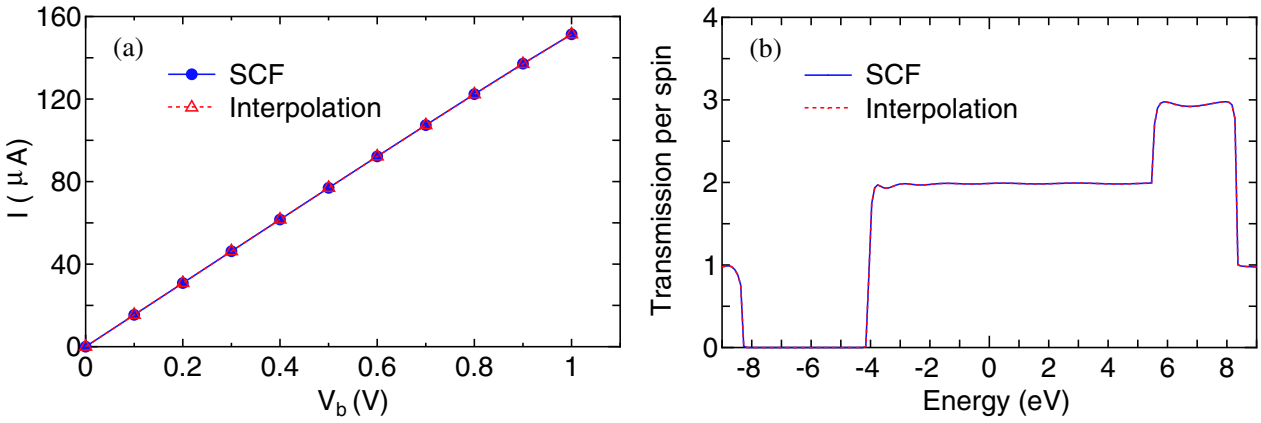

Figure 32: (a) Currents of the linear carbon chain calculated by the SCF calculations (solid line) and the interpolation scheme (dotted line). (b) Transmission of the linear carbon chain under a bias voltage of 0.3 V, calculated by the SCF calculations (solid line) and the interpolation scheme (dotted line). The imaginary part of 0.01 and the grid spacing of 0.01 eV are used for the integration of the nonequilibrium term in the density matrix.

```
NEGF.tran.interpolate.file2  c1-negf-1.0.tranb
NEGF.tran.interpolate.coes    0.7 0.3          # default=1.0 0.0
```

When you perform the interpolation, the keyword 'NEGF.tran.interpolate' should be 'on'. In this case, files 'c1-negf-0.5.tranb' and 'c1-negf-1.0.tranb' specified by the keywords 'NEGF.tran.interpolate.file1' and 'NEGF.tran.interpolate.file2' are the results under bias voltages of 0.5 and 1.0 V, respectively, and the transmission and current at $V = 0.7 * 0.5 + 0.3 * 1.0 = 0.65[V]$ are evaluated by the interpolation scheme, where the weights of 0.7 and 0.3 are specified by the keyword 'NEGF.tran.interpolate.coes'.

A comparison between the fully self consistent and the interpolated results is shown with respect to the current and transmission in the linear carbon chain in Figs. 32(a) and (b). In this case, the SCF calculations at three bias voltages of 0, 0.5, and 1.0 V are performed, and the results at the other bias voltages are obtained by the interpolation scheme. For comparison we also calculate the currents via the SCF calculations at all the bias voltages. It is confirmed that the simple interpolation scheme gives notably accurate results for both the calculations of the current and transmission. Although the proper selection of bias voltages used for the SCF calculations may depend on systems, the result suggests that the simple scheme is very useful to interpolate the effect of the bias voltage while keeping the accuracy of the calculations.

38.7 Parallelization of NEGF

In the current implementation the NEGF calculation is parallelized by MPI. In addition to the MPI parallelization, if you use ACML or MKL, the matrix multiplication and the inverse calculation of matrix in the evaluation of the Green function are also parallelized by OpenMP. In this case, you can perform a hybrid parallelization by OpenMP/MPI which may lead to shorter computational time. The way for the parallelization is completely same as before.

In Fig. 33 we show the speed-up ratio in the elapsed time for the evaluation of the density matrix of 8-zigzag graphene nanoribbon(ZGNR) under a finite bias voltage of 0.5 eV. The energy points of 197 (101 and 96 for the equilibrium and nonequilibrium terms, respectively) are used for the evaluation

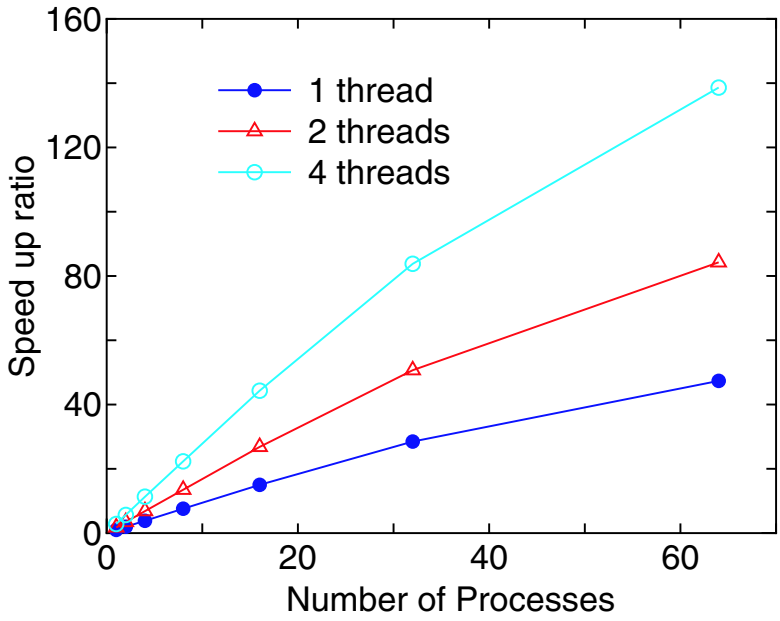

Figure 33: Speed-up ratio in the parallel computation of the calculation of the density matrix for the FM junction of 8-zigzag graphene nanoribbon (ZGNR) by a hybrid scheme using MPI and OpenMP. The speed-up ratio is defined by T_1/T_p, where T_1 and T_p are the elapsed times by a single core and a parallel calculations. The cores used in the MPI and OpenMP parallelizations are called *process* and *thread*, respectively. The parallel calculations were performed on a CRAY-XT5 machine consisting of AMD opteron quad core processors (2.3GHz). In the benchmark calculations, the number of processes is taken to be equivalent to that of processors. Therefore, in the parallelization using 1 or 2 threads, 3 or 2 cores are idle in a quad core processor.

of the density matrix. Only the Γ point is employed for the **k**-point sampling, and the spin polarized calculation is performed. Thus, the combination of 394 for the three indices are parallelized by MPI. It is found that the speed-up ratio of the flat MPI parallelization, corresponding to 1 thread, reasonably scales up to 64 processes. Furthermore, it can be seen that the hybrid parallelization, corresponding to 2 and 4 threads, largely improves the speed-up ratio. By fully using 64 quad core processors, corresponding to 64 processes and 4 threads, the speed-up ratio is about 140, demonstrating the good scalability of the NEGF method. For the details see also Ref. [54]. It should be also noted that the number of processes in the MPI parallelization can exceed the number of atoms in OpenMX Ver. 3.7.

38.8 NEGF method for the non-collinear DFT

OpenMX Ver. 3.7 supports the NEGF method coupled with the non-collinear DFT method, which can be regarded as a full implementation of NEGF within NC-DFT. The spin-orbit coupling, the DFT+U method, and the constraint schemes to control direction of spin and orbital magnetic moments supported for NC-DFT are all compatible with the implementation of the NEGF method. Thus, it is expected that a wide variety of problems can be treated, such as transport through magnetic domains with spiral magnetic structure. The usage of the functionality is basically the same as that for the collinear DFT case. Only the difference between the collinear and NC versions is that the step 3 is performed by a program code 'TranMain_NC', which can be compiled in the source directory as follows:

```
% make TranMain_NC
```

There is no other difference in using the functionality compared to the collinear version.

As an example, we show a result for zigzag graphene nanoribbon calculated by the NEGF method coupled with NC-DFT in Fig. 34. It is assumed that spin moments at the zigzag edges align upward and rightward in the left and right leads, respectively. Those calculations were performed by the conventional NC band structure method with the constraint scheme as the step 1. Then, any constraint was not applied in the calculation of the step 2. After getting the SCF convergence in the step 2, it is found that the spin direction gradually rotates in the central region as shown in Fig. 34(a). The calculations can be traced by input files 'Lead-L-8ZGNR-NC.dat', 'Lead-R-8ZGNR-NC.dat', and 'NEGF-8ZGNR-NC.dat' stored in the directory 'work/negf_example'. Also, you will find another example for input files of a gold chain in the same directory.

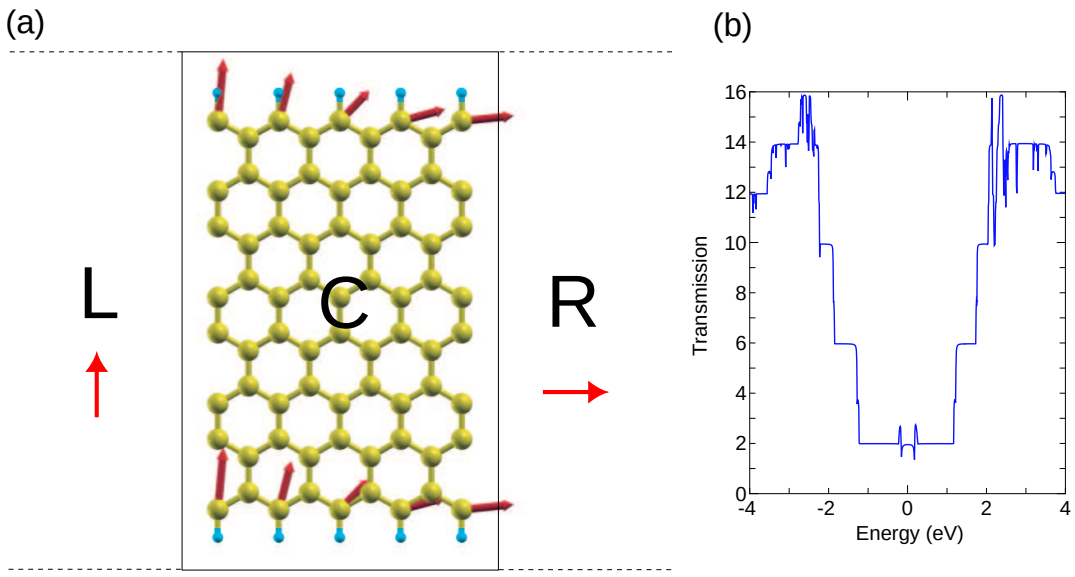

Figure 34: (a) Zigzag graphene nanoribbon with non-collinear spin direction represented by arrow. The length of the arrow corresponds to magnitude of the spin moment. In calculations of the step 1, the constraint scheme to control spin direction was applied so that spin moments at the zigzag edges can align upward and rightward in the left and right leads, respectively. (b) Transmission of electron through the channel region C shown in Fig. 34(a).

38.9 Examples

For user's convenience, input files for five examples can be found in 'work/negf_example' as follows:

- Carbon chain under zero bias voltage

  Step 1: Lead-Chain.dat
  Step 2: NEGF-Chain.dat

- Graphene sheet under zero bias voltage

  Step 1: Lead-Graphene.dat
  Step 2: NEGF-Graphene.dat

- 8-zigzag graphene nanoribbon with an antiferromagnetic junction under a finite bias voltage of 0.3 V

  Step 1: Lead-L-8ZGNR.dat, Lead-R-8ZGNR.dat
  Step 2: NEGF-8ZGNR-0.3.dat

- 8-zigzag graphene nanoribbon with a non-collinear magnetic junction under zero bias

  Step 1: Lead-L-8ZGNR-NC.dat, Lead-R-8ZGNR-NC.dat
  Step 2: NEGF-8ZGNR-NC.dat

- Gold chain by NEGF coupled with NC-DFT under zero bias

  Step 1: Lead-Au-Chain-NC.dat
  Step 2: NEGF-Au-Chain-NC.dat

38.10 Automatic running test of NEGF

To check whether the NEGF calculation part is properly installed or not, an automatic running test for the NEGF calculation can be performed by

For the MPI parallel running

```
% mpirun -np 16 openmx -runtestNEGF
```

For the OpenMP/MPI parallel running

```
% mpirun -np 8 openmx -runtestNEGF -nt 2
```

Then, OpenMX will run with five test cases including calculations of the steps 1 and 2, and compare calculated results with the reference results which are stored in 'work/negf_example'. The comparison (absolute difference in the total energy and force) is stored in a file 'runtestNEGF.result' in the directory 'work'. The reference results were calculated using 16 MPI processes of a 2.6GHz Xeon machine. If the difference is within last seven digits, we may consider that the installation is successful.

39 Maximally Localized Wannier Function

39.1 General

The following are descriptions on how to use OpenMX to generate maximally localized Wannier function (MLWF) [78, 79]. Keywords and settings for controlling the calculations are explained. The style of keywords are closely following those originally in OpenMX. Throughout the section, a couple of results for silicon in the diamond structure will be shown for convenience. The calculation can be traced by openmx code with an input file 'Si.dat' in 'work/wf_example'. There is no additional post processing code. After users may get the convergent result for the conventional SCF process for the electronic structure calculation, the following procedure explained below will be repeated by changing a couple of parameters with the restart file until desired MLWFs are obtained.

To acknowledge in any publications by using the functionality, the citation of the reference [58] would be appreciated:

Switching on generating MLWFs

To switch on the calculation, a keyword 'Wannier.Func.Calc' should be explicitly set as 'on'. Its default value is 'off'.

```
Wannier.Func.Calc        on         #default off
```

Setting the number of target MLWFs

The number of target MLWFs should be given explicitly by setting a keyword 'Wannier.Func.Num' and no default value for it.

```
Wannier.Func.Num       4          #no default
```

Energy window for selecting Bloch states

The MLWFs will be generated from a set of Bloch states, which are selected by defining an energy window covering the eigenenergies of them. Following Ref. [79], two energy windows are introduced. One is so-called outer window, defined by two keywords, 'Wannier.Outer.Window.Bottom' and 'Wannier.Outer.Window.Top', indicating the lower and upper boundaries, respectively. The other one is inner window, which is specified by two similar key words, 'Wannier.Inner.Window.Bottom' and 'Wannier.Inner.Window.Top'. All these four values are given in units eV relative to Fermi level. The inner window should be fully inside of the outer window. If the two boundaries of inner window are equal to each other, it means inner window is not defined and not used in calculation. There is no default values for outer window, while 0.0 is the default value for two boundaries of inner window. One example is as following:

```
Wannier.Outer.Window.Bottom   -14.0   #lower boundary of outer window, no default value
Wannier.Outer.Window.Top        0.0   #upper boundary of outer window, no default value
Wannier.Inner.Window.Bottom     0.0   #lower boundary of inner window, default value 0.0
Wannier.Inner.Window.Top        0.0   #upper boundary of outer window, default value 0.0
```

To set these two windows covering interested bands, it is usually to plot band structure and/or density of states before the calculation of MLWFs. If you want to restart the minimization of MLWFs by reading the overlap matrix elements from files, the outer window should not be larger than that used for calculating the stored overlap matrix. Either equal or smaller is allowed. The inner window can be varied within the outer window as you like when the restart calculation is performed. This would benefit the restarting calculation or checking the dependence of MLWFs on the size of both the windows. For the restarting calculation, please see also the section (7) 'Restart optimization without calculating overlap matrix'.

Initial guess of MLWFs

User can choose whether to use initial guess of target MLWFs or not by setting the keyword 'Wannier.Initial.Guess' as 'on' or 'off'. Default value is 'on', which means we recommend user to use an initial guess to improve the convergence or avoid local minima during the minimization of spread function.

If the initial guess is required, a set of local functions with the same number of target MLWFs should be defined. Bloch wave functions inside the outer window will be projected on to them. Therefore, these local functions are also called as projectors. The following steps are required to specify a projector.

A. Define local functions for projectors

Since the pseudo-atomic orbitals are used for projectors, the specification of them is the same as for the basis functions. An example setting, for silicon in diamond structure, is as following:

```
Species.Number          2

<Definition.of.Atomic.Species
  Si       Si7.0-s2p2d1    Si_CA11
  proj1    Si5.5-s1p1d1f1  Si_CA11
Definition.of.Atomic.Species>
```

In this example, since we employ PAOs from Si as projectors, an additional specie 'proj1' is defined as shown above. Inside the pair keywords '<Definition.of.Atomic.Species' and 'Definition.of.Atomic.Species>', in addition to the first line used for Si atoms, one species for the projectors is defined. Its name is 'proj1' defined by 'Si5.5-s1p1d1f1' and the pseudopotential 'Si_CA'. In fact, the pseudopotential defined in this line will not be used. It is given just for keeping the consistence of inputting data structure. One can use any PAO as projector. Also the use of only a single basis set is allowed for each l-component. We strongly recommend user to specify 's1p1d1f1' in all cases to avoid possible error.

B. Specify the orbital, central position and orientation of a projector

Pair keywords '<Wannier.Initial.Projectos' and 'Wannier.Initial.Projectos>' will be used to specify the projector name, local orbital function, center of local orbital, and the local z-axis and x-axis for orbital orientation.

An example setting is shown here:

```
<Wannier.Initial.Projectors
   proj1-sp3   0.250  0.250  0.250   -1.0 0.0 0.0    0.0  0.0 -1.0
   proj1-sp3   0.000  0.000  0.000    0.0 0.0 1.0    1.0  0.0  0.0
Wannier.Initial.Projectors>
```

Each line contains the following items. For example, in the first line, the species name, 'proj1', is defined in pairing keywords 'Definition.of.Atomic.Species'. '-' is used to connect the projector name and the selected orbitals. 'sp3' means the sp3 hybridized orbitals of this species is used as the initial guess of four target Wannier functions (see also Table 6 for all the possible orbitals and their hybrids). The projectors consisting of hybridized orbitals are centered at the position given by the following 3 numbers, '0.25 0.25 0.25', which are given in unit defined by keyword 'Wannier.Initial.Projectors.Unit' (to be explained below). The next two sets of three numbers define the z-axis and x-axis of the local coordinate system, respectively, where each axis is specified by the vector defined by three components in xyz-coordinate. In this example, in the first line the local z-axis defined by '-1.0 0.0 0.0' points to the opposite direction to the original x-axis, while the local x-axis defined by '0.0 0.0 -1.0' points to the opposite direction to the original z-axis. In the second line the local axes are the same as the original coordinate system.

The orbital used as projector can be the original PAOs or any hybrid of them. One must be aware that the total number of projectors defined by 'sp3' is 4. Similarly, 'sp' and 'sp2' contain 2 and 3 projectors, respectively. A list of supported PAOs and hybridizations among them can be found in Table 6. Any name other than those listed is not allowed.

The projector can be centered anywhere inside the unit cell. To specify its location, we can use the fractional (FRAC) coordinates relative to the unit cell vectors or Cartesian coordinates in atomic unit (AU) or in angstrom (ANG). The corresponding keyword is 'Wannier.Initial.Projectors.Unit'.

```
Wannier.Initial.Projectors.Unit     FRAC     #AU, ANG or FRAC
```

K grid mesh and b vectors connecting neighboring k-points

The Monkhorst-Pack k grid mesh is defined by keyword 'Wannier.Kgrid'. There is no default setting for it. To use finite difference approach for calculating k-space differentials, **b** vectors connecting neighboring k points are searched shell by shell according to the distance from a central k point. The maximum number of searched shells is defined by keyword 'Wannier.MaxShells'. Default value is 12 and it should be increased if failure in finding a set of proper **b** vectors. The problem may happen in case of a system having a large aspect ratio among unit vectors, and in this case you will see an error message, while the value 12 works well in most cases. A proper setting of 'Wannier.Kgrid' will also help to find **b** vectors, where the grid spacing by the discretization for each reciprocal lattice vector should be nearly equivalent to each other.

Table 6: Orbitals and hybrids used as projector. The hybridization is done within the new coordinate system defined by z-axis and x-axis.

Orbital name	Number of included projector	Description
s	1	s orbital from PAOs
p	3	p_x, p_y, p_z from PAOs
px	1	p_x from PAOs
py	1	p_y from PAOs
pz	1	p_z from PAOs
d	5	$d_{z^2}, d_{x^2-y^2}, d_{xy}, d_{xz}, d_{yz}$ from PAOs
dz2	1	d_{z^2} from PAOs
dx2-y2	1	$d_{x^2-y^2}$ from PAOs
dxy	1	d_{xy} from PAOs
dxz	1	d_{xy} from PAOs
dyz	1	d_{xy} from PAOs
f	7	$f_{z^3}, f_{xz^2}, f_{yz^2}, f_{zx^2}, f_{xyz}, f_{x^3-3xy^2}, f_{3yx^2-y^3}$ from PAOs
fz3	1	f_{z^3} from PAOs
fxz2	1	f_{xz^2} from PAOs
fyz2	1	f_{yz^2} from PAOs
fzx2	1	f_{zx^2} from PAOs
fxyz	1	f_{xyz} from PAOs
fx3-3xy2	1	$f_{x^3-3xy^2}$ from PAOs
f3yx2-y3	1	$f_{3yx^2-y^3}$ from PAOs
sp	2	Hybridization between s and px orbitals, including $\frac{1}{\sqrt{2}}(s+p_x)$ and $\frac{1}{\sqrt{2}}(s-p_x)$
sp2	3	Hybridization among s, px, and py orbitals, including $\frac{1}{\sqrt{3}}s-\frac{1}{\sqrt{6}}p_x+\frac{1}{\sqrt{2}}p_y$, $\frac{1}{\sqrt{3}}s-\frac{1}{\sqrt{6}}p_x-\frac{1}{\sqrt{2}}p_y$ and $\frac{1}{\sqrt{3}}s+\frac{2}{\sqrt{6}}p_x$
sp3	4	Hybridization among s, px, py and pz orbitals: $\frac{1}{\sqrt{2}}(s+p_x+p_y+p_z)$, $\frac{1}{\sqrt{2}}(s+p_x-p_y-p_z)$ $\frac{1}{\sqrt{2}}(s-p_x+p_y-p_z)$, $\frac{1}{\sqrt{2}}(s-p_x-p_y+p_z)$
sp3dz2	5	Hybridization among s, p_x, p_y, p_z and d_{z^2} orbitals: $\frac{1}{\sqrt{3}}s-\frac{1}{\sqrt{6}}p_x+\frac{1}{\sqrt{2}}p_y$, $\frac{1}{\sqrt{3}}s-\frac{1}{\sqrt{6}}p_x+\frac{1}{\sqrt{2}}p_y$, $\frac{1}{\sqrt{3}}s-\frac{2}{\sqrt{6}}p_x$ $\frac{1}{\sqrt{2}}p_z+\frac{1}{\sqrt{2}}d_{z^2}$, $-\frac{1}{\sqrt{2}}p_z+\frac{1}{\sqrt{2}}d_{z^2}$
sp3deg	6	Hybridization among s, p_x, p_y, p_z and $d_{z^2}, d_{x^2-y^2}$ orbitals: $\frac{1}{\sqrt{6}}s-\frac{1}{\sqrt{2}}p_x-\frac{1}{\sqrt{12}}d_{z^2}+\frac{1}{2}d_{x^2-y^2}$, $\frac{1}{\sqrt{6}}s+\frac{1}{\sqrt{2}}p_x-\frac{1}{\sqrt{12}}d_{z^2}+\frac{1}{2}d_{x^2-y^2}$, $\frac{1}{\sqrt{6}}s-\frac{1}{\sqrt{2}}p_y-\frac{1}{\sqrt{12}}d_{z^2}-\frac{1}{2}d_{x^2-y^2}$, $\frac{1}{\sqrt{6}}s+\frac{1}{\sqrt{2}}p_y-\frac{1}{\sqrt{12}}d_{z^2}-\frac{1}{2}d_{x^2-y^2}$, $\frac{1}{\sqrt{6}}s-\frac{1}{\sqrt{2}}p_z+\frac{1}{\sqrt{3}}d_{z^2}$, $\frac{1}{\sqrt{6}}s+\frac{1}{\sqrt{2}}p_z+\frac{1}{\sqrt{3}}d_{z^2}$

```
Wannier.MaxShells          12          # default value is 12.
Wannier.Kgrid           8  8  8        # no default value
```

Minimizing spread of WF

For entangled band case [79], two steps are needed to find the MLWFs. The first step is to minimize the gauge invariant part of spread function by disentangling the non-isolated bands. The second step is the same as isolated band case [78]. The gauge dependent part is optimized by unitary transformation of the selected Bloch wave functions according to the gradient of spread function. For the first step, three parameters are used to control the self-consistence loop. They are 'Wannier.Dis.SCF.Max.Steps', 'Wannier.Dis.Conv.Criterion', and 'Wannier.Dis.Mixing.Para'. They are the maximum number of SCF loops, the convergence criterion, and the parameter to control the mixing of input and output subspace projectors, respectively.

```
Wannier.Dis.SCF.Max.Steps         2000         # default 200
Wannier.Dis.Conv.Criterion        1e-12        # default 1e-8
Wannier.Dis.Mixing.Para           0.5          # default value is 0.5
```

For the second step, three minimization methods are available. One is a steepest decent (SD) method, and the second one is a conjugate gradient (CG) method. The third one is a hybrid method which uses the SD method firstly and then switches to the CG method. The keyword 'Wannier.Minimizing.Scheme' indicates which method to be used. '0', '1', and '2' mean the simple SD method, the CG method, and hybrid method, respectively. The step length for the SD method is set by the keyword 'Wannier.Minimizing.StepLength'. In the CG method, a secant method is used to determine the optimized step length. The maximum secant steps and initial step length is specified by 'Wannier.Minimizing.Secant.Steps' and 'Wannier.Minimizing.Secant.StepLength', respectively. The maximum number of minimization step and convergence criterion are controlled by 'Wannier.Minimizing.Max.Steps' and 'Wannier.Minimizing.Conv.Criterion', respectively.

```
Wannier.Minimizing.Scheme             2     # default 0, 0=SD 1=CG 2=hybrid
Wannier.Minimizing.StepLength        2.0    # default 2.0
Wannier.Minimizing.Secant.Steps       5     # default 5
Wannier.Minimizing.Secant.StepLength 2.0    # default 2.0
Wannier.Minimizing.Conv.Criterion   1e-12   # default 1e-8
Wannier.Minimizing.Max.Steps         200    # default 200
```

In the hybrid minimization scheme, SD and CG have the same number of maximum minimization steps as specified by 'Wannier.Minimizing.Max.Steps'.

Restarting optimization without calculating overlap matrix

If the overlap matrix $M_{mn}^{(\mathbf{k},\mathbf{b})}$ has been calculated and stored in a disk file, the keyword 'Wannier.Readin.Overlap.Matrix' can be set as 'on' to restart generating MLWF without calculating $M_{mn}^{(\mathbf{k},\mathbf{b})}$ again.

```
Wannier.Readin.Overlap.Matrix       off      # default is on
```

This can save the computational time since the calculation of overlap matrix is time consuming. The code will read the overlap matrix as well as the eigenenergies and states from the disk file. One should keep in mind that the outer window and k grid should be the same as those used for calculating the stored overlap matrix and eigenvalues. Consistence will be checked in the code. The inner window, initial guess of MLWF as well as the convergence criteria can be adjusted for restarting optimization. If 'Wannier.Readin.Overlap.Matrix' is set as 'off', the overlap matrix will be calculated and automatically stored into a disk file. The file name is defined by 'System.Name' with extension '.mmn'. The eigenenergies and states are also stored in the disk file with extension '.eigen'.

39.2 Analysis

Plotting interpolated band structure

To plot the interpolated band structure, set 'Wannier.Interpolated.Bands' to be 'on'.

```
Wannier.Interpolated.Bands              on    # on|off, default=off
```

Other necessary settings, like k-path and sampling density along each path, are borrowed from those for plotting band dispersion in OpenMX. Therefore, the keyword 'Band.dispersion' should be set as 'on' in order to draw interpolated band structure. After convergence, interpolated band dispersion data will be found in a file with the extension name '.Wannier_Band', which has the same format as '.Band' file. As an example, the interpolated band structure of Si in diamond structure is shown together with its original band structure in Fig. 35(a).

Plotting MLWF

To plot the converged MLWFs, change the keyword 'Wannier.Function.Plot' to be 'on'. The default value of it is 'off'.

```
Wannier.Function.Plot                    on          # default off
Wannier.Function.Plot.SuperCells      1 1 1          # default=0 0 0
```

If it is turned on, all the MLWFs will be plotted. They are written in Gaussian Cube file format with the extension file name like '.mlwf1_4_r.cube'. The file is named in the same style as HOMO or LUMO molecular orbitals files. The first number after '.mlwf' indicates the spin index and the following one are index of MLWFs and the last letter 'r' or 'i' means the real or imaginary part of the MLWF. Users can set the supercell size for plotting MLWF. It is defined by the keyword 'Wannier.Function.Plot.SuperCells'. '1 1 1' in the above example means that the unit cell is extended by one in both the plus and minus directions along the a-, b-, and c-axes by putting the home unit cell at the center, and therefore the MLWFs are plotted in an extended cell consisting of 27 (= (1∗2+1)∗(1∗2+1)∗(1∗2+1)) cells in this case. Figure 35(b) shows one of the eight converged MLWFs from four valence states and four conduction states near Fermi level of Si in diamond structure.

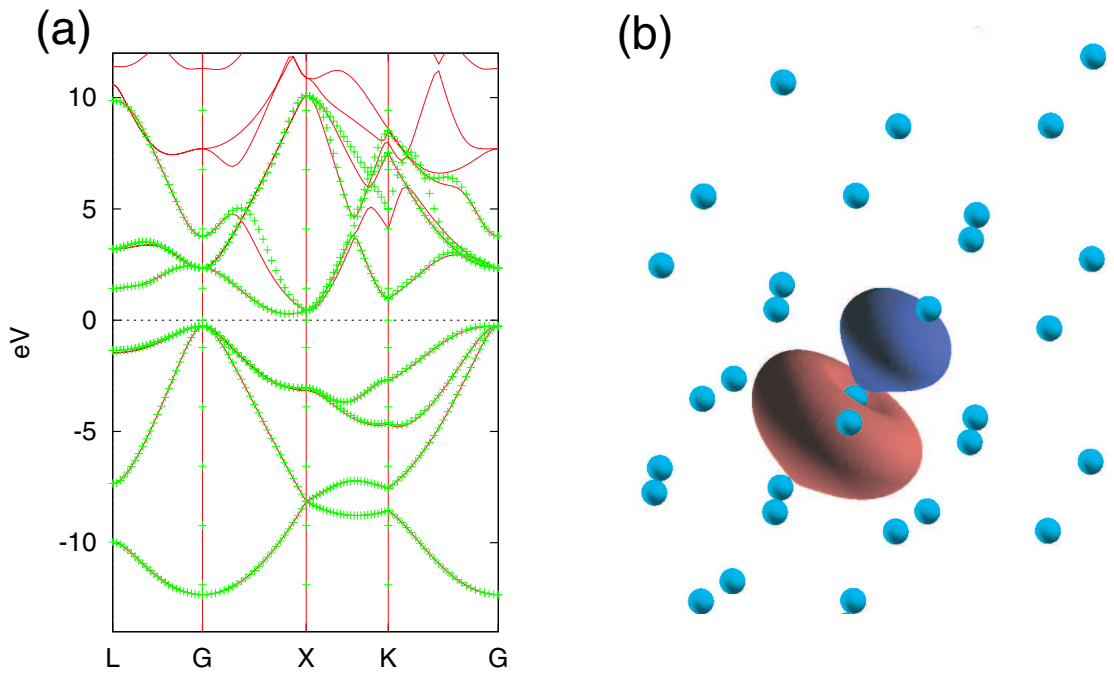

Figure 35: (a) The interpolated band structure (symbolic line) of Si in diamond structure is compared with original band structure (solid line). (b) One of the eight converged MLWFs from four valence states and four conduction states near Fermi level of Si in diamond structure. It is obtained with an initial guess of sp3 hybrid.

39.3 Monitoring Optimization of Spread Function

The output during optimization steps is printed to standard output. To monitor the optimization progress, the following method may be helpful. For convenient, we assume the standard output is stored in a file 'stdout.std'. The following example is for Si.dat which can be found in openmx*.*/work/wf_example, and each user can trace the same calculation.

DISE

Monitor the self-consistent loops for disentangling progress (the first step of optimization):

```
% grep "DISE" stdout.std

|  Iter  | Omega_I (Angs^2) | Delta_I (Angs^2) |  ---> DISE
|     1  |   18.371525257652|   18.371525257652|  ---> DISE
|     2  |   17.955767336391|   -0.415757921261|  ---> DISE
|     3  |   17.659503060694|   -0.296264275698|  ---> DISE
|     4  |   17.454033576174|   -0.205469484520|  ---> DISE
|     5  |   17.311180447271|   -0.142853128902|  ---> DISE
|     6  |   17.210945408916|   -0.100235038355|  ---> DISE
|     7  |   17.139778800398|   -0.071166608519|  ---> DISE
|     8  |   17.088603102826|   -0.051175697572|  ---> DISE
```

```
|     9  |   17.051329329614|   -0.037273773211|  ---> DISE
|    10  |   17.023842837298|   -0.027486492316|  ---> DISE
........
.....
...
.
```

where 'Iter', 'Omega_I', and 'Delta_I' mean the iteration number, the gauge invariant part of the spread function, and its difference between two neighboring steps. The criterion given by the keyword 'Wannier.Dis.Conv.Criterion' is applied to 'Delta_I'.

CONV

Monitor the optimization of the gauge dependent part of the spread function (the second step of optimization):

```
 % grep "CONV" stdout.std

Opt Step |Mode of Gradient|d_Omega_in_steps|     d_Omega   | (in Angs^2) ---> CONV
| SD    1 | 6.52434844E-01 | 5.41612774E-04 |-5.41340331E-04|  ---> CONV
| SD    2 | 6.51123660E-01 | 5.40524307E-04 |-5.40253165E-04|  ---> CONV
 .....
 .....
| SD  200 | 4.77499752E-01 | 3.96392019E-04 |-3.96271308E-04|  ---> CONV
|Opt Step |Mode of Gradient|     d_Omega    | (Angs^2) ---> CONV
| CG    1 | 8.61043764E-01 | -3.24716990E-01|  ---> CONV
 .....
 .....
| CG   58 | 1.67083857E-12 | -5.37225101E-13|  ---> CONV
| CG   59 | 5.44431651E-13 | -1.98972260E-13|  ---> CONV
************************************************************ ---> CONV
                  CONVERGENCE ACHIEVED !                     ---> CONV
************************************************************ ---> CONV
                  CONVERGENCE ACHIEVED !                     ---> SPRD
```

where 'Opt Step' and 'Modu.of Gradient' are the optimization step in either 'SD' or 'CG' method and the modulus of gradient of the spread function. The difference between two neighboring steps in the gauge dependent spread functions is calculated in two different way in the SD method, giving 'd_Omega_in_steps' and 'd_Omega'. 'd_Omega_in_steps' is given by

$$d\Omega = \epsilon \sum_{\mathbf{k}} ||G^{(\mathbf{k})}||^2,$$

where ϵ is the step length, $G^{(\mathbf{k})}$ is the gradient of the spread function. The details of the equation can be found in Ref. [78]. On the other hand, 'd_Omega' is given by

$$d\Omega = \Omega^{(n+1)} - \Omega^{(n)},$$

where n is the iteration number. In the CG method, only 'd_Omega' is evaluated. The criterion given by the keyword 'Wannier.Minimizing.Conv.Criterion' is applied to 'Modu.of Gradient'.

SPRD

Monitor the variation of spread of the Wannier functions:

```
 % grep "SPRD" stdout.std

|Opt Step |     Omega_I     |     Omega_D     |     Omega_OD  |    Tot_Omega   | (in Angs^2) ---> SPRD
| SD    1 |   16.93053479   |    0.13727387   |    6.57748455 |   23.64529321  |  ---> SPRD
| SD    2 |   16.93053479   |    0.13724827   |    6.57696989 |   23.64475295  |  ---> SPRD
| SD    3 |   16.93053479   |    0.13722279   |    6.57645620 |   23.64421378  |  ---> SPRD
| SD    4 |   16.93053479   |    0.13719743   |    6.57594347 |   23.64367569  |  ---> SPRD
 .....
 .....
| SD  199 |   16.93053479   |    0.13399285   |    6.48989479 |   23.55442243  |  ---> SPRD
| SD  200 |   16.93053479   |    0.13398326   |    6.48950811 |   23.55402616  |  ---> SPRD
|Opt Step |     Omega_I     |     Omega_D     |     Omega_OD  |    Tot_Omega   | (Angs^2) ---> SPRD
| CG    1 |    16.93053479  |     0.15480701  |    6.14396737 |   23.22930917  |  ---> SPRD
| CG    2 |    16.93053479  |     0.17172507  |    5.87830203 |   22.98056189  |  ---> SPRD
| CG    3 |    16.93053479  |     0.17012089  |    5.78940789 |   22.89006357  |  ---> SPRD
 .....
 .....
| CG   57 |    16.93053479  |     0.16557875  |    5.73752928 |   22.83364282  |  ---> SPRD
| CG   58 |    16.93053479  |     0.16557876  |    5.73752928 |   22.83364282  |  ---> SPRD
| CG   59 |    16.93053479  |     0.16557876  |    5.73752928 |   22.83364282  |  ---> SPRD
************************************************************ ---> SPRD
                 CONVERGENCE ACHIEVED !                      ---> SPRD
************************************************************ ---> SPRD
```

where 'Opt Step' is the optimization step in either 'SD' or 'CG' method. 'Omega_I' is the gauge invariant part of spread function. 'Omega_D' and 'Omega_OD' are the gauge dependent diagonal and off-diagonal contribution, respectively. 'Tot_Omega' is the sum up of all the above three components of the spread function.

CENT

Monitor the variation of Wannier function center:

```
% grep "CENT" stdout.std
WF   1 ( 1.14164289, 1.14164298, 1.14164266) |   2.95573380  --->CENT
WF   2 ( 1.55716251, 1.55716342, 1.14164203) |   2.95572597  --->CENT
WF   3 ( 1.55716191, 1.14164295, 1.55716190) |   2.95572978  --->CENT
WF   4 ( 1.14164389, 1.55716087, 1.55716055) |   2.95572957  --->CENT
WF   5 ( 0.20775982, 0.20775967, 0.20775893) |   2.95572677  --->CENT
WF   6 ( 0.20776045,-0.20775959,-0.20775914) |   2.95572605  --->CENT
WF   7 (-0.20775851, 0.20775981,-0.20775888) |   2.95572925  --->CENT
WF   8 (-0.20775787,-0.20775767, 0.20775933) |   2.95573335  --->CENT
Total Center ( 5.39761509, 5.39761243, 5.39760738) sum_spread  23.64583455 --->CENT
 SD     1 ------------------------------------------------------------------------> CENT
```

```
WF   1 ( 1.14164582, 1.14164592, 1.14164559) |   2.95566613  --->CENT
WF   2 ( 1.55715957, 1.55716049, 1.14164497) |   2.95565831  --->CENT
WF   3 ( 1.55715897, 1.14164588, 1.55715897) |   2.95566211  --->CENT
WF   4 ( 1.14164683, 1.55715794, 1.55715761) |   2.95566190  --->CENT
WF   5 ( 0.20775689, 0.20775673, 0.20775599) |   2.95565910  --->CENT
WF   6 ( 0.20775752,-0.20775666,-0.20775620) |   2.95565838  --->CENT
WF   7 (-0.20775558, 0.20775687,-0.20775594) |   2.95566158  --->CENT
WF   8 (-0.20775493,-0.20775474, 0.20775639) |   2.95566569  --->CENT
Total Center ( 5.39761509, 5.39761243, 5.39760738) sum_spread  23.64529321 --->CENT
 SD     2 ------------------------------------------------------------------------> CENT
 .....
 .....
 CG    59 ------------------------------------------------------------------------> CENT
WF   1 ( 1.14585349, 1.14584696, 1.14584386) |   2.85421846  --->CENT
WF   2 ( 1.55295615, 1.55294970, 1.14584792) |   2.85422167  --->CENT
WF   3 ( 1.55296133, 1.14584610, 1.55295139) |   2.85421070  --->CENT
WF   4 ( 1.14584053, 1.55296761, 1.55296391) |   2.85417080  --->CENT
WF   5 ( 0.20356211, 0.20355857, 0.20355600) |   2.85418933  --->CENT
WF   6 ( 0.20355119,-0.20355008,-0.20355192) |   2.85422458  --->CENT
WF   7 (-0.20355306, 0.20355395,-0.20355905) |   2.85420611  --->CENT
WF   8 (-0.20355603,-0.20356000, 0.20355520) |   2.85420117  --->CENT
Total Center ( 5.39761571, 5.39761281, 5.39760730) sum_spread  22.83364282 --->CENT
```

where the optimization method and step is indicated by starting with 'SD' or 'CG'. Lines starting with 'WF' show the center of each Wannier function with (x, y, z) coordinates in $\mathring{A}$ unit. and its spread in $\mathring{A}^2$. The sum up of all the Wannier functions center and spread are given in the the line starting with 'Total Center'.

39.4 Examples for generating MLWFs

Examples for different materials are prepared in the installation directory: work/wf_example.

- Benzene.dat

  for generating six p_z-orbital like Wannier functions from benzene's six π molecular orbitals.

- GaAs.dat

  for generating maximally localized Wannier functions from four valence bands of GaAs.

- Si.dat

  for generating eight Wannier functions by including both valence and conduction bands of Si. The initial guess is sp3 hybrids.

- symGra.dat

  for generating the Wannier function for graphene sheet. The initial guess is sp2 hybrids and p_z orbitals on carbon atoms.

- pmCVO.dat

  for generating t_{2g}-like Wannier functions for cubic perovskite $CaVO_3$ without spin polarization calculation.

- NC_CVO.dat

  similar to the case of pmCVO.dat except for the inclusion of spin-orbit coupling.

- GaAs_NC.dat

  similar to the case of GaAs.dat but spin-orbit coupling is included.

- VBz.dat

  for generating Wannier functions for Vanadium-Benzene infinite chain, which is studied in Ref. [58].

39.5 Output files

Additional four files generated by the calculation are explained below. They have different extension names. '.mmn' file is for storing the overlap matrix elements $M_{mn}^{(\mathbf{k},\mathbf{b})}$. '.amn' is for the initial guess projection matrix element $A_{mn}^{(\mathbf{k})}$. '.eigen' is for the eigenenergies and eigenstates at each k point. The '.HWR' file is for the hopping integrals among MLWFs on a set of lattice vectors which lies in the Wigner-Seitz supercells conjugated with the sampled k grids. For restarting optimization calculation, '.mmn' file will be read instead of written. More detailed information of the four files will be given below.

A. File format of '.mmn' file

This file structure is closely following that in Wannier90 [87]. The first line of this file is the description of the numbers in the second line. The numbers from left to right in the second line are the number (N_{win}) of included bands within the outer window, the number of k points, the number of **b** vectors, the number of spin component, respectively. The next lines are data blocks of $M_{mn}^{(\mathbf{k},\mathbf{b})}$. The most outer loop is for spin component. The next is the loop of **k** points and then **b** vectors. The most inner loops are the band index n and m, respectively. In each block, the first line are 5 numbers. The first two numbers are the index of present **k** point and the index of neighboring point **k+b**, respectively. The next three numbers indicates in which unit cell **k+b** point lies. From the second line are the real and imaginary part of each matrix element. In each block, there are $N_{win} \times N_{win}$ complex numbers. An example file, generated by the input file 'Si.dat', is shown here:

```
Mmn_zero(k,b). band_num, kpt_num, bvector num, spinsize
           10           512            8            1
    1  512    0    0    0
    0.571090282808   -0.819911068319
    0.000031357498   -0.000045367307
   -0.000149292597    0.000215591228
   -0.003821911756    0.005522040495
    0.028616452988    0.019804944108
```

```
 0.003677357735    0.002544970842
-0.006610037555   -0.004574771451
-0.000950861169   -0.000658076633
-0.000000008855    0.000000005272
 ........
 .....
 ...
 .
```

B. File format of '.amn' file

This file structure is closely following that in Wannier90 [87]. The first line of the file is the description of the whole file. Obviously, the four numbers in the second line are the number (N_{win}) of bands within the outer window, the number of k points, the number of target MLWFs and the number of spin component, respectively. Similarly, the data blocks are written in loops. The most outer loop is spin component and then **k** points, target MLWFs and number of bands. As described in the first line of this file. In each block, the first three integers are the band index, the index of MLWFs and index of k points, respectively. The next are real and imaginary of that matrix element. An example file, generated by the input file 'Si.dat', is shown here:

```
Amn. Fist line BANDNUM, KPTNUM, WANNUM, spinsize. Next is m n k...
          10          512            8            1
    1    1    1    0.053943539299    0.000161703961
    2    1    1   -0.000525446164   -0.000000008885
    3    1    1    0.002498021589    0.000000084311
    ... ...
    ... ...
   10    1    1   -0.000000023582   -0.000000000069
    1    2    1    0.053943534952    0.000161703965
    2    2    1    0.033382665372    0.000000493665
    3    2    1   -0.051189536188   -0.000001480360
    ........
    .....
    ...
    .
```

C. File format of '.eigen' file

This file contains the eigenenergies and eigenstates at each k point. The first line is the Fermi level of system. The number of bands is indicated in the second line of the file. The next data are mainly in two parts. The first part is the eigenenergies and the second one is the corresponding eigenstates. In each part, the loop of spin component is the most outer one. The next loop is k points, followed by band index. For eigenstates, there is one more inner loop for the basis set. An example file, generated by the input file 'Si.dat', is shown here:

```
Fermi level -0.112747
Number of bands 10
    1    1   -0.566228100179
    2    1   -0.122518136808
    3    1   -0.122518129040
    4    1   -0.122518115949
```

```
    5    1   -0.026598417854
    ... ...
    ... ...
WF kpt 1 (0.00000000,0.00000000,0.00000000)
1 1   0.4790338281  -0.0014359768
1 2   0.0440709749  -0.0001321095
1 3  -0.0000003333  -0.0000000000
    ........
    .....
    ...
    .
```

D. File format of '.HWR' file

This file contains the hopping integrals between the mth MLWF, $|m, \mathbf{0}\rangle$, in the home unit cell and the nth MLWF, $|n, \mathbf{R}\rangle$, in the unit cell at $\mathbf{R}$. The matrix element $\langle m, \mathbf{0}|\hat{H}|n, \mathbf{R}\rangle$ is written in the following way. In '.HWR' file, the first line is just a description. The number of MLWFs, number of lattice vectors inside of Wigner-Seitz supercell are in the second and third line, respectively. The unit cell vectors are given in the fifth, sixth and seventh lines. Spin polarization, whether it is a non-spin polarized calculation or a spin polarized one with collinear or noncollinear magnetic configuration, is given in the eighth line. The ninth line gives the Fermi level. From the tenth line, the block data starts. The outer most loop is spin component. The next loop is for $\mathbf{R}$ and the last two are loops of m and n, respectively. Each $\mathbf{R}$ is written at the first line of each block together with its degeneracy. The index of m and n is printed and followed by the real and imaginary parts of hopping integrals in each line. An example file, generated by the input file 'Si.dat', is shown here:

```
Real-space Hamiltonian in Wannier Gauge on Wigner-Seitz supercell.
Number of Wannier Function 8
Number of Wigner-Seitz supercell 617
Lattice vector (in Bohr)
   5.10000    0.00000    5.10000
   0.00000    5.10000    5.10000
   5.10000    5.10000    0.00000
collinear calculation spinsize 1
Fermi level -0.112747
R (   -6    2    2 )    4
   1     1     -0.000078903162   -0.000000003750
   1     2      0.000024237763   -0.000000000148
   1     3      0.000024237691   -0.000000000341
   1     4      0.000024238375    0.000000004117
   1     5      0.000072656918   -0.000000000196
   1     6     -0.000022470544   -0.000000000859
   1     7     -0.000022481557    0.000000000750
   1     8     -0.000022492706    0.000000000148
   2     1      0.000024238091    0.000000000049
```

```
2     2     -0.000078901874   -0.000000000011
2     3      0.000024234912   -0.000000000023
 ........
 .....
 ...
 .
```

39.6 Automatic running test of MLWF

To check whether the MLWF calculation part is properly installed or not, an automatic running test for the NEGF calculation can be performed by

For the MPI parallel running

```
% mpirun -np 16 openmx -runtestWF
```

For the OpenMP/MPI parallel running

```
% mpirun -np 8 openmx -runtestWF -nt 2
```

Then, OpenMX will run with eight test cases, and compare calculated results with the reference results which are stored in 'work/wf_example'. The comparison (absolute difference in the spread and Ω functions) is stored in a file 'runtestWF.result' in the directory 'work'. The reference results were calculated using a Xeon cluster machine. If the difference is within last seven digits, we may consider that the installation is successful.

40 Numerically exact low-order scaling method for diagonalization

A numerically exact low-order scaling method is supported for large-scale calculations [80]. The computational effort of the method scales as $O(N(\log N)^2)$, $O(N^2)$, and $O(N^{7/3})$ for one, two, and three dimensional systems, respectively, where N is the number of basis functions. Unlike $O(N)$ methods developed so far the approach is a numerically exact alternative to conventional $O(N^3)$ diagonalization schemes in spite of the low-order scaling, and can be applicable to not only insulating but also metallic systems in a single framework. The well separated data structure is suitable for the massively parallel computation as shown in Fig. 36. However, the advantage of the method can be obtained only when a large number of CPU cores are used for parallelization, since the prefactor of computational efforts can be large. When you calculate low-dimensional large-scale systems using a large number of CPU cores, the method can be a proper choice. To choose the method for diagonzalization, you can specify the keyword 'scf.EigenvalueSolver' as

```
scf.EigenvalueSolver     cluster2
```

The method is supported only for colliear DFT calculations of cluster systems or periodic systems with the Γ point for the Brillouin zone sampling. As well as the total energy calculation, the force

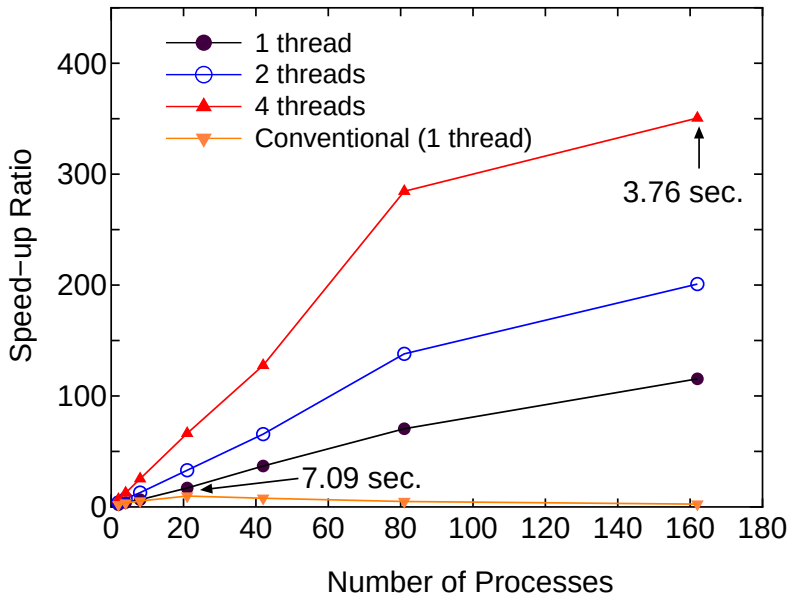

Figure 36: Speed-up ratio in the parallel computation of the diagonalization in the SCF calculation for DNA by a hybrid scheme using MPI and OpenMP. The speed-up ratio is defined by $2T_2/T_p$, where T_2 and T_p are the elapsed times obtained by two MPI processes and by the corresponding number of processes and threads. The parallel calculations were performed on a CRAY-XT5 machine consisting of AMD opteron quad core processors (2.3 GHz). The electric temperature of 700 K and 80 poles for the contour integration are used. For comparison, the speed-up ratio for the parallel computation of the conventional scheme using Householder and QR methods is also shown for the case with a single thread. The elapsed time at cases pointed by arrow is also shown for both the low-order scaling and conventional methods.

Table 7: Total energy of a C60 molecule calculated by the numerically exact low-order scaling method and conventional method, and its computational time (sec.) for the diagonalization using 8 processes in the MPI parallelization. The input file is *C60_LO.dat* in the directory 'work'.

Method	Total energy (Hartree)	Computational time (sec.)
Low-order	-343.896238929370	69.759
Conventional	-343.896238929326	2.784

calculation by the low-order scaling method is supported. Thus, it is possible to perform geometry optimization. However, calculations of density of states and wave functions are not supported yet. The number of poles in the contour integration [55] is controlled by a keyword:

```
scf.Npoles.ON2              90
```

The number of poles to achieve convergence does not depend on the size of system [80], but depends on the spectrum radius of system. If the electronic temperature more 300 K is used, the use of 100 poles is enough to get sufficient convergence for the total energy and forces. As an illustration, we show a calculation by the numerically exact low-order scaling method using an input file 'C60_LO.dat' stored in the directorty 'work'.

```
% mpirun -np 8 openmx C60_LO.dat
```

As shown in Table 7, the total energy by the low-order scaling method is equivalent to that by the conventional method within double precision, while the computational time is much longer than that of the conventional method for such a small system. We expect that the crossing point between the low-order scaling and the conventional methods with respect to computational time is located at around 300 atoms when using more than 100 cores for the parallel computation, although it depends on the dimensionality of system.

41 Effective screening medium method

41.1 General

The effective screening medium (ESM) method is a first-principles computational method for charged or biased systems consisting of a slab [81, 82, 83, 84]. In this method, a 2-dimensional periodic and 1-dimensional optional boundary conditions are imposed on a model cell (Fig. 37(a)), and the Poisson's equation is solved under those set of boundary conditions by using the Green's function method. An isolated slab, charged slab, and a slab under an uniform electric field can be treated by introducing the following combinations of semi-infinite media (ESMs).

(a) Isolated slab: vacuum (relative permittivity $\varepsilon = 1$) + vacuum

(b) Charged slab: vacuum + ideal metal (relative permittivity $\varepsilon = \infty$)

(c) Slab under an electric filed: ideal metal + ideal metal

Here 'slab' means a system consisting of molecules spaced out 2-dimensionally as well as a slab generally used as a surface model. An isolated slab model can be used for investigations of a polarized substrate, and charged slab model is applicable to a simulation of an electrode surface. A slab model under an electric filed sandwiched between two ideal-metal media would be appropriate for a material located in a metal capacitor. In OpenMX, a unit cell used in an ESM-method calculation is constructed as follows (see Fig. 37(a)):

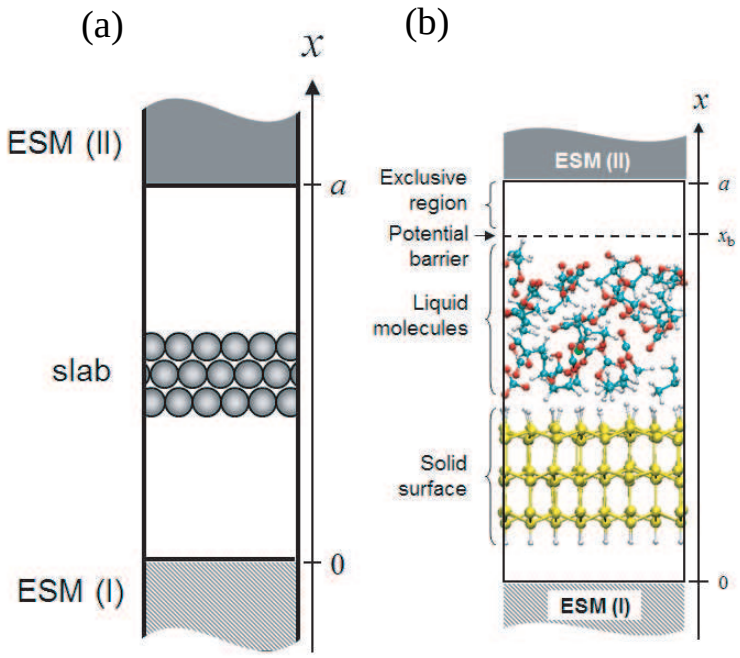

Figure 37: (a) Schematic view of a slab with semi-infinite media (ESMs). ESM (I) and (II) are placed at cell-boundaries, x = 0 and a (a: the length of the cell along x-axis), respectively. (b) An example of a unit cell for a MD calculation of solid surface-liquid interface model system with the ESM method. The slab and ESMs are placed parallel to the y-z plane.

1. The a-axis of the cell is perpendicular to the **b-c** plane and is parallel to the x-axis.
2. Two periodic boundary conditions are set in y- and z-axis directions
3. ESMs are placed at the cell-boundaries (x = 0 and a).
4. The origin of the x-axis is set at the cell boundary.
5. A fractional coordinate for x-axis is designated between 0 and 1.

A calculation based on an ESM-method can be performed by the following keyword:

```
ESM.switch              on3      # off, on1=v|v|v, on2=m|v|m, on3=v|v|m, on4=on2+EF
ESM.buffer.range        4.5      # default=10.0 (ang),
```

where on1, on2, on3, and on4 represent combinations of ESMs, 'vacuum + vacuum', 'ideal metal + ideal metal', 'vacuum + ideal metal', and 'ideal metal + ideal metal under an electric field', respectively. The keyword 'ESM.buffer.range' indicates the width of a exclusive region for atoms with ESM (unit is Å), which is necessary in order to prevent overlaps between wave functions and ESM.

1. ESM.switch = on1:

   Both ESM (I) and (II) are semi-infinite vacuum media. In this case, note that the total charge of a calculation system should be neutral. The keyword 'scf.system.charge' should be set to be zero.

2. ESM.switch = on2:

   Both ESM (I) and (II) are semi-infinite ideal-metal media. One can deal with charged systems. The keyword 'scf.system.charge' can be set to be a finite value.

3. ESM.switch = on3:

   ESM (I) and (II) are a semi-infinite vacuum and ideal metal medium, respectively. One can deal with charged systems. The keyword 'scf.system.charge' can be set to be a finite value.

4. ESM.switch = on4:

   An electric field is imposed on the system with the same combination of ESMs to 'on2'. By using the following keyword, one can impose a uniform electric field on a calculation system;

   ```
   ESM.potential.diff        1.0      # default=0.0 (eV),
   ```

   where one inputs a potential difference between two semi-infinite ideal-metal media with reference to the bottom ideal metal (unit is eV). The electric filed is decided by the length of the cell, a, and the potential difference.

5. In case of MD calculations with the ESM method:

   One can implement MD calculations of solid surface-liquid interface systems with any combinations of ESMs. A surface-model slab and a liquid region should be located as shown in Fig. 37(b). In order to restrict liquid molecules within a given region, an cubic barrier potential can be introduced by using the following keyword (see Fig. 37(b)):

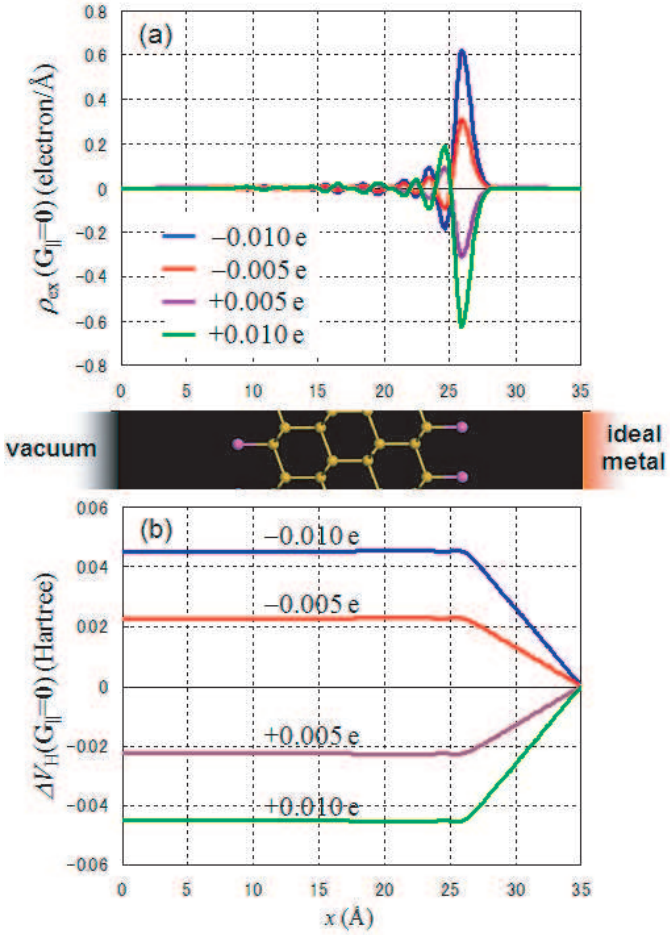

Figure 38: Al-Si(111) slab model with vacuum and ideal-metal ESMs; (a) Distributions of excess charge in Al-Si(111) slab, $\rho_{\rm ex}$; (b) Bias-induced changes of Hartree potentials of Al-Si(111) slab, $\Delta V_{\rm H}$. The number of doped charge is -0.01, -0.005, +0.005, and +0.01 e. Each plot is obtained as a difference in difference charge or difference Hartree potential with reference to a neutral slab with the same ESMs.

```
ESM.wall.position          6.0       # default=10.0 (ang)
ESM.wall.height          100.0       # default=100.0 (eV),
```

where 'ESM.wall.position' denotes the distance between the upper edge of the cell and the origin of the barrier potential, $a - x_b$, and 'ESM.wall.height' is the height of the potential (value of potential energy) at $x = x_b + 1.0$ (Å). It is also recommended to fix positions of atoms on the bottom of a surface-model slab during a MD run.

41.2 Example of test calculation

Let us show effects of ESMs on the electronic structure of a system. As a demonstration calculation, the distribution of excess charge $\rho_{\rm ex}$ in a 1×1 Al-terminated Si(111) slab under the boundary condition, 'vacuum + ideal metal' (ESM.switch = on3), is presented in Fig. 38(a) (the input file of this test

calculation 'Al-Si111_ESM.dat' is found in the work directory). It can be seen that segregation of the doped charge in the slab happened due to the attractive interaction between the doped and the corresponding mirror charges. Figure 38(b) indicates the change of the Hartree potential ΔV_{H} corresponding to each condition indicated in Fig. 38(a), where the potential inside the Al-Si(111) slab and the electric field between the slab and the ideal-metal medium change according to the amount of the doped charge.

42 Nudged elastic band (NEB) method

42.1 General

To search a minimum energy path (MEP) in geometrical phase space connecting two stable structures, a nudged elastic band (NEB) method based on Ref. [85] is supported in OpenMX Ver. 3.7. The detail of the implementation is summarized as follows:

- Calculation of tangents based on Eqs. (8)-(11) in Ref. [85]
- Calculation of perpendicular forces based on Eq. (4) in Ref. [85]
- Calculation of parallel forces based on Eq. (12) in Ref. [85]
- Optimization method based on a hybrid DIIS+BFGS optimizer

In order to minimize user's efforts in using it, the functionality of NEB has been realized as one of geometry optimizers with the following features:

- Easy to use
- Hybrid OpenMP/MPI parallelization
- Initial path by the straight line or user's definition
- Only three routines added

42.2 How to perform

The NEB calculation is performed by the following three steps:

1. Geometry optimization of a precursor
2. Geometry optimization of a product
3. Optimization of a minimum energy path (MEP) connecting the precursor and product

where in the three calculations users have to keep the same computational parameters such as unit cell, cutoff energy, basis functions, pseudopotentials, and electronic temperatures to avoid numerical inconsistency. After the calculations 1 and 2, files '*.dat#' are generated. By using the atomic coordinates in the files '*.dat#', one can easily construct an input file for the calculation 3. Once you have an input file for the calculation 3, the execution of the NEB calculation is the same as for the conventional OpenMX calculation such as

```
% mpirun -np 32 openmx input.dat -nt 4
```

42.3 Examples and keywords

Two input files are provided as example:

- C2H4_NEB.dat

  Cycloaddition reaction of two ethylene molecules to cyclobutane

- Si8_NEB.dat

  Diffusion of an interstitial hydrogen atom in the diamond Si

The input file 'C2H4_NEB.dat' will be used to illustrate the NEB calculation in the proceeding explanation.

Providing two terminal structures

The atomic coordinates of the precursor are specified in the input file by

```
<Atoms.SpeciesAndCoordinates
   1    C   -0.66829065594143    0.00000000101783   -2.19961193219289     2.0     2.0
   2    C    0.66817412917689   -0.00000000316062   -2.19961215251205     2.0     2.0
   3    H    1.24159214112072   -0.92942544650857   -2.19953308980064     0.5     0.5
   4    H    1.24159212192367    0.92942544733979   -2.19953308820323     0.5     0.5
   5    H   -1.24165800644131   -0.92944748269232   -2.19953309891389     0.5     0.5
   6    H   -1.24165801380425    0.92944749402510   -2.19953309747076     0.5     0.5
   7    C   -0.66829065113509    0.00000000341499    2.19961191775648     2.0     2.0
   8    C    0.66817411530651   -0.00000000006073    2.19961215383949     2.0     2.0
   9    H    1.24159211310925   -0.92942539308841    2.19953308889301     0.5     0.5
  10    H    1.24159212332935    0.92942539212392    2.19953308816332     0.5     0.5
  11    H   -1.24165799549343   -0.92944744948986    2.19953310195071     0.5     0.5
  12    H   -1.24165801426648    0.92944744880542    2.19953310162389     0.5     0.5
Atoms.SpeciesAndCoordinates>
```

The atomic coordinates of the product are specified in the input file by

```
<NEB.Atoms.SpeciesAndCoordinates
   1    C   -0.77755846408657   -0.00000003553856   -0.77730141035137     2.0     2.0
   2    C    0.77681707294741   -0.00000002413166   -0.77729608216595     2.0     2.0
   3    H    1.23451821718817   -0.88763832172374   -1.23464057728123     0.5     0.5
   4    H    1.23451823170776    0.88763828275851   -1.23464059022330     0.5     0.5
   5    H   -1.23506432458023   -0.88767426830774   -1.23470899088096     0.5     0.5
   6    H   -1.23506425800395    0.88767424658723   -1.23470896874564     0.5     0.5
   7    C   -0.77755854665393    0.00000000908006    0.77730136931056     2.0     2.0
   8    C    0.77681705017323   -0.00000000970885    0.77729611199476     2.0     2.0
   9    H    1.23451826851556   -0.88763828740000    1.23464060936812     0.5     0.5
  10    H    1.23451821324627    0.88763830875131    1.23464061208483     0.5     0.5
  11    H   -1.23506431230451   -0.88767430754577    1.23470894717613     0.5     0.5
  12    H   -1.23506433587007    0.88767428525317    1.23470902573029     0.5     0.5
NEB.Atoms.SpeciesAndCoordinates>
```

Keywords for the NEB calculation

The NEB calculation can be performed by setting the keyword 'MD.Type' as

```
MD.Type                 NEB
```

The number of images in the path is given by

```
MD.NEB.Number.Images        8           # default=10
```

where the two terminals are excluded from the number of images.
The spring constant is given by

```
MD.NEB.Spring.Const         0.1         # default=0.1(hartee/borh^2)
```

In most cases, the obtained path does not largely depend on the value.
The optimization of MEP is performed by a hybrid DIIS+BFGS scheme which is controlled by the following keywords:

```
MD.Opt.DIIS.History           4         # default=7
MD.Opt.StartDIIS             10         # default=5
MD.maxIter                  100         # default=1
MD.Opt.criterion         1.0e-4         # default=1.0e-4 (Hartree/Bohr)
```

The specification of these keywords are the same as for the geometry optimization. So, see the section 'Geometry optimization' in the manual for the details. Also, it is also possible to fix the atomic position by the keyword 'MD.Fixed.XYZ'.

Execution of the NEB calculation

One can perform the NEB calculation with the input file 'C2H4_NEB.dat' by

```
% mpirun np 16 openmx C2H4_NEB.dat
```

If the calculation is successfully completed, more than 24 files will be generated. Some of them are listed below:

```
c2h4.neb.opt          history of optimization for finding MEP
c2h4.neb.ene          total energy of each image
c2h4.neb.xyz          atomic coordinates of each image in XYZ format
C2H4_NEB.dat#         input file for restarting.
C2H4_NBE.dat_0        input file for the precursor
C2H4_NBE.dat_1        input file for the image 1
C2H4_NBE.dat_2        input file for the image 2
C2H4_NBE.dat_3        input file for the image 3
C2H4_NBE.dat_4        input file for the image 4
C2H4_NBE.dat_5        input file for the image 5
C2H4_NBE.dat_6        input file for the image 6
C2H4_NBE.dat_7        input file for the image 7
C2H4_NBE.dat_8        input file for the image 8
C2H4_NBE.dat_9        input file for the product
c2h4_0.out            output file for the precursor
```

```
c2h4_1.out            output file for the image 1
c2h4_2.out            output file for the image 2
c2h4_3.out            output file for the image 3
c2h4_4.out            output file for the image 4
c2h4_5.out            output file for the image 5
c2h4_6.out            output file for the image 6
c2h4_7.out            output file for the image 7
c2h4_8.out            output file for the image 8
c2h4_9.out            output file for the product
```

'c2h4.neb.opt' contains history of optimization for finding MEP as shown in Fig. 39(a). One can see the details at the header of the file as follows:

```
************************************************************
************************************************************
        History of optimization by the NEB method
************************************************************
************************************************************

  iter   SD_scaling     |Maximum force|   Maximum step        Norm        Sum of Total Energy of Images
                        (Hartree/Bohr)        (Ang)       (Hartree/Bohr)       (Hartree)

 1       0.37794520       0.12552253       0.04583483       0.49511548    -223.77375997
 2       0.37794520       0.08735938       0.03172307       0.35373414    -223.85373393
 3       0.37794520       0.05559291       0.01919790       0.25650527    -223.89469352
 4       0.37794520       0.03970051       0.01254863       0.20236344    -223.91689564
 5       0.45353424       0.03132536       0.01360864       0.17275416    -223.93128189
 6       0.45353424       0.02661456       0.01202789       0.15142709    -223.94412534
 7       0.45353424       0.02367627       0.01068250       0.13703973    -223.95422398
 .....
 ...
 .
```

Also, 'c2h4.neb.ene' and 'c2h4.neb.xyz' can be used to analyze the change of total energy as a function of the distance (Bohr) from the precursor and the structural change as shown in Fig. 39(b). The content of 'c2h4.neb.ene' is as follows:

```
#
# 1st column: index of images, where 0 and MD.NEB.Number.Images+1 are the terminals
# 2nd column: Total energy (Hartree) of each image
# 3rd column: distance (Bohr) between neighbors
# 4th column: distance (Bohr) from the image of the index 0
#
    0     -28.02131967       0.00000000       0.00000000
    1     -28.02125585       0.82026029       0.82026029
    2     -28.02086757       0.82124457       1.64150486
    3     -28.01974890       0.82247307       2.46397794
    4     -28.01724274       0.82231749       3.28629543
    5     -28.01205847       0.82220545       4.10850088
    6     -27.98707448       0.82271212       4.93121300
```

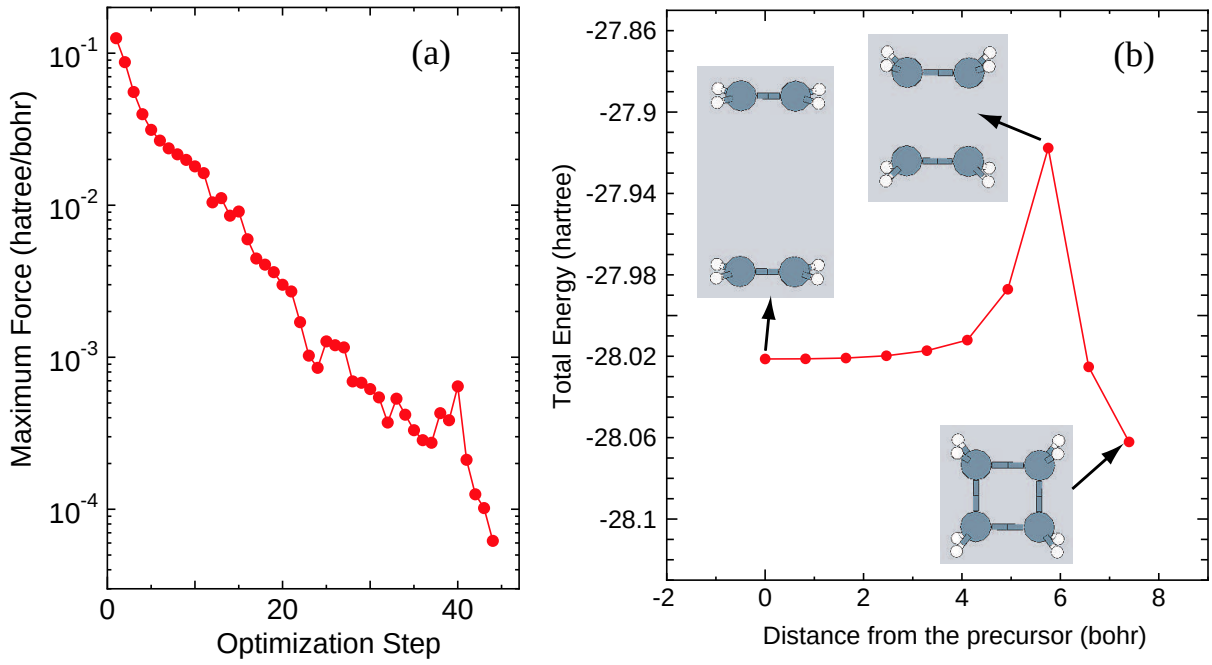

Figure 39: (a) History of optimization (c2h4.neb.opt) for the NEB calculation for a cycloaddition reaction of two ethylene molecules to a cyclobutane molecule, (b) change of total energy (c2h4.neb.ene) of two ethylene molecules as a function of the distance (Bohr) from the precursor and the corresponding geometrical structures (c2h4.neb.xyz) of images on the minimum energy path. The input file used for the NEB calculation is 'C2H4_NEB.dat' in the directory 'work'.

```
7      -27.91765377      0.82175187      5.75296486
8      -28.02520689      0.82164937      6.57461423
9      -28.06207901      0.82095145      7.39556568
```

where the first column is a serial number of image, while 0 and 9 correspond to the precursor and product, respectively. The second column is the total energy of each image. The third and fourth columns are interval (Bohr) between two neighboring images and the distance (Bohr) from the precursor in geometrical phase space. A file '*.dat_#', where '*' is 'System.Name' and '#' is a serial number for each image, is also generated, since each calculation for each image is basically done as an independent OpenMX calculation with a different input file. A corresponding output file '*_#.out' is also generated, which may be useful to analyze how the electronic structure changes on MEP.

As well as the case of 'C2H4_NEB.dat', one can perform the NEB calculation by 'Si8_NEB.dat'. After the successful calculation, you may get the history of optimization and change of total energy along MEP as shown in Fig. 40.

42.4 Restarting the NEB calculation

It often happens that the convergence is not achieved even after the maximum optimization step. In such a case, one has to continue the optimization as a new job starting from the last optimization step in the previous job. A file '*.dat#' is generated after every optimization step. The file contains a

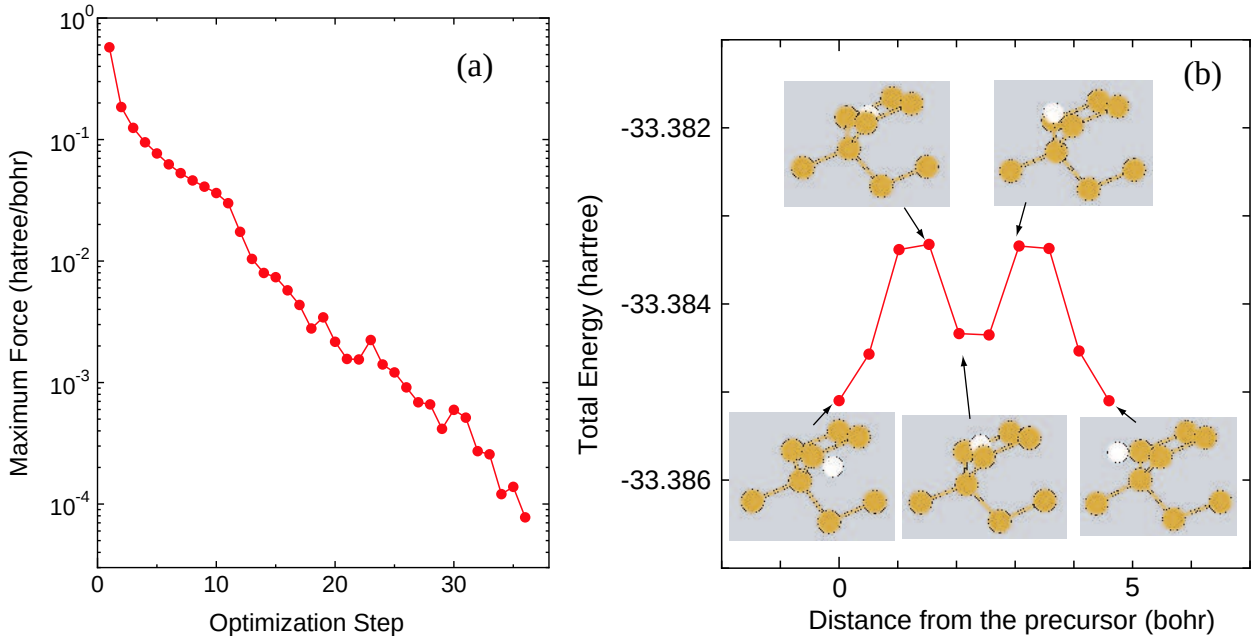

Figure 40: (a) History of optimization (si8_neb.neb.opt) for the NEB calculation for diffusion of an interstitial hydrogen atom in the diamond Si, (b) change of total energy (si8_neb.neb.ene) as a function of the distance (Bohr) from the precursor and the corresponding geometrical structures (si8_neb.neb.xyz) of images on the minimum energy path. The input file used for the NEB calculation is 'Si8_NEB.dat' in the directory 'work'.

series of atomic coordinates for images in the last step. One can restart the optimization using a file '*.dat#'.

42.5 User defined initial path

As default, the initial path connecting the precursor and the product is a straight line connecting them. However, in some cases the geometrical structure of images generated on the straight line can be very erratic so that distance between atoms can be too close to each other. In this case, one should explicitly provide the atomic coordinates of images. The user defined initial path can be provided by the same way as for the restarting. Then, one has to provide atomic coordinates for each image by the following keywords:

```
<NEB1.Atoms.SpeciesAndCoordinates
   1    Si    -0.12960866043083     0.13490502997627    -0.12924862991035      2.0      2.0
   2    Si    -0.40252421446808     5.19664433048606     4.91248322056082      2.0      2.0
   ...
NEB1.Atoms.SpeciesAndCoordinates>

<NEB2.Atoms.SpeciesAndCoordinates
   1    Si    -0.08436294149342    -0.02173837971883    -0.08374099211565      2.0      2.0
   2    Si    -0.33677725120015     5.10216241168093     5.01087499461541      2.0      2.0
   ...
NEB2.Atoms.SpeciesAndCoordinates>
```

For all the images of which number is given by 'MD.NEB.Number.Images', the atomic coordinates need to be provided. Also, it is required for a keyword to be switched on as

```
scf.restart     on
```

42.6 Monitoring the NEB calculation

In the NEB calculation, the standard output will display only that for the image 1, and those for the other images will not be displayed. However, there is no guarantee that the SCF iteration converges for all the images. In order to monitor the SCF convergence for all the images, temporary files can be checked by users. In the NEB calculation, an input file is generated for each image, whose name is '*.dat_#', where '#' runs from 0 to MD.NEB.Number.Images+1, and 'system.name' is modified as the original system.name_#. So, one can check the SCF convergence by monitoring a file 'system.name.DFTSCF', whether it converges or not.

42.7 Parallel calculation

In the NEB calculation, the setting for the parallelization will be automatically done depending on the number of processes and threads. However, it would be better to provide a proper number of processes for the MPI parallelization which can be divisible by the number of images given by 'MD.NEB.Number.Images', in order to achieve a good load balance in the MPI parallelization. It is noted that the number of processes for the MPI parallelization can exceed the number of atoms unlike the conventional calculation. The hybrid parallelization by OpenMP/MPI is also supported.

Although the default parallelization scheme works well in most cases, a memory shortage can be a serious problem when a small number of the MPI processes is used for large-scale systems. In the default MPI parallelization, the images are preferentially parallelized at first. When the number of MPI processes exceeds the number of images, the calculation of each image starts to be parallelized, where the memory usage starts to be parallelized as well. In this case, users may encounter a segmentation fault due to the memory shortage if many CPU cores are not available. To avoid such a situation, the following keyword is available.

```
MD.NEB.Parallel.Number    3
```

In this example, the calculations of every three images are parallelized at once where the MPI processes are classified to three groups and utilized for the parallelization of each image among the three images. In order to complete the calculations of all the images, the grouped calculations are repeated by floor[(the number of images)/(MD.NEB.Parallel.Number)] times. The scheme may be useful for the NEB calculation of a large-scale system. If the keyword is not specified in your input file, the default parallelization scheme is employed.

42.8 Other tips

It would be better to provide atomic coordinates for bulk systems in Ang or AU instead of FRAC, since the atomic position tends to be translated in FRAC to keep the fractional coordinate within 0 to 1. The translation tends to generate a confusing movie in the visualization of the result.

Only three routines are added to implement the NEB functionality. They are neb.c, neb_run.c, and neb_check.c. The main routine is neb.c. It may be easy to implement related methods in neb.c.

43 STM image by the Tersoff-Hamann scheme

Scanning tunneling microscope (STM) image can be obtained by the Tersoff-Hamann scheme [52]. The method is nothing but calculation of partial charge density in an energy window measured from the chemical potential. The calculation of the partial charge density is performed by the following keywords:

```
partial.charge                  on       # on|off, default=off
partial.charge.energy.window    0.0      # in eV
```

where the second keyword defines an energy window (in eV) measured from the chemical potential (a plus value means conduction band and negative valence). Since the calculation of the partial charge density is performed during calculation of the density of states (DOS), the following keywords have to be specified as well:

```
Dos.fileout                    on        # on|off, default=off
Dos.Erange               -20.0  20.0     # default = -20 20
Dos.Kgrid                   5 5 5        # default = Kgrid1 Kgrid2 Kgrid3
```

After the calculation with the keywords, you will get '*.pden.cube' which can be used for the STM simulation within the Tersoff-Hamman approximation. As an example, a simulated STM image of a graphene layer is shown in Fig. 41.

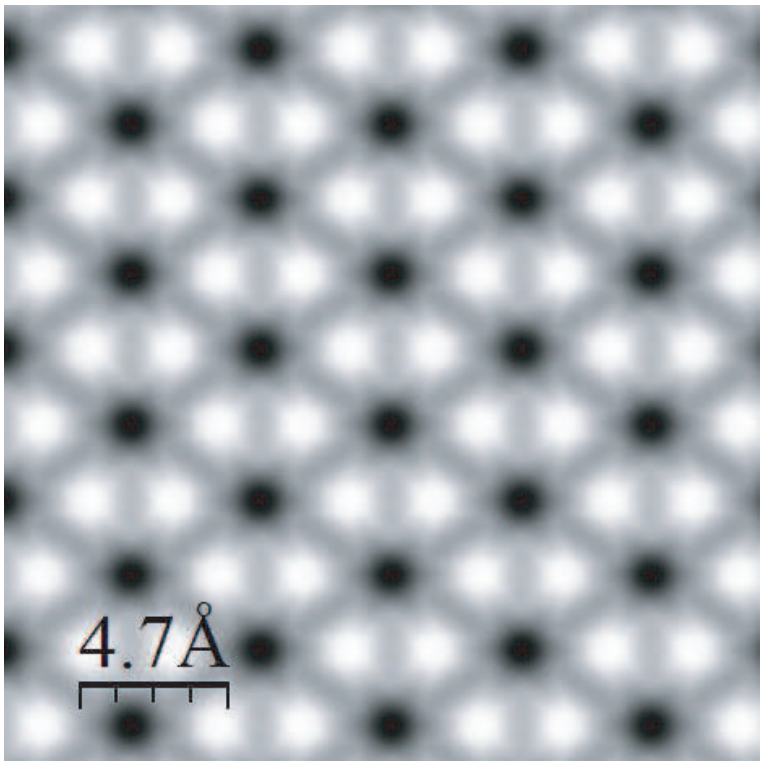

Figure 41: Simulated STM image of a graphene layer, where 'partial.charge.energy.window' of 2 eV was used in the calculation, and the input file is 'Graphene_STM.dat' in the directory 'work'. The cube file 'Graphene_STM.pden.cube' was visualized with an isovalue of 0.0001 by a software WSxM [92].

44 DFT-D2 method for vdW interaction

The DFT-D2 method by Grimme [86] is supported to include a vdW interaction. The following keywords are relevant to the DFT-D2 method.

```
scf.dftD                    on          # on|off, default=off
DFTD.Unit                  Ang          # Ang|AU
DFTD.rcut_dftD           100.0          # default=100 (DFTD.Unit)
DFTD.d                    20.0          # default=20
DFTD.scale6               0.75          # default=0.75
DFTD.IntDirection        1 1 1          # default=1 1 1 (1:on 0:off)
```

When you include the vdW correction, switch on 'scf.dftD'. The cutoff radius for the pairwise interaction is given by 'DFTD.rcut_dftD', where the unit is given by 'DFTD.Unit'. The 'd' value in Eq. (12) in Grimme's paper [86] is given by 'DFTD.d', while the default value is 20. The scaling factor in Eq. (11) in Grimme's papar [86] is given by 'DFTD.scale6', while the default value for the PBE functional is 0.75. Also, the interaction can be cut along the **a**-, **b**-, and **c**-axes by 'DFTD.IntDirection', where 1 means that the interaction is included, and 0 not. Also, the periodicity for each atom can be controlled by

```
<DFTD.periodicity
   1   1
   2   1
   3   1
   4   1
  ....
DFTD.periodicity>
```

where the first column is a serial number which is the same as in the 'Atoms.SpeciesAndCoordinates', and the second column is a flag which means that 1 is periodic, and 0 is non-periodic for the corresponding atom. By considering the periodicity or non-periodicity of each atom, the interaction is automatically cut when they are non-periodic.

The main modifications are placed at only two routines: DFTDvdW_init.c and Calc_EdftD() of Total_Energy.c. In DFTDvdW_init.c, you can easily change the parameters for the vdW correction, and in Calc_EdftD() of Total_Energy.c you can confirm how they are calculated.

Since OpenMX uses localized orbitals as basis function, it is very important to take account of basis set superposition error (BSSE) when we investigate an effect of a weak interaction such as vdW interaction. To estimate BSSE, the counterpoise (CP) method [33, 34] can be used. As for the CP method, see the Section 'Empty atom scheme'.

45 Calculation of Energy vs. lattice constant

45.1 Energy vs. lattice constant

The calculation of Energy vs. lattice constant is supported by the following keywords:

```
MD.Type                    EvsLC      #
MD.EvsLC.Step               0.4       # default=0.4%
MD.maxIter                  32        # default=1
```

When 'MD.Type' is set to 'EvsLC', the total energy is calculated step by step by changing unit cell vectors, **a**, **b**, and **c**. The change of unit cell vectors is done uniformly by expanding them by a percentage, where the reference is the initial vectors, specified with 'MD.EvsLC.Step'. The number of steps is specified by the keyword 'MD.maxIter'. After the calculation, you will obtain a file '*.EvsLC', where '*' is 'System.Name'. The columns in the file '*.EvsLC' are arranged in order of a_x, a_y, a_z, b_x, b_y, b_z, c_x, c_y, c_z in Å, and the total energy in Hartree, where $a(b,c)_x$, $a(b,c)_y$, and $a(b,c)_z$ are x-, y-, and z-coordinates of the **a**(**b**,**c**) vector, respectively. As an example, calculation of Energy vs. lattice for the fcc Mn bulk is shown in Fig. 42, where the equilibrium lattice constant and bulk modulus were evaluated by fitting the data to the Murnaghan equation of state with a code 'murn.f' provided on the web site [88].

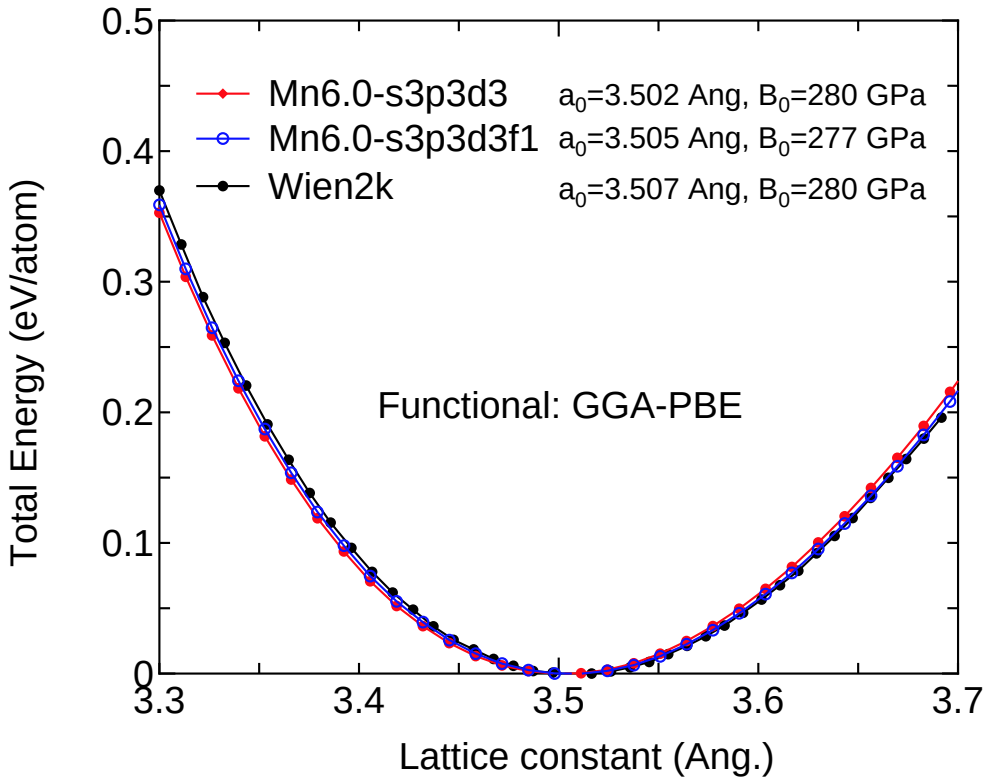

Figure 42: Total energy vs. lattice constant for the fcc Mn bulk calculated by the keyword 'EvsLC'. The input file used for the calculation is 'Mnfcc-EvsLC.dat' in the directory 'work'.

45.2 Delta factor

As well as 'EvsLC', a similar functionality is provided as

```
MD.Type                         DF
```

by which OpenMX automatically calculates the total energy of the system with volumes of -6, -4, -2, 0, 2, 4, and 6 %, where the original structure given in the input file is taken to be the reference. The regulation of volume is simply performed by considering uniform change of lattice vectors, **a**-, **b**-, and **c**-axes. The volume and the corresponding total energy are output to a file '*.DF'. The data can be used to calculate the delta factor proposed in Ref. [27].

46 Fermi surface

The Fermi surface is visualized by XCrySDen [61]. When you perform calculations of the density of states by the following keywords:

```
Dos.fileout                 on          # on|off, default=off
Dos.Erange              -20.0  20.0     # default = -20 20
Dos.Kgrid                 61 61 61      # default = Kgrid1 Kgrid2 Kgrid3
```

you will obtain a file '*.FermiSurf0.bxsf', where '*' is 'System.Name', and the file can be visualized by XCrySDen [61]. As well as 'Dos.Fileout', 'DosGauss.fileout' can be also used for the purpose. In case of spin-polarized calculations, two files are generated as '*.FermiSurf0.bxs' and '*.FermiSurf1.bxs' for spin-up and spin-down states, respectively. In case of non-collinear calculations, a file '*.FermiSurf.bxs' is generated. It is noted that a large number of **k**-points should be used in order to obtain a smooth Fermi surface. As an example, Fermi surfaces of the fcc Ca bulk are shown in Fig. 43. The input file used for the calculation is 'Cafcc_FS.dat' in the directory 'work'.

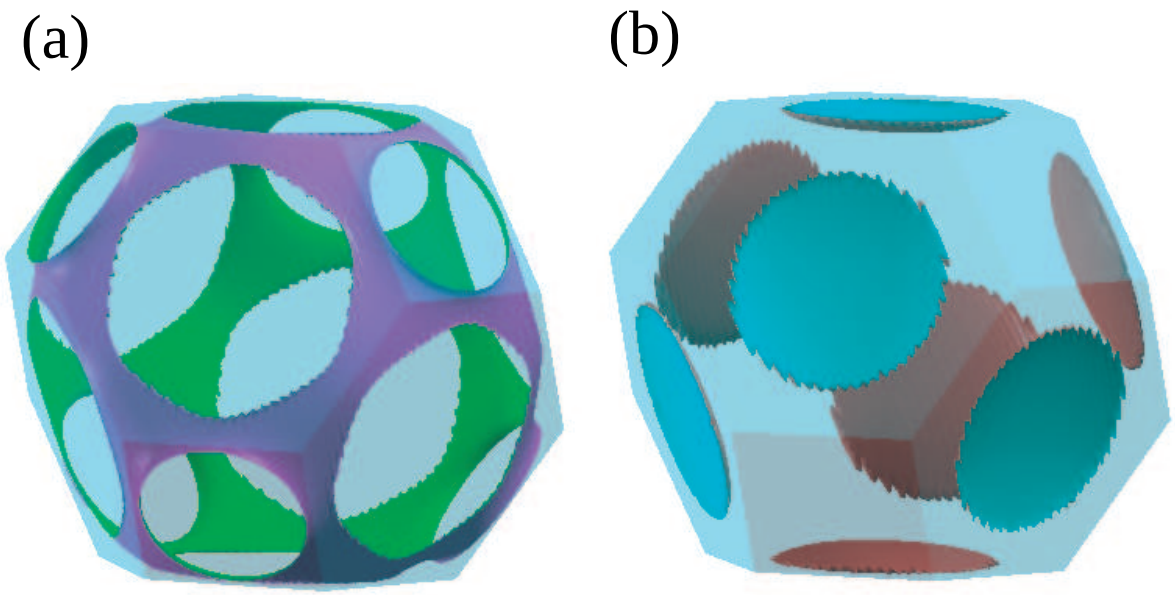

Figure 43: Fermi surfaces of the fcc Ca bulk visualized by XCrySDen [61]. Since two sorts of bands intersect with the Fermi energy (chemical potential), two Fermi surfaces are shown in (a) and (b). The input file used for the calculation is 'Cafcc_FS.dat' in the directory 'work'.

47 Analysis of difference in two Gaussian cube files

A utility tool is provided to generate a Gaussian cube file which stores the difference between two Gaussian cube files for total charge density, spin density, and potentials. If you analyze the difference between two states, this tool would be useful.

(1) Compiling of diff_gcube.c

There is a file 'diff_gcube.c' in the directory 'source'. Compile the file as follows:

```
% gcc diff_gcube.c -lm -o diff_gcube
```

When the compile is completed normally, then you can find an executable file 'diff_gcube' in the directory 'source'. Please copy the executable file to the directory 'work'.

(2) Calculation of the difference

If you want to know the difference between two Gaussian cube files 'input1.cube' and 'input2.cube', and output the result to a file 'output.cube', then perform the executable file as follows:

```
% ./diff_gcube input1.cube input2.cube output.cube
```

The difference is output to 'output.cube' in the Gaussian cube format. Thus, you can easily visualize the difference using many software, such XCrySDen [61] and Molekel [60]. In fact, Fig. 22 in the Section 'Electric field' was made by this procedure.

48 Analysis of difference in two geometrical structures

A utility tool is provided to analyze the difference between two geometrical coordinates in two xyz files which store Cartesian coordinates. The following three analyses are supported: a root mean square of deviation (RMSD) between two Cartesian coordinates defined by

$$\mathrm{RMSD} = \sqrt{\frac{\sum_i^{N_{\mathrm{atom}}} (R_i - R_i^0)^2}{N_{\mathrm{atom}}}}$$

a mean deviation (MD) between two Cartesian coordinates defined by

$$\mathrm{MD} = \frac{\sum_i^{N_{\mathrm{atom}}} |R_i - R_i^0|}{N_{\mathrm{atom}}}$$

and a mean deviation between bond lengths (MDBL) defined by

$$\mathrm{MDBL} = \frac{\sum_i^{N_{\mathrm{bond}}} |BL_i - BL_i^0|}{N_{\mathrm{bond}}}$$

where N_{atom} and N_{bond} are the number of atoms and the number of bonds with bond length (BL) within a cutoff radius. Also, the deviation vector between xyz coordinate of each atom is output to a xsf file 'dgeo_vec.xsf' in the XCrySDen format. If you analyze the difference between two geometries, this tool would be useful.

(1) Compiling of diff_gcube.c

There is a file 'diff_gcube.c' in the directory 'source'. Compile the file as follows:

```
% gcc diff_geo.c -lm -o diff_geo
```

When the compile is completed normally, then you can find an executable file 'diff_geo' in the directory 'source'. Please copy the executable file to the directory 'work'.

(2) Calculation of the difference

You can find the following usage in the header part of diff_geo.c.

```
usage:
        ./diff_geo file1.xyz file2.xyz -d rmsd

   option
      -d rmsd      a root mean square of deviation
      -d md        a mean deviation
      -d mdbl 2.2  a mean deviation between bond lengths,
                   2.2 (Ang) means a cutoff bond length which
                   can be taken into account in the calculation
```

If you want to know RMSD between two Cartesian coordinates, run as follows:

```
% ./diff_geo file1.xyz file2.xyz -d rmsd
```

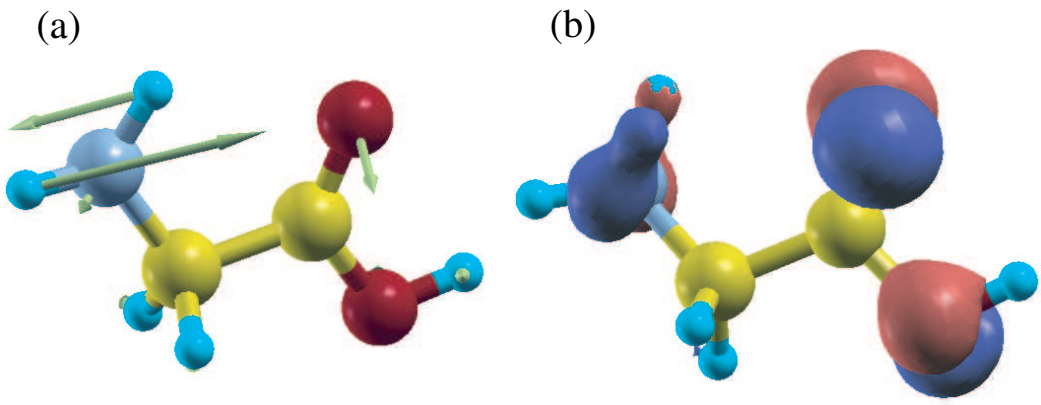

Figure 44: (a) Vectors corresponding to the deviation of atomic coordinates in optimized structures and (b) the difference of total charge density between a neutral and one electron doped glycine molecule. These figures were visualized by XCrySDen. In Fig. (b) blue and red colors indicate the decrease and increase of total charge density, respectively.

The calculated result appears in the standard output (your display). Also, a xsf file 'dgeo_vec.xsf' is generated in the XCrySDen format, which stores the difference between Cartesian coordinates of each atom in a vector form. This file can be visualized using 'Display→Forces' in XCrySDen. When MDBL is calculated, please give a cutoff bond length (Å). Bond lengths below the cutoff bond length are taken into account for the RMSD calculation. Figure 44 shows vectors corresponding to the deviation of atomic coordinates in optimized structures and the difference of total charge density between a neutral and one electron doped glycine molecule. We see that the large structural change seems to take place together with the large charge deviation. This example illustrates that the tool would be useful when we want to know how the structure is changed by the charge doping and the electric field.

49 Analysis of difference charge density induced by the interaction

The redistribution of charge (spin) density induced by the interaction between two systems A and B can be analyzed by the following procedure:

(i) calculate the composite system consisting of A and B

Then, you will have a cube file for charge (spin) density. Let it be 'AB.cube'. Also, you will find 'Grid_Origin' in the standard output which gives x-, y-, and z-components of the origin of the regular grid as:

```
Grid_Origin  xxx  yyy  zzz
```

The values will be used in the following calculations (ii) and (iii).

(ii) calculate the system A

This calculation must be performed by the same calculation condition with the same unit cell as in the composite system consisting of A and B. Also, the coordinates of the system A must be the same as in the calculation (i). To use the same origin as in the calculation (i) rather than the use of an automatically determined origin, you have to include the following keyword in your input file:

```
scf.fixed.grid  xxx  yyy  zzz
```

where 'xxx yyy zzz' is the coordinate of the origin you got in the calculation (i). Then, you will have a cube file for charge (spin) density. Let it be 'A.cube'.

(iii) calculate the system B

As well as the calculation (ii), this calculation must be performed by the same calculation condition with the same unit cell as in the composite system consisting of A and B. Also, the coordinates of the system B must be the same as in the calculation (i). To use the same origin as in the calculation (i) rather than the use of an automatically determined origin, you have to include the following keyword in your input file:

```
scf.fixed.grid  xxx  yyy  zzz
```

where 'xxx yyy zzz' is the coordinate of the origin you got in the calculation (i). Then, you will have a cube file for charge (spin) density. Let it be 'B.cube'.

(iv) compile two codes

compile two codes as follows:

```
% gcc diff_gcube.c -lm -o diff_gcube
% gcc add_gcube.c -lm -o add_gcube
```

(v) generate a cube file for difference charge (spin) density

First, generate a cube file for the superposition of two charge (spin) densities of the systems A and B by

```
% ./add_gcube A.cube B.cube A_B.cube
```

The file 'A_B.cube' is the cube file for the superposition of charge (spin) density of two isolated systems. Then, you can generate a cube file for the difference charge (spin) density induced by the interaction as follows:

```
% ./diff_gcube AB.cube A_B.cube dAB.cube
```

The file 'dAB.cube' is the cube file for the difference charge (spin) density induced by the interaction, where the difference means (AB - A_B).

50 Automatic determination of the cell size

When you calculate an isolated system, you are required to provide a super cell so that the isolated system does not overlap with the image systems in the repeated cells. The larger cell size can cause a numerical inefficiency, since a larger number of grids are used in the solution of the Poisson's equation in this case. Therefore, the use of the minimum cell size is desirable in terms of computational efficiency. OpenMX supports the requirement. If you remove the specification for the cell size, that is, from '<Atoms.UnitVectors' to 'Atoms.UnitVectors>', then OpenMX automatically determines an appropriate cell which does not overlap the next cells and fulfills the required cutoff energy. The determined cell vectors are displayed in the standard output like this:

```
<Set_Cluster_UnitCell> automatically determined UnitCell(Ang.)
<Set_Cluster_UnitCell> from atomic positions and Rc of PAOs (margin= 10.00%)
<Set_Cluster_UnitCell> 6.614718 0.000000 0.000000
<Set_Cluster_UnitCell> 0.000000 6.041246 0.000000
<Set_Cluster_UnitCell> 0.000000 0.000000 6.614718

widened unit cell to fit energy cutoff (Ang.)
A = 6.744142 0.000000 0.000000 (48)
B = 0.000000 6.322633 0.000000 (45)
C = 0.000000 0.000000 6.744142 (48)
```

51 Interface for developers

An interface for developers is provided. If you want to use the Kohn-Sham Hamiltonian, the overlap, and the density matrices, Then these data can be utilized by the following steps.

1. HS.fileout

   Include the keyword, HS.fileout, in your input file as follows:

   ```
   HS.fileout                      on      # on|off, default=off
   ```

   Then, these data are output to a file '*.scfout' where * means System.Name in your input file.

2. make analysis_example

   In the directory 'source' compile by

   ```
   % make analysis_example
   ```

   Then, an executable file, analysis_example, is generated in the directory, 'work'.

3. ./analysis_example *.scfout

   Move to the directory 'work', and then perform the program as follows:

   ```
   % ./analysis_example *.scfout
   or
   % ./analysis_example *.scfout > HS.out
   ```

   You can find the elements of the Hamiltonian, the overlap, and the density matrices in a file 'HS.out'

4. explanation of analysis_example

   In a file 'analysis_example.c' you can find a detailed description for these data. A part of the description is as follows:

   ```
   ************************************************************
     You can utilize a filename.scfout which is generated by the SCF
     calculation of OpenMX by the following procedure:

      1. Define your main routine as follows:

            int main(int argc, char *argv[])

      2. Include a header file, "read_scfout.h", in your main routine
         (if you want, also in other routines) as follows:

            #include "read_scfout.h"

      3. Call a function, read_scfout(), in the main routine as follows:

            read_scfout(argv);
   ************************************************************
   ```

52 Automatic force tester

An effective way of assuring the reliability of implementation of many functionalities is to compare analytic and numerical forces. If any program bug is introduced, they will not be consistent with each other. To do this, one can run an automatic tester by

For serial running

```
% ./openmx -forcetest 0
```

For parallel running

```
% ./openmx -forcetest 0 "mpirun -np 4 openmx"
```

where '0' is a flag to specify energy terms to be included in the consistency check, and one can change 0 to 8. Each number corresponds to

flag	0	1	2	3	4	5	6	7	8
Kinetic	1	0	1	0	0	0	0	0	0
Non-local	1	0	0	1	0	0	0	0	0
Neutral atom	1	0	0	0	1	0	0	0	0
diff Hartree	1	0	0	0	0	1	0	0	0
Ex-Corr	1	0	0	0	0	0	1	0	0
E. Field	1	0	0	0	0	0	0	1	0
Hubbard U	1	0	0	0	0	0	0	0	1

where '1' means that it is included in the force consistency check. In a directory 'work/force_example', there are 36 test inputs which are used for the force consistency check. After finishing the test, a file 'forcetest.result' is generated in the directory 'work'. You will see results of the comparison as follows:

```
force_example/C2_GGA.dat
  flag= 0
  Numerical force= -(Utot(s+ds)-Utot(s-ds))/(2*ds)
  ds=   0.0003000000
  Forces (Hartree/Bohr) on atom 1
                              x              y              z
  Analytic force       -1.676203071292 -1.397113794193 -1.117456296887
  Numerical force      -1.676101156844 -1.397036485449 -1.117288361652
  diff                 -0.000101914447 -0.000077308744 -0.000167935235

force_example/C2_LDA.dat
  flag= 0
  Numerical force= -(Utot(s+ds)-Utot(s-ds))/(2*ds)
  ......
  ....
```

53 Automatic memory leak tester

In OpenMX, the memory used is dynamically allocated when it is required. However, the dynamic memory allocation causes often a serious memory leak which wastes the memory used as the MD steps increase. To check the memory leak, one can run OpenMX as follows:

For serial running

```
% ./openmx -mltest
```

For parallel running

```
% ./openmx -mltest "mpirun -np 4 openmx"
```

By monitoring VSZ and RSS actually used at the same monitoring point in the program code for 13 test inputs in a directory 'work/ml_example', one can find whether the memory leak takes place or not. After finishing the run, a file 'mltest.result' is generated in the directory 'work'. You will see the monitored VSZ and RSS as a function of MD steps as follows:

```
   1     ml_example/Co4.dat

                   CPU (%)     VSZ (kbyte)    RSS (kbyte)
MD_iter=   1      92.900      49756          15736
MD_iter=   2      84.900      73344          57208
MD_iter=   3      81.200      73344          57212
MD_iter=   4      85.900      98672          82548
MD_iter=   5      82.800      98672          82548
MD_iter=   6      83.800      98672          82548
MD_iter=   7      84.200      98672          82548
MD_iter=   8      84.600      98824          82688
MD_iter=   9      85.000      98824          82688
MD_iter=  10      87.300      98824          82688
MD_iter=  11      87.500      98824          82688
MD_iter=  12      87.400      98824          82688
MD_iter=  13      85.700      98824          82688
MD_iter=  14      84.500      98824          82688
MD_iter=  15      86.100      98824          82688
MD_iter=  16      86.300      98824          82688
MD_iter=  17      86.500      98824          82688
MD_iter=  18      86.400      98824          82688
MD_iter=  19      86.500      98824          82688
MD_iter=  20      87.500      98824          82688

   2     ml_example/Co4+U.dat

                   CPU (%)     VSZ (kbyte)    RSS (kbyte)
```

```
MD_iter=   1      92.800      50048          15924
MD_iter=   2      84.700      73628          57476
MD_iter=   3      84.700      73628          57496
MD_iter=   4      85.300      73628          57496
MD_iter=   5      85.100      98828          82684
MD_iter=   6      85.000      98828          82684
   ......
   ....
```

54 Analysis of memory usage

The memory usage can be found by analyzing files '*.memory0', '*.memory1',..., and '*.memory#', where '*' is the file name specified by the keyword 'System.Name' and the number in the file extension corresponds to process ID in the MPI parallelization. The files are output by setting the keyword 'memory.usage.fileout' as

```
memory.usage.fileout   on   # default=off, on|off
```

As an example 'met.memory0' is shown below

```
Memory: SetPara_DFT: Spe_PAO_XV                                0.01 MBytes
Memory: SetPara_DFT: Spe_PAO_RV                                0.01 MBytes
Memory: SetPara_DFT: Spe_Atomic_Den                            0.01 MBytes
Memory: SetPara_DFT: Spe_PAO_RWF                               0.57 MBytes
Memory: SetPara_DFT: Spe_RF_Bessel                             1.03 MBytes
Memory: SetPara_DFT: Spe_VPS_XV                                0.01 MBytes
Memory: SetPara_DFT: Spe_VPS_RV                                0.01 MBytes
Memory: SetPara_DFT: Spe_Vna                                   0.01 MBytes
Memory: SetPara_DFT: Spe_VH_Atom                               0.01 MBytes
Memory: SetPara_DFT: Spe_Atomic_PCC                            0.01 MBytes
Memory: SetPara_DFT: Spe_VNL                                   0.11 MBytes
Memory: SetPara_DFT: Spe_VNLE                                  0.00 MBytes
Memory: SetPara_DFT: Spe_VPS_List                              0.00 MBytes
.....
....
...
Memory: Poisson: array0                                        4.00 MBytes
Memory: Poisson: array1                                        4.00 MBytes
Memory: Poisson: request_send                                  0.00 MBytes
Memory: Poisson: stat_send                                     0.00 MBytes
Memory: Poisson: request_recv                                  0.00 MBytes
Memory: Poisson: stat_recv                                     0.00 MBytes
Memory: Force: Hx                                              0.00 MBytes
Memory: Force: Hy                                              0.00 MBytes
Memory: Force: Hz                                              0.00 MBytes
Memory: Force: CDM0                                            0.00 MBytes
Memory: Data_Grid_Copy_B2C_1: Work_Array_Snd_Grid_B2C          0.72 MBytes
Memory: Data_Grid_Copy_B2C_1: Work_Array_Rcv_Grid_B2C          0.72 MBytes
Memory: total                                                256.99 MBytes
```

The file can be obtained by setting the keyword in the input file 'Methane.dat' and performing a single process. Note that memory usages for most of arrays are listed in the file, but the list is not complete.

55 Output of large-sized files in binary mode

Large-scale calculations produce large-sized files in text mode such as cube files. The IO access to output such files can be very time consuming in machines of which IO access is not fast. In such a case, it is better to output those large-sized files in binary mode. The procedure is supported by the following keyword:

```
OutData.bin.flag    on    # default=off, on|off
```

Then, all large-sized files will be output in binary mode. The default is 'off'.

The output binary files are converted using a small code 'bin2txt.c' stored in the directory 'source' which can be compiled as

```
gcc bin2txt.c -lm -o bin2txt
```

As a post processing, you will be able to convert as

```
./bin2txt *.bin
```

The functionality will be useful for machines of which IO access is not fast.

56 Examples of the input files

For your convenience, the input files of examples shown in the manual are available in the directory 'work' as listed below:

```
Molecules or clusters
    C60.dat             SCF calc. of a C60 molecule
    C60_DC.dat          DC calc. of a C60 molecule
    CG15c_DC.dat        DC calc. of DNA
    Cr2_CNC.dat         Constrained DFT calc. of a Cr2 dimer
    Doped_NT.dat        SCF calc. of doped carbon nanotube
    Fe2.dat             SCF calc. of a Fe2 dimer
    Gly_NH.dat          Nose-Hoover MD of a glycine molecule
    Gly_VS.dat          Velocity scaling MD of a glycine molecule
    H2O.dat             Geometry opt. of a water molecule
    MCCN.dat            DC calc. of a a multiply connected carbon nanotube
    Methane2.dat        Geometry opt. of a distorted methane molecule
    Methane.dat         SCF calc. of a  methane molecule
    Methane_OO.dat      Orbital optimization of a methane molecule
    Mn12.dat            SCF calc. of a single molecular magnet, Mn12
    Mol_MnO_NC.dat      Non-collinear SCF calc. of a MnO molecule
    Nitro_Benzene.dat   SCF calc. of a nitro benzene molecule under E-field
    Pt13.dat            SCF calc. of a Pt13 cluster
    Pt63.dat            SCF calc. of a Pt63 cluster
    SialicAcid.dat      SCF calc. of a sialic acid molecule
    Valorphin_DC.dat    DC calc. of valorphin molecule
    C2H4_NEB.dat        NEB calc. of C2H4 dimer
    C60_LO.dat          Low-order scaling calc. of a C60 molecule

Bulk
    Cdia.dat            SCF calc. of bulk diamond
    MnO_NC.dat          Non-collinear SCF calc. of bulk MnO
    FeO_NC.dat          Non-collinear SCF calc. of bulk FeO
    CoO_NC.dat          Non-collinear SCF calc. of bulk CoO
    NiO_NC.dat          Non-collinear SCF calc. of bulk NiO
    Crys-NiO.dat        SCF calc. of bulk NiO
    DIA64_Band.dat      SCF calc. of bulk diamond including 64 atoms
    DIA8_DC.dat         DC calc. of bulk diamond including 8 atoms
    DIA64_DC.dat        DC calc. of bulk diamond including 64 atoms
    DIA216_DC.dat       DC calc. of bulk diamond including 216 atoms
    DIA512_DC.dat       DC calc. of bulk diamond including 512 atoms
    DIA512-1.dat        Krylov O(N) calc. of bulk diamond including 512 atoms
    Febcc2.dat          SCF calc. of bcc Fe
    GaAs.dat            Non-collinear calc. of bulk gallium arsenide
    NaCl.dat            SCF calc. of bulk NaCl
```

```
NaCl_FC.dat        SCF calc. of bulk NaCl with a Cl-site vacancy
Si8.dat            Geometry opt. of distorted Si bulk
Al-Si111_ESM.dat   ESM calc. of Al-Si interface
Cafcc_FS.dat       Fermi surface calc. of the fcc Ca bulk
Graphite_STM.dat   STM image of graphene
Mnfcc-EvsLC.dat    E vs. lattice constant calc. of the fcc Mn bulk
Si8_NEB.dat        NEB calc. for hydrogen in Si
```

57 Known problems

- Overcompleteness of basis functions

  When a large number of basis functions is used for dense bulk systems with fcc, hcp, and bcc like structures, the basis set tends to be overcomplete. In such a case, you may observe erratic eigenvalues. To avoid the overcompleteness, a small number of optimized basis functions should be used. Another way to avoid the problem is to switch off the keyword 'scf.ProExpn.VNA' as

  ```
  scf.ProExpn.VNA      off       # on|off, default = on
  ```

  In this case, you may need to increase the cutoff energy for the numerical grid in real space by the keyword 'scf.energycutoff'.

- Difficulty in getting the SCF convergence

  For large-scale systems with a complex (non-collinear) magnetic structure, a metallic electric structure, or the mixture, it is quite difficult to get the SCF convergence. In such a case, one has to mix the charge density very slowly, indicating that the number of SCF steps to get the convergence becomes large unfortunately.

- Difficulty in getting the optimized structure

  For weak interacting systems such as molecular systems, it is not easy to obtain a completely optimized structure, leading that the large number of iteration steps is required. Although the default value of criterion for geometrical optimization is 10^{-4} Hartree/Bohr for the largest force, it would be a compromise to increase the criterion from 10^{-4} to 5×10^{-4} in such a case.

58 OpenMX Forum

For discussion of technical issues on OpenMX and ADPACK, there is a forum (http://www.openmx-square.org/forum/patio.cgi). It is expected that the forum is utilized for sharing tips in use of OpenMX and for further code development. Points of concern for use of this forum can be found in http://www.openmx-square.org/forum/note.html

59 Others

Program

The program package is written in the C and F90 languages, including one makefile

`makefile,`

21 header files

exx_debug.h	exx_file_eri.h	exx.h	exx_interface_openmx.h
exx_rhox.h	exx_step2.h	exx_xc.h	Inputtools.h
mimic_sse.h	read_scfout.h	tran_variables.h	exx_def_openmx.h
exx_file_overlap.h	exx_index.h	exx_log.h	exx_step1.h
exx_vector.h	f77func.h	lapack_prototypes.h	openmx_common.h
tran_prototypes.h			

and 265 routines

add_gcube.c	get_elpa_row_col_comms.f90	SCF2File.c
Allocate_Arrays.c	Get_OneD_HS_Col.c	Set_Aden_Grid.c
analysis_example.c	Get_Orbitals.c	Set_Allocate_Atom2CPU.c
AngularF.c	GR_Pulay_DM.c	Set_Density_Grid.c
Band_DFT_Col.c	Hamiltonian_Band.c	Set_Hamiltonian.c
Band_DFT_Dosout.c	Hamiltonian_Band_NC.c	Set_Initial_DM.c
Band_DFT_kpath.c	Hamiltonian_Cluster.c	Set_Nonlocal.c
Band_DFT_MO.c	Hamiltonian_Cluster_NC.c	Set_OLP_Kin.c
Band_DFT_NonCol.c	Hamiltonian_Cluster_SO.c	Set_Orbitals_Grid.c
bandgnu13.c	init_alloc_first.c	SetPara_DFT.c
Bench_MatMul.c	init.c	Set_ProExpn_VNA.c
BentNT.c	Initial_CntCoes2.c	Set_Vpot.c
bin2txt.c	Initial_CntCoes.c	Set_XC_Grid.c
BroadCast_ComplexMatrix.c	Init_List_YOUSO.c	Show_DFT_DATA.c
BroadCast_ReMatrix.c	Input_std.c	Simple_Mixing_DM.c
check_lead.c	Inputtools.c	Smoothing_Func.c
Cluster_DFT.c	io_tester.c	solve_evp_complex.f90
Cluster_DFT_Dosout.c	iterout.c	solve_evp_real.f90
Cluster_DFT_ON2.c	iterout_md.c	Spherical_Bessel.c
Cont_Matrix0.c	jx.c	test_mpi2.c
Cont_Matrix1.c	Kerker_Mixing_Rhok.c	test_mpi3.c
Cont_Matrix2.c	Krylov.c	test_mpi4.c
Cont_Matrix3.c	KumoF.c	test_mpi.c
Cont_Matrix4.c	lapack_dstedc1.c	test_openmp2.c
Contract_Hamiltonian.c	lapack_dstedc2.c	test_openmp3.c
Contract_iHNL.c	lapack_dstedc3.c	test_openmp.c
Cutoff.c	lapack_dstegr1.c	Tetrahedron_Blochl.c
dampingF.c	lapack_dstegr2.c	Timetool.c
deri_dampingF.c	lapack_dstegr3.c	Total_Energy.c
DFT.c	lapack_dsteqr1.c	TRAN_Add_ADensity_Lead.c
DFTDvdW_init.c	lapack_dstevx1.c	TRAN_Add_Density_Lead.c
diff_gcube.c	lapack_dstevx2.c	TRAN_adjust_Ngrid.c
diff_geo.c	lapack_dstevx3.c	TRAN_Allocate.c
DIIS_Mixing_DM.c	lapack_dstevx4.c	TRAN_Allocate_NC.c
DIIS_Mixing_Rhok.c	lapack_dstevx5.c	TRAN_Apply_Bias2e.c
Divide_Conquer.c	Lapack_LU_inverse.c	TRAN_Calc_CentGreen.c
Divide_Conquer_Dosout.c	LU_inverse.c	TRAN_Calc_CentGreenLesser.c

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Dr_KumoF.c
Dr_RadialF.c
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Eff_Hub_Pot.c
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Eigen_lapack.c
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esp.c
EulerAngle_Spin.c
expao.c
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mpi_non_blocking.c
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Nonlocal_RadialF.c
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OutData.c
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Overlap_Cluster.c
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PhiF.c
Poisson.c
Poisson_ESM.c
polB.c
Pot_NeutralAtom.c
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PrintMemory_Fix.c
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RadialF.c
readfile.c
read_scfout.c
ReLU_inverse.c
RestartFileDFT.c
RF_BesselF.c
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Runtest.c
TRAN_Calc_GridBound.c
TRAN_Calc_Hopping_G.c
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TRAN_Calc_SelfEnergy.c
TRAN_Calc_SurfGreen.c
TRAN_Calc_SurfGreen_Sanvito.c
TRAN_Check_Input.c
TRAN_Check_Region.c
TRAN_Check_Region_Lead.c
TRAN_Credit.c
TRAN_Deallocate_Electrode_Grid.c
TRAN_Deallocate_RestartFile.c
TRAN_DFT.c
TRAN_DFT_Dosout.c
TRAN_DFT_NC.c
TRAN_Distribute_Node.c
TRAN_Input_std_Atoms.c
TRAN_Input_std.c
TranMain.c
TranMain_NC.c
TRAN_Output_HKS.c
TRAN_Output_HKS_Write_Grid.c
TRAN_Output_Trans_HS.c
TRAN_Poisson.c
TRAN_Print.c
TRAN_Print_Grid.c
TRAN_Read.c
TRAN_RestartFile.c
TRAN_Set_CentOverlap.c
TRAN_Set_CentOverlap_NC.c
TRAN_Set_Electrode_Grid.c
TRAN_Set_IntegPath.c
TRAN_Set_MP.c
TRAN_Set_SurfOverlap.c
TRAN_Set_SurfOverlap_NC.c
TRAN_Set_Value.c
truncation.c
unit2xyz.c
VH_AtomF.c
VNAF.c
Voronoi_Charge.c
Voronoi_Orbital_Moment.c
XC_CA_LSDA.c
XC_Ceperly_Alder.c
XC_EX.c
XC_PBE.c
XC_PW92C.c
xyz2spherical.c
zero_cfrac.c
zero_fermi.c

In addition, the following library packages are linked:

```
lapack,
```

```
blas,
fftw,
MPICH or LAM
omp
```

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The distribution of this program package follows the practice of the GNU General Public License [59]. Moreover, the author, Taisuke Ozaki, possesses the copyright of the original version of this program package. We cannot offer any guarantee in your use of this program package. However, when you report program bugs, we will cooperate and work well as much as possible together with you to remove the problems.

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