NRLMOL Tutorials and Documentation Documentation

Release 0

NRLMOL users

January 21, 2014

CONTENTS

CHAPTER

ONE

CONTENTS

1.1 Features

NRLMOL, the Naval Research Laboratory Molecular Orbital Library is a massively parallel code for electronic structure calculations on large molecules and clusters. The code is based on Kohn-Sham formulation of density functional theory and solves Kohn-Sham equations by expressing the Kohn-Sham orbitals as a linear combination of Gaussian orbitals. NRLMOL is principally developed by Mark Pederson and collaborators.

Some of the features of NRLMOL or the things that you can do with NRLMOL.

Use of full point group symmetry- you can specify the symmetry operations

Full or partial structure optimization using Cartesian or internal coordinates

Vibrational frequencies

Infra-red spectra

Raman spectra

Density of States

Projected density of states

Vibrational density of states

Polarizability

Vibrational Polarizability

Magnetic anisotropy

~~Spin Hamiltonians~~

~~Site specific polarizabilities~~

~~Perturbative Delta SCF for the charge transfer excitations~~

~~Fragment Analysis~~

~~Population analysis - MESP~~

~~Population analysis - AIM~~

~~Population analysis - NBO (interface to NBO)~~

1.2 Compiling the code.

Once you have procured the code from repository. Go to the directory containing sources and edit makefile to suite for your platform. A number of routines in NRLMOL were written in mid and late eighties and require static allocation of arrays. The code needs to compiled for appropriate array sizes for the system under study. These parameters are listed in file called **PARAMS**. Please change them to your needs and compile the code by typing **make** at the command line.

1. To compile serial version uncomment the line

   ./condcomp < $*.ftn > $*.f

2. To compile MPI version uncomment the line ./condcomp -DMPI < $*.ftn > $*.f
3. To compile MPI with SCALAPACK uncomment the line ./condcomp -DMPI -DSCALAPCK < $*.ftn > $*.f

If you are a beginner, he serial option is probably the best for you. *TIP* You will need the BLAS and LAPACK to compile the code. It is highly recommended that you use optimized BLAS and LPACK libraries if they are available to you. Examples of these are vendor provided libraries, e.g. MKL libraries by Intel or GotoBLAS library. In the limited set of tests, it was found that the performance of the code is best with MKL libraries. However linking MKL libraries can be difficult. Use the examples from the Makefile.

An example **PARAM** file containing parameters used is listed below for your convenience with explanation of parameters.

```
C
       IMPLICIT REAL*8 (A-H,O-Z)
C
C ***************************************************
C THESE ARE THE PARAMETERS THAT SHOULD BE ADJUSTED  *
C ***************************************************
C
C MX_PROC: MAXIMUM NUMBER OF PROCESSORS (ONLY RELEVANT FOR MPI)
C
       PARAMETER (MX_PROC=32)
C
C MXSPN: 1 FOR SPIN UNPOLARIZED, 2 FOR SPIN POLARIZED
C
       PARAMETER (MXSPN=2)
C
C MAX_PTS: MAX. NUMBER OF MESH POINTS
C
       PARAMETER (MAX_PTS=850000)
C
C MAX_FUSET: MAX. NUMBER OF FUNCTION SETS
C
       PARAMETER (MAX_FUSET=1)
C
C MAX_IDENT: MAX. NUMBER OF INEQUIVALENT ATOMS
C
       PARAMETER (MAX_IDENT=50)
C
C MX_CNT: MAX. NUMBER OF EQUIVALENT ATOMS
C
       PARAMETER (MX_CNT=380)
C PARAMETERS NEEDED FOR LBFGS... (?)
       PARAMETER (MXATMS=MX_CNT, NMUPMAX=7)

C
C MAX_BARE: MAX. NUMBER OF BARE GAUSSIANS PER ATOM
```

```
C
       PARAMETER (MAX_BARE=20)
C
C MAX_CON: MAX. NUMBER OF CONTRACTED FUNCTIONS PER ANGULAR MOMENTUM
C
       PARAMETER (MAX_CON=10)
C
C MAX_OCC: MAX. NUMBER OF OCCUPIED STATES
C
       PARAMETER (MAX_OCC=2500)
C
C MAXUNSYM: MAX. TOTAL NUMBER OF CONTRACTED ORBITALS FOR ONE ATOM
C
       PARAMETER (MAXUNSYM=50)
C
C NDH: MAX. DIMENSION OF A BLOCK MATRIX TO DIAGONALIZE
C
       PARAMETER (NDH=3500)
C
C NDH_TOT: MAX. NUMBER OF NONZERO ELEMENTS FOR HAMILTONIAN
C
       PARAMETER (NDH_TOT=NDH*(NDH+1)/2)
C
C MX_GRP: MAX. NUMBER OF GROUP OPERATIONS.
C
       PARAMETER (MX_GRP=1)
C
C MAX_REP: MAX. NUMBER OF IRREDUCIBLE GROUP REPRESENTATIONS
C
       PARAMETER (MAX_REP=4)
C
C MAXSLC: MAX. NUMBER OF SALCS ON A SHELL
C         SALC = SYMMETRY ADAPTED LINEAR COMBINATION OF GAUSSIANS
C         SHOULD BE EQUAL TO MAXUNSYM*M WHERE M IS THE MAXIMUM NUMBER
C         OF EQUIVALENT ATOMS CORRESPONDING TO ONE INEQUIVALENT ATOM
C
       PARAMETER (MAXSLC=1500)
C
C PARAMETERS DEPENDING ON THE CURRENT POINT GROUP
C LOCMAX SHOULD BE EQUAL TO 6*M WHERE M IS THE MAXIMUM NUMBER
C OF EQUIVALENT ATOMS CORRESPONDING TO ONE INEQUIVALENT ATOM
C MAXSYMSALC SHOULD BE EQUAL TO THE SUM OF ALL DIMENSIONS OF
C ALL REPRESENTATIONS (32 FOR IH, 20 FOR OH)
C
       PARAMETER (LOCMAX=720)
       PARAMETER (ISMAX=18)
       PARAMETER (MAXSYMSALC=32)
C
C MXRPSP: MAXIMUM NUMBER OF RADIAL POINTS FOR INTEGRATION OF
C         NONLOCAL PART OF PSEUDOPOTENTIAL
C
       PARAMETER (MXRPSP=100)
C
C MXPTAB: MAXIMUM SIZE OF TABLE FOR TABULATED PSEUDOPOTENTIALS
C
       PARAMETER (MXPTAB=100)
C
C MXLPSP: HIGHEST ANGULAR MOMENTUM ALLOWED FOR NONLOCAL PART OF
```

```
C         PSEUDOPOTENTIAL
C
       PARAMETER (MXLPSP=2)
C
C
C MXKPT: MAXIMUM NUMBER OF KPTS IN FORMFAK
C
       PARAMETER (MXKPT=1)
C
C ***************************************************************
C THE OPTIMUM SETTING FOR THESE PARAMETERS IS MACHINE-DEPENDENT *
C ***************************************************************
C
C MPBLOCK: BLOCK SIZE FOR GENERAL TEMPORARY STORAGE
C
       PARAMETER (MPBLOCK=100)
C
C MXPOISS: BLOCK SIZE IN POISSON1 AND COUPOT1
C
       PARAMETER (MXPOISS=100)
C
C NSPEED: SMALLER BLOCK SIZE TO SPEED UP DENSITY EVALUATION
C         A BLOCK OF SIZE MPBLOCK WILL BE BROKEN UP INTO BLOCKS
C         OF SIZE NSPEED
C
       PARAMETER (NSPEED=25)
C
C *************************************************
C THESE PARAMETERS USUALLY DON’T NEED ADJUSTMENTS *
C *************************************************
C
C LDIM: SIZE OF HIGHEST IMPLEMENTED ANGULAR MOMENTUM (S=1, P=2, ETC)
C DO NOT CHANGE THIS UNLESS YOU KNOW EXACTLY WHAT YOU ARE DOING
C
       PARAMETER (LDIM=3)
C
C CUTEXP: CUTOFF FOR EXPONENTIALS (EXP(-CUTEXP) IS VIRTUALLY ZERO)
C
       PARAMETER (CUTEXP=40.0D0)
C
C MX_SPH: MAX. NUMBER OF SPHERES FOR MESH POINTS
C
       PARAMETER (MX_SPH=MAX_PTS/100)
C
C MAX_VIRT_PER_SYM: MAX NUMBER OF STORED ORBITALS PER REPRESENTATION
C
       PARAMETER (MAX_VIRT_PER_SYM=NDH/3)
c        PARAMETER (MAX_VIRT_PER_SYM=400)
C
C MAXIMUM NUMBER OF GAUSSIANS FOR STARTING POTENTIAL FIT
C
       PARAMETER (MAXGFIT=15)
C
C MAXIMUM NUMBER OF GAUSSIANS FOR GENERAL LEAST-SQUARE FITS
C
       PARAMETER (MAXLSQF=50)
C
C TEMPORARY STORAGE IN OVERLAP
```

```
C
      PARAMETER (MTEMP=75000)
C
```

1.3 Setting up calculation

How to set up a calculation?

Basic input file for the NRLMOL is called “CLUSTER”. It requires minimal input from the user and most parameters required from the calculations are obtained using default values. If you are using a recent versions (after 2012) then you can specify some parameters that control the calculations in the file called “NRLMOL_INPUT.DAT”. This file is optional, in that, if it doesn’t exist it will be created automatically with default choices. We will discuss the details of the parameters in the **NRLMOL_INPUT.DAT** later.

For now let’s work on setting up of the **CLUSTER** file. It is the minimal input needed to run the NRLMOL code. The structure of the “CLUSTER” file is as below.

You can set up **CLUSTER** file in number of different ways.

1. You can cut and paste it from these pages and adapt it by hand using the editor of your choice.
2. You can use a script called **xmol-dat_2_CLUSTER.pl** to create it from the **XMOL.DAT**. The **XMOL.DAT** is a file in the *xyz* format and has atomic numbers in the place of the atomic labels (symbols). To convert standard **xmol2xyz.pl**. This way of creating **CLUSTER** will not make use of point group symmetry. If the molecules or your system has symmetry it is advisable to make use of point group symmetry as it results in significant computational savings. To use symmetry, use the following approach. Also, ensure that your spin (moment) is correctly specified. The script will set it to 1 for odd electron systems and to 0 for an even electron system. You may want to adapt *charge* and *spin* to your needs.
3. Let’s suppose your systems of interest is in “XMOL.DAT”, then execute the following command **echo “@XMOL.DAT” > CLUSTER**

   This will insert a line “@XMOL.DAT” in the CLUSTER file. Now execute the NRLMOL on the command line. NRLMOL will try to identify the available symmetry. It will find the symmetry operations and write them in the file called **GRPMAT** and it will create the **CLUSTER**. The CLUSTER file created will have fewer atoms (only inequivalent atoms are listed). The entire structure can be generated using the symmetry operations and the positions of the ineqivalent atoms. Note that often for the systems containing high symmetry (e.g, *icosahedral*), NRLMOL will usually find lower point group symmetry. To overcome this you can use you can combine step 1 and step 3. It advisable to ensure that the resultant XMOL.xyz or XMOL.DAT generated during the calculations is the system of your interest.
4. Use the **NRLMOL GUI**. NRLMOL GUI allows setting up of CLUSTER file and visualization of results produced by the NRLMOL. For the visulalizatin of results like DOS, it also requires the *gnuplot* software to be installed.

1.4 Exchange correlation functionals

The available LDA exchange-correlation functionals are:

- **LDA functionals**
    1. VWN
    2. Ceperly-Adler
    3. Perdew-Zunger 81

4. RPA
5. Wigner Interpolation Functional
6. Kohn-Sham exchange only (Xalpha with alpha =2/3)
7. Gunnarsson-Lundquist

The first GGA functional (PW91) was implemented in 1991. THe following GGA functionals are currently available.

- **GGA functionals**
    1. Becke 1988 exchange functional (B88)
    2. Perdew-Wang 91 functional (PW91)
    3. Perdew-Burke-Ernzerhof 96 functional (PBE)
    4. Revised Perdew-Burke-Ernzerhof 96 functional (PBE)
    5. RPBE

The PBE functional is the default functional. In the above lines, the words in the bracket are the keywords that you can use to select the exchange and correlation functional of your choice. THis is specified in the file called(CLUSTER) file. For example, to specify use the “BPW91” functional you will use **GGA-B88*GGA-PW91** in the first line in the CLUSTER file.

Work on implementation of Minnesota functionals is in progress.

1.5 NRLMOL_INPUTS

The **NRLMOL_INPUT.DAT** is an auxiliary input file that allows setting of parameters for calculation. If it does not exist then the it will be created during the run using default values.

The NRLMOL_INPUT.DAT with default values of parameters as of today (December 09, 2013) is given below. They are described in detail.

```
# Put Y,N or number next to the equal sign to determiner execution
# Don’t forget thew quotation marks for the letters
# All variables in this list end with v

&input_data
ATOMSPHV       = ’N’
CALCTYPEV      = ’LBFGS’
DIAG1V         = 0   ! diagonalization to use on regular arrays (diagge.f90)
DIAG2V         = 0   ! diagonalization to use on packed arrays (diag_dspgv.f90)
DOSOCCUV       = ’N’ ! Controls wether to calculate density of states
EXCITEDV       = ’N’ ! Determines if this is an excited state calculation
FORMFAKV       = ’N’ ! this controls if FORMFAK is executed
JNTDOSV        = ’N’ ! this controls whether excite is executed
MATDIPOLEV     = ’N’
NONSCFV        = ’N’ ! Set to Y to do a non SCF calculation
DFTD3V         = ’N’ ! Set to Y to do include Grimmes DFT-D3 dispersion
NONSCFFORCESV = ’N’ ! Set to Y to calculate forces in a non SCF calculation
WFGRIDV        = ’N’
&end
```

Here **N** means *NO*. If **Y** then the calculation of a given property is requested. Note that certain calculations such as, for example, the calculation of joint density of states is often useful only at the final converged geometry.

1. ATOMSPHV : Default is **N**. THis will place an atomic sphere around each nucleus and integrates electron density within the sphere. THis is a sort of population analysis and can be used to obtain local magnetic moment.

2. CALCTYPEV: Default is 'LBFGS'. Available choices: **SCF-ONLY**, **CONJUGATE-GRADIENT**, **INTERNAL**, **POLARIZABILITY**

    - **SCF-ONLY** for the SCF calculations, t
    - **Polarizability** for the Polarizability by finite-field using energies.
    - **CONJUGATE-GRADIENT** : Geometry optimization by conjugate-gradient.
    - **INTERNAL** : Geometry optimization by internal-coordinates.
    - **VERLET** : Geometry optimization by VERLET.

3. **DIAG1V = 0 ! diagonalization to use on regular arrays (diagge.f90)**

    The diagonalization of matrices.

    (a) DSGVX (LAPACKL: computes selected eigenvalues, and optionally eigenvectors). This is default and only a few eigenvectors are obtained.

    (b) DSGVD (Default if matrix size is below 100). Uses a divide and conquer algorithm to compute eigenvectors.

    (c) DSGV (This is slowest of the available) option.

0. DIAG2V = 0 Diagonalization of Hamiltonian (using packed storage for memory savings). Set using **idiag2** variable in the code. Note that the old Dirk's singular value decomposition routine for the diagonalization has been removed. It is very very slow compared to any of the following.

    Available:

    (a) DSPGVX (LAPACK: computes selected eigenvalues, and optionally eigenvectors). This is default and only a few eigenvectors are obtained.

    (b) DSPGVD (Default if matrix size is below 100). Uses a divide and conquer algorithm to compute eigenvectors.

    (c) DSPGV (QR- factorization. This is slowest of the available) option.

    The option 1 (DSPGVD) is the fastest if all eigenvectors are required otherwise use the default 0. * Note that the **SCALAPACK** is also available but you will have to build the executable by enabling **SCALAPACK**.

0. DOSOCCUV = 'N' ! Controls whether to calculate density of states

1. EXCITEDV = 'N' ! Determines if this is an excited state calculation

2. FORMFAKV = 'N' ! this controls if FORMFAK is executed

3. JNTDOSV = 'N' ! this controls whether excite is executed (Calculation of joint density of states).

4. MATDIPOLEV = 'N' ! Set this to true during the site-specific polarizability. This will compute contributio to the dipole moment from individual atom. This is particularly useful in computation of site-specific polarizabilities. It will by itself not provide site-specific polarizability.

5. NONSCFV = 'N' ! Set to Y to do a non SCF calculation

6. DFTD3V = 'N' ! Set to Y to do include Grimmes DFT-D3 dispersion This will include Stefan Grimme's empirical dispersion correction. The parameters set used for the dispersion in the NRLMOL is set for the PBE functional. Also, the zero damping scheme is used by default. Use these for optimization of non-bonded systems. For details, please refer to S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, J. Chem. Phys. 132, 154104 (2010); DOI:10.1063/1.3382344.

7. NONSCFFORCESV = ‘N’ ! Set to **Y** to calculate forces in a non SCF calculation This will do a non SCF calculation. Not very useful. Sometimes you already have converged wavefunctions and you want to calculate the JOINT DOS or any post convergence property. Then it is recommended that you perform at least one SCF iteration and compute the properties of interest.
8. WFGRIDV = ‘N’ ! When set to **Y**, it will generate CUBE file for 5 molecular orbitals densities around the HOMO and LUMO.

1.6 NRLMOL Mesh

In the NRLMOL, mesh is generated by specifying the accuracy of various intergals. The mesh is refined until the specified accuracy of the integrals is accomplished. In this sense, the mesh is variational. There are two types of meshes used in the calculation. One is the radial mesh used for calculations within the atomic spheres and the other is the interstitial mesh (mesh between atomic spheres). The defaults for these are 1.E-06. The mesh parameters are stored in the MESHDAT file. The default will look like It is possible to change the default mesh by the user. The parameters used in creating the mesh are listed in the MESHDAT file. The default MESHDAT file contains the following parameters :

```
 F                                                                      line 1
0.10000E-06   1.2000                                                      line 2
 6                                                                        line 3
0.20000      0.40000      0.60000       1.0000       1.6000               line 4
 4                                                                        line 5
 2.1000       10.100       18.100                                         line 6
 2   1   3   5   5   7   9  11  19  21                                    line 7
 4   1   3   5   5   7   9  11  19  21                                    line 8
 4   1   3   6   5   7   9  11  19  21                                    line 9
 6   1   3   6   7   7   9  11  19  21                                    line 10
0.20000E-06   1.2000                                                      line 11
 2.0000       8                                                           line 12
 2.0000                                                                   line 13
```

As noted above are two types of meshes used in the calculation. One is the radial mesh use for calculations within atomic spheres and the other is the interstitial mesh.

Line 1:

Line 2: The numbers in this line pertains to the radial mesh. The radial mesh is constructed to give integrations involving various Gaussians from short to long range. The small number is the error allowed in integration by the mesh. The second number 1.2 separates the exponentials of the Gaussians which are tested i.e. the n+1st exponential is 1.2 times nth exponent. Decreasing the error tolerance will result in increase in number of mesh points and better integrals.

Line 3: The atomic sphere is divided into different concentric regions with different numbers of mesh points. The number of such radial zones is written in line 3.

Line 4: The outer radii of the radial zones.

Line 5: The mesh has to be different for different atoms. Hence the periodic table (upto Z=56) is divided in 4 types of meshes.

Line 6: This line shows the 4 types of meshes for atoms : first one for Z<2.1, second one for Z<10.1 and third on for Z<18.1 and the last one for Z>18.

Line 7,8,9,10: The four lines contain the parameters for each type of atomic mesh. The numbers are

NPATS, NPIST, NTHET, NPHI, LMAX FOR EACH RADIAL ZONE

NPATS :

NPIST, NTHET, NPHI : Before creating the mesh, the space is divided into boxes such that each atom is contained in one box. Then a sphere around the atom is assumed and the radial mesh is created. The space at the box corners between the atomic sphere and the rectangular box is divided in a different mesh. The parameters NPIST, NTHET and NPHI correspond to the mesh at the box corners.

LMAX : LMAX for the each radial zone. This mesh will integrate a function of the type r lmax exp(-. r2) within the given error limit in this region. Increasing LMAX results in a more refined mesh.

Line 11 : This line contains the same parameters as line 2 but for the interstitial mesh. Decreasing the error limit results in more accurate integrals in the interstitial region.

Line 12: Cutfac, mx1d

CUTFAC: If a box transforms into itself due to symmetry, it will be split if it is larger than cutfac times the distance to the closest atom.

MX1D: max. number of points in a one-dimensional interstitial partition

Line 13: Splrat

SPLRAT: largest allowed ratio for: the size of an atomic box divided by the distance of another atom to the box boundary

> NRLMOL allows setting of these paramaters by user to excersize control over the quality of calculation. Above values are default. Perhaps the simplest thing you can do to improve mesh is to improve the quality of interstial mesh by changing the line 11. *Warning* When taking energy differeces and comparing the energies it advisable to ensure that same quality of mesh was used in all pertaining calculations.

1.7 NRLMOL files: INPUTS and OUTPUTS

The main required input file for NRLMOL is called **CLUSTER**. Using the minimal structural information one can set up NRLMOL calculation using default values for the most of the paramters. An auxillary input file is called **NRLMOL_INPUT.DAT**. Besides these a number of INPUT files can be used as input files if provided by users to control the job calculations. In practically most cases you will be with **CLUSTER** and **NRLMOL_INPUT.DAT** files. Following is the list of files that NRLMOL will generate when executed. They contain variours information about the calculations.

- LIST of FILES

1. ATOMSPHNN: Charge and spin charge in each inequivalent atom integrated over a sphere of specified radius.
2. CLUSTER : Main input file.
3. CLUSTER.MOLDEN : This contains the geometry and converged molecular orbtials in the molden format. The file can be visualized using *MOLDEN* or *JMOL* moleclar viewers. The visualization of XMOL.xyz, CLUSTER.MOLDEN, and WFHOMO* files is *highly* recommended.
4. DIPOLE : Contains x, y, z components of dipole moments in the atomic units.
5. DOSOCU, DOSVIRT, DOSJNT : Contain density of states information for the occupied, virtual and total states.
6. EVALUES : The eigenvalues, their spin, symmetry representation, degeneracy and occupancy, Fermi energy for the current SCF cycle. It can also be used as an input file to specify fixed occupation numbers.
7. **EVALNNN** [The eigenvalues, their spin, symmetry representation, degeneracy and occupancy,]
   Fermi energy for each iteration number NNN.

8. FRCOUT : Total energy, forces on each atom, dipole moment, applied electric field . Written at every optimization step.
9. GEOCNVRG : Convergence criteria, Total energy , largest force, information about geometry optimization. Is written after every complete SCF cycle.
10. HISTORY: Contains history of the geometry optimization. To see the energy as function of optimization step do 'grep -i TR HISTORY' in the directory.
11. JNTOUT : Joint density of states and absoprtion spectra.
12. MAJNNN : Majority spin density of states for the atom number NNN.
13. MINNNN : Minority spin density of states for the atom number NNN.
14. RHOTOT : Total density on a specified grid. Is written in Gaussian cubic format.
15. RHOSPN : Spin density on a specified grid. Is written in Gaussian cubic format.
16. RUNS : Control restart of calculation. Caculations can be restarted from Hamiltonian (**HAMOLD**), wavefunctions (**WFOUT**), or potential (**COUPOT**).
17. **SPNRES: Gamma matrices, anisotropy energy, energy eigenvalue with spin-orbit coupling** (more description later).
18. SUMMARY : Total energy, electronic charge, kinetic energy and trace of hamiltonian for each iteration.
19. VIBINP: VIBINP is of the input files for the vibrational calculations. It contains, the last geometry (optimized), forces, electric field, dipole moment etc.
20. **WFHOMONN: Orbital density on a specified grid. Is written in Gaussian cubic format. NN is** 00 for HOMO and is positive for states above HOMO. NN is negative for states below HOMO.
21. XMOL.DAT : Goemetry in the xyz format. The first column contains atomic numbers. The atomic coordinates are in Angstrom.
22. XMOL.xyz : Goemetry in the xyz format. The first column contains atomic labels. The atomic coordinates are in Angstrom. Use **JMOL** to visuliaze this.

1.8 ISYMGEN - Basis sets

The basis set information is in the ISYMGEN file which is created when you run NRLMOL. This file contains the basis set for each identity atom. For each orbital of a given atom, same set of primitive Gaussians is used. For example, the default basis set for carbon is written as below :

The following is the Pederson-Porezag (NRLMOL default) basis in the **ISYMGEN** . The newer version allows use of few other basis sets such as : 6-31G*, 6-311G**, STO-3G, TZVP, DGDZVP etc. The Pederson-Porezag (NRLMOL default) is specially optimized for the PBE functional.

```
   6   6                       ELECTRONIC AND NUCLEAR CHARGE
ALL                            ALL-ELECTRON ATOM TYPE
   3                           NUMBER OF ATOMS OF TYPE CAR
ALL-CAR001
ALL-CAR002
ALL-CAR003
EXTRABASIS         CONTROLS USAGE OF SUPPLEMENTARY BASIS FUNCTIONS
 12                NUMBER OF BARE GAUSSIANS
   5   4   3       NUMBER OF S,P,D FUNCTIONS
   0   0   1       SUPPLEMENTARY S,P,D FUNCTIONS
 0.22213361D+05      0.33317370D+04      0.75790135D+03
 0.21454372D+03      0.69924889D+02      0.25086135D+02
 0.95910418D+01      0.38024557D+01      0.14891854D+01
 0.57487653D+00      0.21494732D+00      0.77209650D-01

 0.19792249D+00      0.36998977D+00      0.63644615D+00
 0.10124931D+01      0.14480787D+01      0.17173689D+01
 0.14931932D+01      0.68987161D+00      0.86072247D-01
-0.16566695D-02      0.37766033D-03     -0.47105343D-04

-0.45005260D-01     -0.84621052D-01     -0.14496564D+00
-0.23535601D+00     -0.34215368D+00     -0.44595124D+00
-0.45263971D+00     -0.32216414D+00     -0.12988420D-01
 0.20135471D+00      0.12769913D+00      0.14135467D-01

 0.00000000D+00      0.00000000D+00      0.00000000D+00
 0.00000000D+00      0.00000000D+00      0.00000000D+00
 0.00000000D+00      0.00000000D+00      0.00000000D+00
 0.10000000D+01      0.00000000D+00      0.00000000D+00

 0.00000000D+00      0.00000000D+00      0.00000000D+00
 0.00000000D+00      0.00000000D+00      0.00000000D+00
 0.00000000D+00      0.00000000D+00      0.00000000D+00
 0.00000000D+00      0.10000000D+01      0.00000000D+00

 0.00000000D+00      0.00000000D+00      0.00000000D+00
 0.00000000D+00      0.00000000D+00      0.00000000D+00
 0.00000000D+00      0.00000000D+00      0.00000000D+00
 0.00000000D+00      0.00000000D+00      0.10000000D+01

 0.23138630D-01      0.42649133D-01      0.74658851D-01
 0.12024115D+00      0.18351176D+00      0.24706804D+00
 0.30714219D+00      0.31372706D+00      0.26726340D+00
 0.14756585D+00      0.47585576D-01      0.72796459D-02

 0.00000000D+00      0.00000000D+00      0.00000000D+00
 0.00000000D+00      0.00000000D+00      0.00000000D+00
 0.00000000D+00      0.00000000D+00      0.00000000D+00
 0.10000000D+01      0.00000000D+00      0.00000000D+00


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

Here, the first line specifies the nuclear and electronic charges in the atom. The nuclear and electronic charges specifies the actual atom (e.g. Nuc charge = 6 for carbon) but the electronic charge depends on whether all electron or pseudo potential calculations are used (e.g. for carbon it would be 6 for all electron and 4 for a pseudopotential calculation)

The second line specifies the type of calculation :

ALL for all-electron BHS for BHS pseudopotential TAB for tabulated user-supplied pseudopotential

The third and fourth lines specify the number of total such atoms in the geometry and their symbols in the SYMBOL file. EXTRABASIS =1 in SYMBOL file will signal the program to use the supplementary basis functions. Then comes the number of primitive Gaussians followed by the number of the s, p and d -type contracted Gaussians. The number of supplementary functions of s, p and d type are written next. These informations are followed by some blocks of numbers. The first block lists the exponents of the primitive Gaussians. This is then followed by Ns blocks where Ns is the number of contracted s-type Gaussians. The first block is the coefficients multiplying the primitive Gaussians for the 1s contracted Gaussian, the second block is for 2s Gaussian and so on. After the Ns number of such blocks, comes the Np blocks corresponding to the p-type contracted Gaussians followed by similar Nd number of d-type Gaussians. In the example for carbon atom above, the 1s and 2s contracted Gaussian is a linear combination of the all the primitive Gaussians whereas the higher unoccupied s orbitals are taken as single long-range Gaussians. Similarly for p orbitals where only the 2p orbital is occupied. These are then followed by similar blocks corresponding to the supplementary functions. The supplementary functions are used only when

EXTRABASIS = 1 in the SYMBOL file. These are generally polarization functions and are usually only used for the calculation of IR and Raman intensities and possibly for dipole moments and polarizabilities.

The carbon atom basis set in the example might be called a “12-1211+++G(3d)” basis in Pople/Gaussian parlance if we consider the last s,p,d orbitals as diffuse functions. This means 12 primitive gaussians contracted to the core 1s orbital, then a triple-zeta valence set (three sets of s and three sets of p orbitals) represented by 12, 1 and 1 primitive gaussians, three sets of d polarization functions and three sets of diffuse functions (s,p,d) each represented by a single primitive gaussian. This is an example of a “generally contracted” basis in which the same set of primitives contributes to all the orbitals. If the diffuse functions are considered as valence, then this basis has a quadruple-zeta functions.

~~1.9 Setting up perturbative Delta SCF calculation~~

~~Running excited state calculations using perturbative delta SCF method. This is not automated yet so~~ use the following guidelines to run the excited states calculations. The method works well for the charge transfer excited states. It is a perturbation approach, so the first step is to carry out the ground state SCF. Run a spin-polarized ground state calculation for a chosen system without using any point group symmetry. Each excited state calculation is done in a separate directory. Use the following procedure to run the excited state calculations.

1. Make a directory, say *EXCITED1* and copy the following files from the directory where the ground state calculations were performed to the excited state directory: SYMBOL, GRPMAT, ISYMGEN, HAMOLD, REPMAT, VMOLD.

2. Create RUNS file. Your RUNS file for the excited state calculation should be:

```
-1     N            ITBEG, NCALC
 1     4            START: 0=SCR.NUC, 1=HAM, 2=POT, 3=LSF, 4=WFUNC
 0                  START HAMILTONIAN IS INTERPOLATED: 0=NO, 1=YES
```

   where, *N* is the geometry number of the corresponding geometry in **SYMBOL**. “-1” option allows previously generated mesh; if, for some reason, this does not work, then set it to “1” and rerun. **WARNING** Most of the problems/errors with excited states calculation are due to use of different geometries in the excited state and the ground state. So please ensure that you use correct geometry:- the second field in the top line of the **RUNS** file. Also, for the excited state calculation with perturbative delta SCF method, you always start with Hamiltonian.

3. Run the command “$ echo ”.TRUE.” > RUNTYPE

4. Next create a file called **OCCEXC** with required occupation numbers. (No blank lines). An example *OCCEXC* for the water molecule (H2O) is given below:

```
 1      : Number of excited states to be calculated. For starter keep it 1.
 -76.387242322234A      : Ground state SCF energy
1 5                     : Spin and state indices for the hole
2 6                     : SPin and state indices for the particle
5                       : Number of GS occupied orbitals of spin 1
1 1 1 1 1               : GS occupancy of the states of spin 1
5                       : Number of GS occupied orbitals of spin 2
1 1 1 1 1               : GS occupancy of the states of spin 2
5                       : Number of excited occupied orbitals of spin 1
1 1 1 1 0               : occupancy of the orbitals of spin 1 in excited state
```

```
6                        : Number of excited occupied orbitals of spin 2
1 1 1 1 1 1              : occupancy of the orbitals of spin 2 in excited state
```

5. Compile the NRLMOL for the excited states. Your executable for the ground state may not work as the parameters are different for the excited states. When compiled, copy the executable here and submit the job.

TIP The memory demand for the excited state calculation is much larger than the ground state as both the ground and excited state Hamiltonians are required. If your calculations run out of memory, one possibility is to use fewer cores per node in a parallel job.

1.10 Tutorial 1 Understanding atomic structure using the NRLMOL

Very simple tutorial to get aquainted with advanced electronic structure calculation package NRLMOL. This tutorial will explain how to run the NRLMOL for atomic calculations. For simplicity, we will assume that the open shell atoms are spherically symmetric.

February 6, 2008

The CLUSTER file is the main input file of NRLMOL. It contains the minimal information to set up the calculation. See below the CLUSTER file for the Nitrogen atom:

```
GGA-PBE*GGA-PBE            # Exchange-correlation parametrization
GRP                        # Point group of system
1                          # No. of atoms
0.0 0.0  0.0    7  ALL    # x,y,z coordinates, Atomic number, ALL means all electron
0.0 3.000                 # Charge and Moment

 Spherical atomic calculation. Input auto generated by Perl script,
                Rajendra Zope, EL Paso, TX 79912. Wed Feb  6 15:17:59 CST 2008
```

We will now describe the input structure of this file.

The first line is **GGA-PBE*GGA-PBE**. It means that the exchange-correlation interactions in the systems are modeled within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) parametrization. This is the default functional used in NRLMOL. A few other functionals are also available.

The second line is **GRP** . It refers to point group symmetry. The GRP means the symmetry point group operations will be read from the GRPMAT file. For spherical atoms the GRPMAT will contain a unit matrix. You need not generate GRPMAT file. It will be created automatically.

The third line contains **1**. It specifies the number of atoms in calculations. We're running atomic calculations. So number of atoms is 1. For molecules this number will change. See tutorial on molecular calculations for more details.

The line following third line contains the cartesian position in atomic units of the atom, its atomic number, and string ALL. In this example, we are dealing with only one atom, which can be conveniently put at the origin (0, 0, 0). Followed by the xyz coordinates is the atomic charge. The example listed is for Nitrogen whose atomic number is 7. The string ALL means include all (that is 7 in this case) electrons into calculations.

The fifth line in example has two fields. The first field is **0.0** which means perform calculation for the neutral atom. If it is **1** then the calculations will be performed for singly charged cation of N atoms. The next field which is **3** in this example corresponds to number of unpaired electron in the system. The nitrogen has three unpaired electrons in the 2p orbitals. Lines after Charge and Moment line are ignored.

Now, copy the example input in the file called CLUSTER and run the calculation for nitrogen atom using the following sequences of commands at the prompt. It is recommeded that you run each NRLMOL calculation in a separate directory.

$ **rm -f GEOCNVRG SYMBOL**

$ **./cluster > print.SCF**

Open the **GEOCNVRG** file and write down the energy. If you have done everything correctly then it should be **-54.535482** Hartree.

Now, browse through the file print.SCF and look at the energies printed at each iteration. The difference between total energy in two successive iterations should diminish as the self consistent process progresses. When this difference is smaller than the threshold value set in SCFDAT the SCF process will stop. Also, look at the EVALUES file in which Kohn-Sham eigenvalues and occupation numbers are printed. Try to understand the SCF process, occupation numbers, degeneracy of orbitals.

1.11 Tutorial 2: Understanding electronic structure of molecules using NRLMOL

In this tutorial we will learn to optimize the geometries of diatomic molecules. We choose a case of H2 molecule. Again, as a reminder the **CLUSTER** file is the main input file of NRLMOL. It contains the minimal information to set up the calculation. See below the CLUSTER file for the hydrogen molecule.

```
GGA-PBE*GGA-PBE            # Exchange-correlation parametrization
GRP                        # Point group of system
2                          # No. of atoms
0.0 0.0  0.5    1  ALL    # x,y,z coordinates, Atomic number, ALL means all electron
0.0 0.0 -0.5    1  ALL    # x,y,z coordinates, Atomic number, ALL means all electron
0.0 0.000                 # Charge and Moment

 Hydrogen molecule. Input auto generated by Perl script.
```

We will now describe the input structure of this file. The first line is **GGA-PBE*GGA-PBE**. It means that the exchange-correlation interactions in the systems are modeled within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) parametrization. This is the default functional used in NRLMOL. A few other functionals are also available.

The second line is **GRP**. It refers to point group symmetry. The GRP means the symmetry point group operations will be read from the GRPMAT file. A few selected symmetry groups such as Ih, Td, Th, C3V etc. can also be provided here. In this case the GRPMAT corresponding to specified point group will be automatically generated by NRLMOL. Even though the H2 molecule posses symmetry we will perform calculation without symmetry. We will learn how to use symmetry to speed up calculations in the next tutorial. So keep “GRP” line as it is. The GRPMAT file will be created automatically and will contain the identity matrix only.

The third line specifies the number of inequivalent atoms in calculations. Since our calculation does not use symmetry, the number of inequivalent atoms. Since we are not making use of point group symmetry, the number of inequivalent atoms is same as total number of atoms, which is 2 in this case.

The lines following the third line contain information for each of the inequivalent atoms. The first three numbers are the cartesian positions in atomic units, its atomic number, and string ALL. In this example, we have placed one hydrogen atom at (0,0,Z) and the second one at (0,0,-Z). You can put the atoms anywhere. Atomic positions should be given in atomic units, Bohr. Followed by xyz coordinates is the atomic charge. The example listed is for hydrogen whose atomic number is 1. The string ALL signifies that the calculations are to be performed at the all-electron level. It is also possible to use pseudopotentials. Only the BHS pseudopotentials are hardwired into the code. It is also possible to use user-supplied (numerical) pseudopotentials also, but requires more work and is not recommended for beginners.

The last line in example has two fields. The first field is 0.0 which means perform calculation for the neutral molecule. If it is 1 then the calculations will be performed for singly charged cation of N atoms. The next field which is 0 in this example corresponds to number of unpaired electrons in the system. There are no unpaired electrons. Lines after Charge and Moment line are ignored.

Now, copy the example input in the file called CLUSTER and run the calculation for H2 molecule using the following sequences of commands at the prompt.

> $ **rm -f GEOCNVRG SYMBOL ISYMGEN INPUT RUNS**
>
> $ **./cluster < print.SCF**

Now, browse through the file print.SCF and look at the energies printed at each iteration. Also, look at the EVALUES file in which Kohn-Sham eigenvalues and occupation numbers are printed. Try to understand the SCF process. Now, let's open the GEOCNVRG file:

```
  1.0000000000000000E-003
     CONVERGE FALSE
     ENERGY=   -1.113884538059298
     TOTAL GRADIENT=   0.4658517560326668
     LARGEST NUCLEAR GRADIENT=   0.3294070519678478
```

The number on the first line is the optimization threshold. If the RMS gradient falls below this value then optimization of structure is complete. The following line CONVERGENCE FALSE tells us that the structure is not optimized yet, that is, the atoms have still significant forces. The next line is the total energy in Hartree for the current geometry. The last line print out the maximum rms force. To get more information on the forces, look at the file **FRCOUT**.

```
                -1.1138845381         1 Energy and Symbol NCALC
           0.00000000           0.00000000           0.50000000   1   1
  -0.593228680992D-07  -0.593228686397D-07   0.329406819469D+00
           0.00000000           0.00000000          -0.50000000   1   1
  -0.593227768567D-07  -0.593227770511D-07  -0.329407051968D+00  <--- MAX-FORCE
   0.557780120356D-07   0.557780123507D-07  -0.768552000929D-07
   0.000000000000D+00   0.000000000000D+00   0.000000000000D+00
```

The first line is the total energy in Hartree. It will also be printed in **GEOCNVRG**. Followed by these are atomic positions (x,y,z) components of atom 1, which is followed by the x,y,z component's of forces. Similar, information is printed on subsequent lines. The second last line contains DIPOLE MOMENT while the last line prints out the external electric field. The H2 molecule does not have dipole moment and our calculations are in absence of electric field. Note that since we placed atoms on Z axis only the Z component of force is nonzero. The forces are significant and tell us that atoms should be moved away from each other. Since the forces are significant we need to repeat calculation until the forces vanish (fall below the threshold). So repeat following command until forces are zero which is easy to figure out by looking at **GEOCNVRG**.

> $ **./cluster > print.SCF**

You can also use following script to automate optimization. For the bash shell it is :

```
#!/bin/bash
  export niters=41

  export iter=1
 while [ $iter -le $niters ]; do

    #${mpirun}  -np ${NP}   ./bcluster > print.${iter}
    #${mpirun} -machinefile $PBS_NODEFILE -np ${NP} ./cluster  > print.${iter}
    ./cluster  > print.${iter}

    cat FRCOUT >> FRCOUT-TOT
    cp FRCOUT FRCOUT.${iter}
      if [ -e "EXIT" ]; then
            rm -f EXIT; exit
      fi
```

```
     if [ -e "GEOCNVRG" ]; then
       export x=`cat GEOCNVRG| grep CONV |awk '{print $2}'`
         if [ $x == 'TRUE' ]; then
            echo "Looks like geometry is converged at step ${iter}. \n Stopping..."
            exit
         fi
     fi
  let  iter=${iter}+1
done # end_of_while_loop
```

Cut and paste the above script in a file called **opt.bash**. Then do the following to run it.

$ **chmod +x opt.bash**

$ **./opt.bash &**

The first command will make the file **opt.bash** executable and the second one will run the program in background. The final **GEOCNVRG** file should look something like

```
1.0000000000000000E-003
CONVERGE TRUE
ENERGY=   -1.166529242444089
TOTAL GRADIENT=   4.6930900067498795E-004
LARGEST NUCLEAR GRADIENT=   3.3185157688592808E-004
```

Note the second line says that CONVERGENCE is **TRUE** . This indicates that convergence was obtained for the optimization job, i.e. the structure is optimized. The final forces are in **FRCOUT**.

```
                 -1.1665292424     6 Energy and Symbol NCALC
         -0.00000200          -0.00000200           0.70838900   1   1
 -0.156998838711D-06  -0.156998838805D-06   0.331851502536D-03
         -0.00000200          -0.00000200          -0.70838900   1   1
 -0.156998838240D-06  -0.156998838613D-06  -0.331851502610D-03  <--- MAX-FORCE
  0.311218459833D-06   0.311218459219D-06  -0.930366894636D-13
  0.000000000000D+00   0.000000000000D+00   0.000000000000D+00
```

The final optimized coordinates are stored in “XMOL.DAT” (They are in Angstrom).

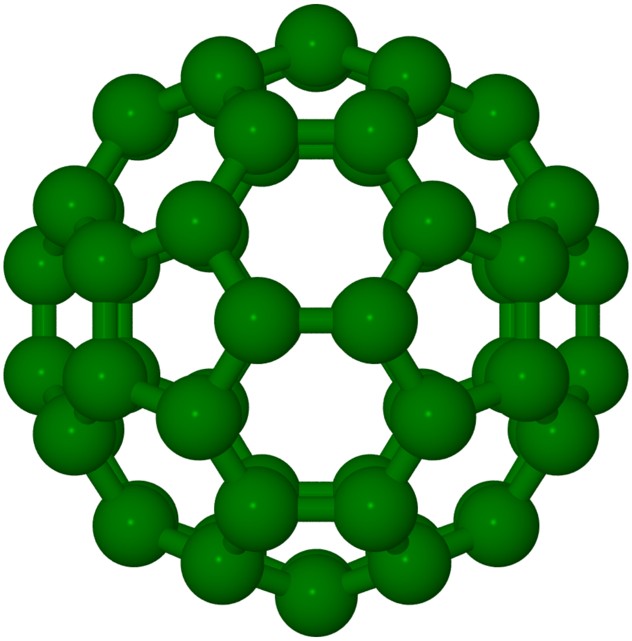
```
   2
Cluster output
    1    0.00000    0.00000    0.37486
    1    0.00000    0.00000   -0.37486
```

So the optimized bond length is 0.749 Angstrom.

1.12 Tutorial 3 Electronic structure of the C60 molecule

This tutorial will explain use of NRLMOL to study the electronic structure of C60 molecule. The C60 molecule is spherical carbon molecule - also called bucky ball. It was found in the laboratory at Rice university in 1985 by Harold Kroto, James R. Heath, Sean O’Brien, Robert Curl, and Richard Smalley. The 1996 nobel prize was awarded to Kroto, Curl and Smalley for the discovery of C60 and related molecules. This molecule posses very high symmetry-icosahedral symmetry.

We will make use of this symmetry in our calculations. All carbon atoms in C60 are equivalent to each other, that is, once the position of one carbon atom is specified the position of remaining carbon atoms can be obtained using the point group operations of the icosahedral group. This tutorial will explain how to accomplish this and make use of symmetry to simplify the calculations.



We assume that the code us compiled with appropriate set of parameters needed for arrays. The following set of parameters will work.

```
IMPLICIT REAL*8 (A-H,O-Z)
PARAMETER ( MX_PROC=          40)
PARAMETER ( MXSPN=           1)
PARAMETER ( MAX_PTS=      100000)
PARAMETER ( MAX_FUSET=           2)
PARAMETER ( MAX_IDENT=          10)
PARAMETER ( MX_CNT=         60)
PARAMETER ( MXATMS= MX_CNT )
PARAMETER ( NMUPMAX=           7)
PARAMETER ( MAX_BARE=          30)
PARAMETER ( MAX_CON=          12)
PARAMETER ( MAX_OCC=        2400)
PARAMETER ( MAXUNSYM=          55)
PARAMETER ( NDH=        1500)
PARAMETER ( NDH_TOT=     1126500)
PARAMETER ( MX_GRP=         120)
PARAMETER ( MAX_REP=          10)
PARAMETER ( MAXSLC=        3300)
PARAMETER ( LOCMAX=         360)
PARAMETER ( ISMAX=          32)
PARAMETER ( MAXSYMSALC=          32)
PARAMETER ( MXRPSP=         100)
PARAMETER ( MXPTAB=         100)
PARAMETER ( MXLPSP=           2)
PARAMETER ( MXKPT=           1)
PARAMETER ( MPBLOCK=         100)
PARAMETER ( MXPOISS=         100)
PARAMETER ( NSPEED=          25)
PARAMETER ( LDIM=           3)
PARAMETER ( CUTEXP=   40.00000000000000     )
PARAMETER ( MX_SPH=        1000)
PARAMETER ( MAX_VIRT_PER_SYM=         500)
```

```
        PARAMETER ( MAXGFIT=          15)
        PARAMETER ( MAXLSQF=          50)
        PARAMETER ( MTEMP=       60000 )
        PARAMETER ( KRHOG=          10 )
```

As you know by now, CLUSTER file is the main input file of NRLMOL. For C60 the CLUSTER file is

```
GGA-PBE*GGA-PBE          (DF TYPE EXCHANGE*CORRELATION)
IH                       (TD, OH, IH, X, Y, XY, ... OR GRP)
1                        (NUMBER OF INEQUIV. ATOMS IN CH4)
0.000000  6.579993  1.321695   6 ALL
0.0 0.0                  (NET CHARGE AND NET SPIN)
```

Note that we have only one atom listed and the point group is listed to be **Ih**. If you are using point group symmetry then only positions of inequivalent atoms need to be listed. The NRLMOL will generate full geometry of the system using the point group operations. It is *strongly* recommended that you visualize the geometry generated - XMOL.DAT or XMOL.xyz files using molecular viewer such as JMOL or MOLEKEL or any other of your choice.

Now run the calculation. $ **rm -f GEOCNVRG SYMBOL**

$ **./cluster > print.SCF**

Open the **GEOCNVRG** file and write down the energy. It should be

```
   1.0000000000000000E-003
 CONVERGE TRUE
 ENERGY=   -2284.358327861622
 TOTAL GRADIENT=   6.9943783981219765E-005
 LARGEST NUCLEAR GRADIENT=   6.9943783981219765E-005
```

and the forces are

```
               -2284.3583278616     1 Energy and Symbol NCALC
           0.00000000           6.57999300           1.32169500   6   6
   0.000000000000D+00  -0.934955152640D-05  -0.693160789707D-04  <--- MAX-FORCE
  -0.213162820728D-13   0.710542735760D-14   0.213162820728D-13
   0.000000000000D+00   0.000000000000D+00   0.000000000000D+00
```

Note that forces on only one atom (inequivalent) are listed.

The eigenvalues are stored in file called "EVALUES". Please inspect it. Look at the degeneracy of the eigenvalues. Identify HOMO, LUMO etc. The file is also displayed below for your convenience.

```
This is an abridged file containing eigenvalues of C60.

 ********* NEW TRY ************, SPIN:            1
 REP:            1 DIM:            1 NUMBER OF BASES:           25
           1          25
   -9.942805     -0.8997024     -0.5549701     -0.4479115     -0.1991965E-01
   0.6689239E-01  0.1684883      0.4065947      0.4303353      0.4932246
   0.6197493      0.8237995       1.064748       1.332207       1.589216
    .
    .
    .
 REP:            2 DIM:            3 NUMBER OF BASES:           60
           3          60
   -9.942771      -9.942283     -0.8811058     -0.6511179     -0.4751674
  -0.4263302     -0.1540616      0.2963368E-01  0.7381854E-01  0.1399013
   0.1454381      0.2194449      0.2953231      0.4100078      0.4159666
   0.5064494      0.5198368      0.5662745      0.6077245      0.6927512
   0.8485903      0.9020563      0.9212636      0.9778088       1.120618
    .
    .
    .
 REP:            3 DIM:            5 NUMBER OF BASES:           95
            5          95
   -9.942707      -9.942522      -9.942192     -0.8455306     -0.7306929
  -0.5751889     -0.4086972     -0.3857767     -0.3299505     -0.2612101
  -0.7485659E-01  0.5984700E-01  0.9606631E-01  0.1289818      0.1606308
   0.2017960      0.2727632      0.3200607      0.3361940      0.3987439
   0.4505640      0.4721895      0.4830797      0.4905669      0.5863982
   0.5938349      0.6509424      0.6840220      0.6948194      0.8087404
   0.8537736      0.9215714      0.9419371      0.9592563      0.9766250
    .
    .
    .
 REP:            4 DIM:            3 NUMBER OF BASES:           60
            3          60
   -9.942610      -9.942173     -0.8087070     -0.6119900     -0.4521482
  -0.3383461     -0.8228363E-01  0.8985531E-01  0.1057484      0.1731967
   0.2351114      0.3167932      0.4029469      0.4170402      0.4388469
   0.5078198      0.5737927      0.6229951      0.7266742      0.7936461
   0.9151430      0.9266100      0.9995002       1.073048       1.199648
    .
    .
    .
 REP:            5 DIM:            4 NUMBER OF BASES:           70
            4          70
   -9.942629      -9.941986     -0.7771414     -0.4280769     -0.3666027
  -0.3181925      0.1970728E-01  0.8832295E-01  0.1412645      0.2453531
   0.3710384      0.3930982      0.4018634      0.4195257      0.5115655
   0.5622322      0.5934607      0.6458433      0.7175404      0.7465492
   0.7555818      0.8274507      0.9549796       1.034820       1.078526
    .
 REP:            6 DIM:            4 NUMBER OF BASES:           70
            4          70
   -9.942545      -9.942070     -0.7135614     -0.5127091     -0.3953816
  -0.2569762     -0.5496157E-02  0.1097230      0.1575782      0.2465148
   0.3105353      0.4047911      0.4485227      0.4531293      0.4763553
   0.4850277      0.5600762      0.6488439      0.6656025      0.7337152
   0.8110428      0.9402047      0.9808577       1.030000       1.105739
 REP:            7 DIM:            5 NUMBER OF BASES:           80
            5          80
   -9.942488      -9.942127     -0.6595450     -0.4869222     -0.3186715
  -0.2144125     -0.2052547E-01  0.1355438      0.2234478      0.2350119
   0.3204446      0.3928607      0.3957610      0.4817556      0.4930063
   0.5036710      0.5642048      0.5714468      0.7307460      0.7358558
   0.7466057      0.8818037      0.9426629      0.9976558       1.047811
    1.088609       1.136037       1.226505       1.297072       1.401576
    2.099996       2.127763       2.167014       2.206178       2.279180
 REP:            8 DIM:            3 NUMBER OF BASES:           45
            3          45
   -9.942249     -0.5708627     -0.1140607      0.1309249      0.1794275
   0.3661029      0.4497591      0.4917586      0.5693141      0.6491583
   0.8200522      0.9194278      0.9646669       1.101807       1.220654
    1.351788       1.480114       1.581128       1.767750       1.927398
    1.952246       2.024065       2.094322       2.217394       2.285956
 REP:            9 DIM:            3 NUMBER OF BASES:           45
            3          45
   -9.941977     -0.3861205      0.3803237E-01  0.2679375      0.3120214
   0.4249118      0.4853449      0.5541875      0.6313738      0.6528077
   0.8270208      0.8480218       1.054382       1.105491       1.275696
    1.421811       1.585232       1.855841       1.955594       1.993680
    2.065630       2.158184       2.230132       2.310101       2.441308
 REP:           10 DIM:           1 NUMBER OF BASES:           10
            1          10
   0.6175634      0.9026151       1.484611       2.284678       2.714255
    3.303272       3.605378       5.801911       5.971903       6.756511
 FERMI LEVEL:  -0.1842370492849899      TEMP:   1.0000000000000000E-004
 SUMMARY OF EVALUES AND THEIR OCCUPANCIES:
    1  REP:  1  DEG:  1  SPIN:  1  ENERGY:   -9.94281      OCC:    1.00000
    2  REP:  2  DEG:  3  SPIN:  1  ENERGY:   -9.94277      OCC:    1.00000
    3  REP:  3  DEG:  5  SPIN:  1  ENERGY:   -9.94271      OCC:    1.00000
    4  REP:  5  DEG:  4  SPIN:  1  ENERGY:   -9.94263      OCC:    1.00000
    5  REP:  4  DEG:  3  SPIN:  1  ENERGY:   -9.94261      OCC:    1.00000
    6  REP:  6  DEG:  4  SPIN:  1  ENERGY:   -9.94254      OCC:    1.00000
    7  REP:  3  DEG:  5  SPIN:  1  ENERGY:   -9.94252      OCC:    1.00000
    8  REP:  7  DEG:  5  SPIN:  1  ENERGY:   -9.94249      OCC:    1.00000
    9  REP:  2  DEG:  3  SPIN:  1  ENERGY:   -9.94228      OCC:    1.00000
   10  REP:  8  DEG:  3  SPIN:  1  ENERGY:   -9.94225      OCC:    1.00000
   11  REP:  3  DEG:  5  SPIN:  1  ENERGY:   -9.94219      OCC:    1.00000
   12  REP:  4  DEG:  3  SPIN:  1  ENERGY:   -9.94217      OCC:    1.00000
   13  REP:  7  DEG:  5  SPIN:  1  ENERGY:   -9.94213      OCC:    1.00000
   14  REP:  6  DEG:  4  SPIN:  1  ENERGY:   -9.94207      OCC:    1.00000
   15  REP:  5  DEG:  4  SPIN:  1  ENERGY:   -9.94199      OCC:    1.00000
   16  REP:  9  DEG:  3  SPIN:  1  ENERGY:   -9.94198      OCC:    1.00000
   17  REP:  1  DEG:  1  SPIN:  1  ENERGY:  -0.899702      OCC:    1.00000
   18  REP:  2  DEG:  3  SPIN:  1  ENERGY:  -0.881106      OCC:    1.00000
   19  REP:  3  DEG:  5  SPIN:  1  ENERGY:  -0.845531      OCC:    1.00000
   20  REP:  4  DEG:  3  SPIN:  1  ENERGY:  -0.808707      OCC:    1.00000
   21  REP:  5  DEG:  4  SPIN:  1  ENERGY:  -0.777141      OCC:    1.00000
   22  REP:  3  DEG:  5  SPIN:  1  ENERGY:  -0.730693      OCC:    1.00000
   23  REP:  6  DEG:  4  SPIN:  1  ENERGY:  -0.713561      OCC:    1.00000
   24  REP:  7  DEG:  5  SPIN:  1  ENERGY:  -0.659545      OCC:    1.00000
   25  REP:  2  DEG:  3  SPIN:  1  ENERGY:  -0.651118      OCC:    1.00000
   26  REP:  4  DEG:  3  SPIN:  1  ENERGY:  -0.611990      OCC:    1.00000
   27  REP:  3  DEG:  5  SPIN:  1  ENERGY:  -0.575189      OCC:    1.00000
   28  REP:  8  DEG:  3  SPIN:  1  ENERGY:  -0.570863      OCC:    1.00000
   29  REP:  1  DEG:  1  SPIN:  1  ENERGY:  -0.554970      OCC:    1.00000
   30  REP:  6  DEG:  4  SPIN:  1  ENERGY:  -0.512709      OCC:    1.00000
   31  REP:  7  DEG:  5  SPIN:  1  ENERGY:  -0.486922      OCC:    1.00000
   32  REP:  2  DEG:  3  SPIN:  1  ENERGY:  -0.475167      OCC:    1.00000
   33  REP:  4  DEG:  3  SPIN:  1  ENERGY:  -0.452148      OCC:    1.00000
   34  REP:  1  DEG:  1  SPIN:  1  ENERGY:  -0.447911      OCC:    1.00000
   35  REP:  5  DEG:  4  SPIN:  1  ENERGY:  -0.428077      OCC:    1.00000
   36  REP:  2  DEG:  3  SPIN:  1  ENERGY:  -0.426330      OCC:    1.00000
   37  REP:  3  DEG:  5  SPIN:  1  ENERGY:  -0.408697      OCC:    1.00000
   38  REP:  6  DEG:  4  SPIN:  1  ENERGY:  -0.395382      OCC:    1.00000
   39  REP:  9  DEG:  3  SPIN:  1  ENERGY:  -0.386121      OCC:    1.00000
   40  REP:  3  DEG:  5  SPIN:  1  ENERGY:  -0.385777      OCC:    1.00000
   41  REP:  5  DEG:  4  SPIN:  1  ENERGY:  -0.366603      OCC:    1.00000
   42  REP:  4  DEG:  3  SPIN:  1  ENERGY:  -0.338346      OCC:    1.00000
   43  REP:  3  DEG:  5  SPIN:  1  ENERGY:  -0.329950      OCC:    1.00000
   44  REP:  7  DEG:  5  SPIN:  1  ENERGY:  -0.318671      OCC:    1.00000
   45  REP:  5  DEG:  4  SPIN:  1  ENERGY:  -0.318192      OCC:    1.00000
   46  REP:  3  DEG:  5  SPIN:  1  ENERGY:  -0.261210      OCC:    1.00000
   47  REP:  6  DEG:  4  SPIN:  1  ENERGY:  -0.256976      OCC:    1.00000
   48  REP:  7  DEG:  5  SPIN:  1  ENERGY:  -0.214412      OCC:    1.00000
```

```
49  REP:  2  DEG:  3  SPIN:  1  ENERGY:  -0.154062      OCC:   0.000000E+00
50  REP:  8  DEG:  3  SPIN:  1  ENERGY:  -0.114061      OCC:   0.000000E+00
51  REP:  4  DEG:  3  SPIN:  1  ENERGY:  -0.822836E-01  OCC:   0.000000E+00
52  REP:  3  DEG:  5  SPIN:  1  ENERGY:  -0.748566E-01  OCC:   0.000000E+00
```

To be added: Discussion of orbital degeneracies- plot of wave functions

~~1.13 Tutorial Running fragment analysis with NRLMOL~~

This tutorial shows how to perform fragment analysis with NRLMOL code, changes have been introduced in the NRLMOL_INPUT.dat file to request fragment analysis and the structure of the input file CLUSTER has been modified to accomodate these changes. If fragment analysis is not requested, the CLUSTER file remains unchanged.

1.13.1 Getting the code

Above all, you will need to obtain the latest NRLMOL version which supports fragment analysis, go to where you have your source code and look for a file called fragment.f90, if it is not present, contact me to update your code.

1.13.2 Steps

Individual Fragment Calculation

This part of the calculation doesn't actually require the latest code to be performed. You just need to perform a single NRLMOL run separately on each of the fragments to be analyzed (single point calculation), we do not want to optimize this individual fragments, because the geometry is different when they are taken as a complex. Once the calculation is done, we will need the generated HAMOLD file from each of the fragments. These files must be renamed HAM.1, HAM.2, etc. depending on the number of fragments of the complex. Also, in the file EVALUES we need to collect the following information:

1. **The number of basis functions:** Get the number next to NUMBER OF BASES:
2. **The number of occupied states:** Count the number of occupied states in the list after SUMMARY OF EVALUES AND THEIR OCCUPANCIES: (count the number of states that have OCC: 1)

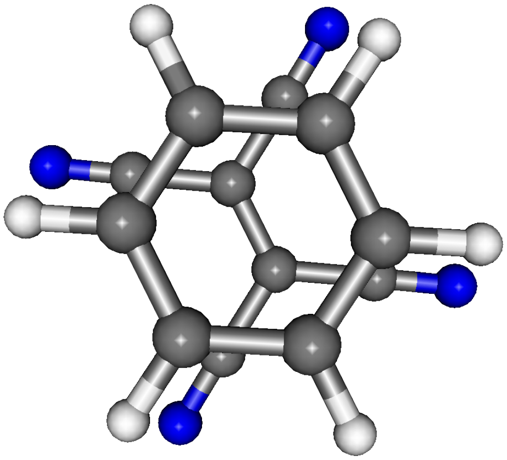
Complex calculation part 1

Now you can perform a calculation on the whole complex, but, there are some considerations that must be taken. NRLMOL reorders the atoms you normally specify in the CLUSTER file, So we lose track of what atoms belong to what fragment, for example: if two fragments of a complex contain Hydrogen, NRLMOL will list all Hydrogens together (in the generated files SYMBOL and ISYMGEN) independently of what fragment they belong to. This is problematic, because the hamiltonian matrix is constructed with this sorted order. But we want it to be written so as to reflect the order of the atoms by fragment. So before you submint your compunded CLUSTER file for execution, some changes to it must be done (besides the format of the CLUSTER file changes when doing a calculation of fragments). First, your CLUSTER file must have the atoms in the order that the fragments are speficied.

1.13.3 Example

Fragments

For an example of a fragment calculation we will use TCNE-Benzene, a small 22 atom complex that can be decomposed into two fragments: a 12 atom benzene ring and the 10 atom TCNE. The complete complex is shown in the figure



We will consider the benzene ring as the first fragment (fig.). It's CLUSTER file is:

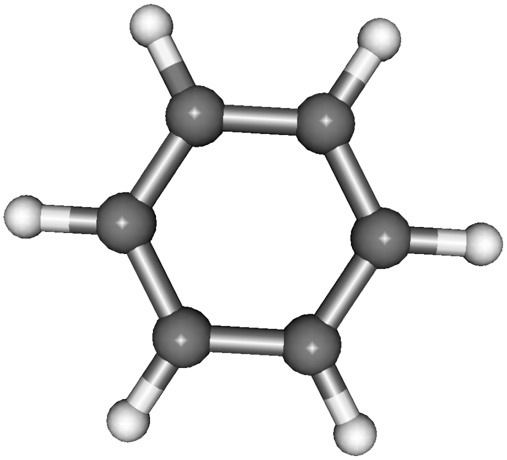
```
GGA-PBE*GGA-PBE
GRP
12
  0.0000      2.6433     -3.9697    6 ALL
  0.0000     -2.6433     -3.9697    6 ALL
  2.2925      1.3220     -3.9702    6 ALL
 -2.2925      1.3220     -3.9702    6 ALL
  2.2925     -1.3220     -3.9702    6 ALL
 -2.2925     -1.3220     -3.9702    6 ALL
  0.0000      4.7079     -3.9776    1 ALL
  0.0000     -4.7079     -3.9776    1 ALL
  4.0794      2.3559     -3.9732    1 ALL
 -4.0794      2.3559     -3.9732    1 ALL
 -4.0794     -2.3559     -3.9732    1 ALL
  4.0794     -2.3559     -3.9732    1 ALL
  0.0000      0.0000
```

Once you run NRLMOL with this fragment, from EVALUES we get this information:

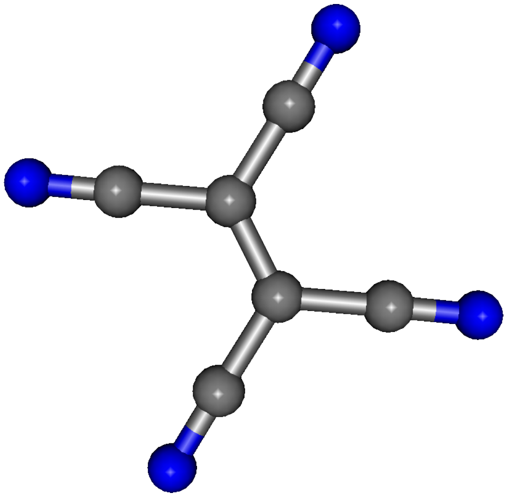
1. **Number of Bases:** 324
2. **Number of occupied states:** 21

Now we run the second fragment (fig.), where the CLUSTER file is:

```
GGA-PBE*GGA-PBE
GRP
10
  0.0000      1.2969      2.9150    6 ALL
  0.0000     -1.2969      2.9150    6 ALL
 -2.3072      2.7100      2.9357    6 ALL
  2.3071      2.7100      2.9357    6 ALL
```



```
 -2.3072     -2.7100      2.9357    6 ALL
  2.3071     -2.7100      2.9357    6 ALL
 -4.1665      3.8824      2.9754    7 ALL
  4.1665      3.8824      2.9754    7 ALL
 -4.1665     -3.8824      2.9754    7 ALL
  4.1665     -3.8824      2.9754    7 ALL
  0.0000      0.0000
```



The results we need from EVALUES are:

1. **Number of Bases:** 350
2. **Number of occupied states:** 32

Complex calculation part 1

Now that we have run the fragments individually, must put them together and run NRLMOL on the complete complex (fig.). Here's were you need the newest version of NRLMOL. The first thing to do is to set Y to FRAGMENTV in the NRLMOL_INPUT.DAT, your file should look something like this:

```
# Put Y,N or number next to the equal ...
# Don't forget thew quotation marks for the letters
# All variables in this list end with v
```

```
 &input_data
 ATOMSPHV      = ’N’
 CALCTYPEV     = ’LBFGS’
 DFTD3V        = ’N’
 DIAG1V        = 0
 DIAG2V        = 0
 DOSOCCUV      = ’N’
 EXCITEDV      = ’N’
 FORMFAKV      = ’N’
 FRAGMENTV     = ’Y’
 JNTDOSV       = ’N’
 MATDIPOLEV    = ’N’
 NONSCFV       = ’N’
 NONSCFFORCESV = ’N’
 WFGRIDV       = ’N’
 &end
```

The CLUSTER file is now a little different:

```
GGA-PBE*GGA-PBE
GRP
22  2
12 10
  0.0000      2.6433     -3.9697    6 ALL
  0.0000     -2.6433     -3.9697    6 ALL
  2.2925      1.3220     -3.9702    6 ALL
 -2.2925      1.3220     -3.9702    6 ALL
  2.2925     -1.3220     -3.9702    6 ALL
 -2.2925     -1.3220     -3.9702    6 ALL
  0.0000      4.7079     -3.9776    1 ALL
  0.0000     -4.7079     -3.9776    1 ALL
  4.0794      2.3559     -3.9732    1 ALL
 -4.0794      2.3559     -3.9732    1 ALL
 -4.0794     -2.3559     -3.9732    1 ALL
  4.0794     -2.3559     -3.9732    1 ALL
  0.0000      1.2969      2.9150    6 ALL
  0.0000     -1.2969      2.9150    6 ALL
 -2.3072      2.7100      2.9357    6 ALL
  2.3071      2.7100      2.9357    6 ALL
 -2.3072     -2.7100      2.9357    6 ALL
  2.3071     -2.7100      2.9357    6 ALL
 -4.1665      3.8824      2.9754    7 ALL
  4.1665      3.8824      2.9754    7 ALL
 -4.1665     -3.8824      2.9754    7 ALL
  4.1665     -3.8824      2.9754    7 ALL
  0.0000      0.0000
```

The changes are:

1. In line 3 we specify the total number of atoms (22)
2. After that, in the same line, we specify the total number of fragments (2)
3. Line 4 specifies the total number of atoms for fragment 1 (12), and
4. The total number of atoms for fragment 2 (10)

By specifying the CLUSTER file this way, we are telling NRLMOL to generate the Hamiltonian matrix (written in Hamold) following this particular order of atoms and not group atoms by type, this was the matrix can be sliced according to the number of basis functions. Speaking of which when this CLUSTER file is run the number of bases from EVALUES is 674, which is the sum of the bases from the fragments. Also, the number of occupied states is 53. Again, a sum of the states of the individual fragments (we will need this value for the next step).

Complex calculation part 2

This is the actual fragment analysis, the two steps before this are only to setup this caclulation. This also invloves a different binary that must be constructed from the Mafile. On the command line construct this binary by issuing the command *make fragment*. This will create another binary called *clusterfrag*, this file runs serially so you can run it directly from the command line (however, it is still reccomended you use a script on external clusters). But before we start the calculation, some inputs are required: 1. create a new directory to run this binary. 2. put the following files there:

1. The HAMOLD files for each of the fragments, renamed as HAM.1,HAM.2, etc.
2. The HAMOLD file from the complex calculation
3. The OVLBABY file from the complex calculation
3. A new file called FRAGMENT.IN must be created, its structure is: 1. Spin of the system (get the value of SPN from the first line in EVALUES) 2. Number of fragments (2 for this case) 3. Number of occupied states (53 for the complex) 4. A listing of the number of bases and occupied states per fragment 5. the following statement: **.FALSE.**

So the FRAGMENT.IN file should look like this:

```
1
2
53
324 21
350 32
.FALSE.
```

Once this binary runs, there should be two files created: **OVERLAP** and **WAVEMO**.

1.14 FREQUENTLY ASKED QUESTIONS ABOUT NRLMOL

1. Which molecular properties are calculated in NRLMOL ?

   The molecular properties one can get from NRLMOL are :

   Electronic structure, density of states, bond lengths, optimized geometry, spin magnetic moment, magnetic anisotropy energy, dipole moment, harmonic vibrational frequencies, infrared and Raman spectra, electronic density, orbital density, electron localization function, ionization potential, electron affinity, optical absorption spectra, joint density of states, atomic charge, screened and unscreened polarizabilities, vibrational polarizability etc.

2. Which exchange-correlation functionals can be used in NRLMOL ? The LDA exchange-correlation functionals are:

   VWN

   CA

   Perdew-Zunger 81

   RPA

   Wigner Interpolation Functional

   Kohn-Sham exchange only

Gunnarsson-Lundquist

The GGA functionals are PW91 and PBE.

3. How can I start a spin-polarized calculation?

   If you specify a spin magnetic moment in the CLUSTER file, the calculation will automatically be spin-polarized. For a system with spin S=0, to run a spin-polarized calculation you have to make changes in the SYMBOL file. IN the SYMBOL file, the number of ELECTRON with down spin should be specified by a '-' sign. e.g. in methane it should be

   ELECTRONS = 5.00000000 -5.00000000

4. What is the basis set used in NRLMOL ?

   The basis set is specified in the ISYMGEN file which is created when you run NRLMOL. This file contains the basis set for each identity atom. For each orbital of a given atom, same set of primitive Gaussians is used. For example, the default basis set for carbon is written as below :

```
   6   6                       ELECTRONIC AND NUCLEAR CHARGE
ALL                            ALL-ELECTRON ATOM TYPE
   3                           NUMBER OF ATOMS OF TYPE CAR
ALL-CAR001
ALL-CAR002
ALL-CAR003
EXTRABASIS         CONTROLS USAGE OF SUPPLEMENTARY BASIS FUNCTIONS
 12                NUMBER OF BARE GAUSSIANS
   5   4   3       NUMBER OF S,P,D FUNCTIONS
   0   0   1       SUPPLEMENTARY S,P,D FUNCTIONS

       0.22213361D+05       0.33317370D+04       0.75790135D+03
       0.21454372D+03       0.69924889D+02       0.25086135D+02
       0.95910418D+01       0.38024557D+01       0.14891854D+01
       0.57487653D+00       0.21494732D+00       0.77209650D-01

       0.19792249D+00       0.36998977D+00       0.63644615D+00
       0.10124931D+01       0.14480787D+01       0.17173689D+01
       0.14931932D+01       0.68987161D+00       0.86072247D-01
      -0.16566695D-02       0.37766033D-03      -0.47105343D-04

      -0.45005260D-01      -0.84621052D-01      -0.14496564D+00
      -0.23535601D+00      -0.34215368D+00      -0.44595124D+00
      -0.45263971D+00      -0.32216414D+00      -0.12988420D-01
       0.20135471D+00       0.12769913D+00       0.14135467D-01

       0.00000000D+00       0.00000000D+00       0.00000000D+00
       0.00000000D+00       0.00000000D+00       0.00000000D+00
       0.00000000D+00       0.00000000D+00       0.00000000D+00
       0.10000000D+01       0.00000000D+00       0.00000000D+00

       0.00000000D+00       0.00000000D+00       0.00000000D+00
       0.00000000D+00       0.00000000D+00       0.00000000D+00
       0.00000000D+00       0.00000000D+00       0.00000000D+00
       0.00000000D+00       0.10000000D+01       0.00000000D+00

       0.00000000D+00       0.00000000D+00       0.00000000D+00
       0.00000000D+00       0.00000000D+00       0.00000000D+00
       0.00000000D+00       0.00000000D+00       0.00000000D+00
       0.00000000D+00       0.00000000D+00       0.10000000D+01

       0.23138630D-01       0.42649133D-01       0.74658851D-01
```

```
0.12024115D+00       0.18351176D+00       0.24706804D+00
0.30714219D+00       0.31372706D+00       0.26726340D+00
0.14756585D+00       0.47585576D-01       0.72796459D-02

0.00000000D+00       0.00000000D+00       0.00000000D+00
0.00000000D+00       0.00000000D+00       0.00000000D+00
0.00000000D+00       0.00000000D+00       0.00000000D+00
0.10000000D+01       0.00000000D+00       0.00000000D+00


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

Here, the first line specifies the nuclear and electronic charges in the atom. The nuclear and electronic charges specifies the actual atom (e.g. Nuc charge = 6 for carbon) but the electronic charge depends on whether all electron or pseudo potential calculations are used (e.g. for carbon it would be 6 for all electron and 4 for a pseudopotential calculation)

The second line specifies the type of calculation :

ALL for all-electron BHS for BHS pseudopotential TAB for tabulated user-supplied pseudopotential

The third and fourth lines specify the number of total such atoms in the geometry and their symbols in the SYMBOL file. **EXTRABASIS =1** in SYMBOL file will signal the program to use the supplementary basis functions. Then comes the number of primitive Gaussians followed by the number of the s, p and d -type contracted Gaussians. The number of supplementary functions of s, p and d type are written next. These informations are followed by some blocks of numbers. The first block lists the exponents of the primitive Gaussians. This is then followed by Ns blocks where Ns is the number of contracted s-type Gaussians. The first block is the coefficients multiplying the primitive Gaussians for the 1s contracted Gaussian, the second block is for 2s Gaussian and so on. After the Ns number of such blocks, comes the Np blocks corresponding to the p-type contracted Gaussians followed by similar Nd number of d-type Gaussians. In the example for carbon atom above, the 1s and 2s contracted Gaussian is a linear combination of the all the primitive Gaussians whereas the higher unoccupied s orbitals are taken as single long-range Gaussians. Similarly for p orbitals where only the 2p orbital is occupied. These are then followed by similar blocks corresponding to the supplementary functions. The supplementary functions are used only when **EXTRABASIS = 1** in the SYMBOL file. These are generally polarization functions and are usually only used for the calculation of IR and Raman intensities and possibly for dipole moments and polarizabilities.

The carbon atom basis set in the example might be called a “12-1211+++G(3d)” basis in Pople/Gaussian parlance if we consider the last s,p,d orbitals as diffuse functions. This means 12 primitive gaussians contracted to the core 1s orbital, then a triple-zeta valence set (three sets of s and three sets of p orbitals) represented by 12, 1 and 1 primitive gaussians, three sets of d polarization functions and three sets of diffuse functions (s,p,d) each represented by a single primitive gaussian. This is an example of a “generally contracted” basis in which the same set of primitives contributes to all the orbitals. If the diffuse functions are considered as valence, then this basis has a quadruple-zeta functions.

5. NRLMOL writes out a bunch of files. Are all of them output files ?

   See the discussion of files at

6. In the self-consistency cycle, the energy oscillates. How can I reach self-consistency ?

   This can for a number of reasons. One of them is that your structure is not correct. Visualize it to ensure that your geometry (and units) are correct. It can also happen when the energy levels near the Fermi energy are degenerate and half-filled. The cure is to increase the electronic temperature in TMPTRE from the default value of 0.0001 Hartree. Doing so will smear the occupancies over all the levels and will help in reaching a self-consistent solution.

7. The geometry optimization seems to get stuck in the same geometry. How do I get out ?

   This seems to happen mostly when the LBFGS scheme is used for geometry optimization. The way out is either delete the .LBF files or use conjugate-gradient method. The later can be started by replacing the LBFGS in the first line of SYMBOL file by CONJUGATE-GRADIENT. The conjugate gradient option seems to be most reliable but often slower than LBFGS by a factor of 2. The user should decide whether to use LBFGS or conjugate-gradient depending on the size of the system and also the smallness of the forces. Using conjugate-gradient towards the end of the optimization seems to be more useful.

8. The geometry changes very little in the optimization and forces are small. But the code does not say that convergence is reached. What do I do ?

   This is numerical problem and can be solved by refining the mesh used in the calculation. To refine a mesh see following question.

9. Is it possible to change the mesh by the user ?

   Please refer to the discussion of MESHDAT file.

10. What are the symmetry groups recognized by NRLMOL ?

    Only a handful of symmetry groups are hard-coded in NRLMOL. These are :

    Ih, Th, Oh, Td, X, Y, Z, XY, YZ, XZ, C3v, ...

    Caution: C3v,... assumes the highest symmetry rotational axis along the z direction. It however allows use of any(most) symmetry group provided corresponding *GRPMAT* file containing symmetry opration matrices is provided. e.g. Point groups D20, D30 can also be used in NRLMOL.

11. How can I know the symmetry of the energy levels ?

    The eigen values are not labeled by its symmetry in NRLMOL. However, it can be easily identified by the representation it belongs to and the character of the representation which is written near the beginning in the screen output.

12. I am doing calculations on a singly or doubly charged anion. The energy eigenvalues near the top of the valence band are positive. Does it mean that these electrons are not bound ?

    Not necessarily. The binding energy of an electron is given by the difference of the total energy E(n)-E(n+1) where n is the number of electron. The positive eigenvalues is an artifact of the inaccuracy in the exchange-correlation functional in the asymptotic region and can be cured by inclusion of self-interaction correction (SIC) in the calculation. However, the SIC version of NRLMOL is not yet fully operational.

13. Can I optimize the geometry in the presence of an electric field ?

    To put in an electric field, make the following changes :

    1. Change the number of files in SYMBOL to 2 as below :

       2 Number of symbolic files

       ISYMGEN = INPUT

       EFLDVIB = EFIELD

       N+3 Number of symbols in list

       N Number of nuclei

1. Also make the following changes in SYMBOL:

   ELECTRONS = Nup Ndn EFIELD = x y z where Nup and Ndn are the number of spin up and down electrons. x,y,and z are the components of the electric field vector. If optimizing a geometry in the presence of an electric field it may be advisable to pin one of the atoms by setting occurrences of “1 1 1” in the SYMBOL file to “0 0 0”. This would be absolutely necessary for a charged molecule or cluster in an electric field. (See item 22)

1. Create a file called EFLDVIB and write EFIELD at the top of the file.

   Can I use the same potential for same nuclear positions but with a different symmetry group ? Yes, it is possible to use the same potential using different symmetry provided the nuclear positions are fixed. Copy the VMOLD and POTOLD files from the old calculation and change the NCALC in RUNS to the value in the old calculation. Make sure NCALC in RUNS exists in the SYMBOL file.

2. Can I fix the spin moment in my calculation ?

   To fix the spin magnetic moment, put the following line at the top of the EVALUES file :

   FIXM

3. Can I specify the occupancies ?

   Yes, it is possible to fix the occupancies of the energy levels in the following way :

   (a) Write the top line of EVALUES as

   OCCU

   (b) Write the number of the spin up states in the first representation and write the occupancies in the following line.

   (c) Repeat step II for all representation.

   (d) Repeat step II and III for spin down states.

```
OCCU
        9
  1.000000       1.000000       1.000000       1.000000       1.000000
  1.000000       1.000000       1.000000       1.000000
        10
  1.000000       1.000000       1.000000       1.000000       1.000000
  1.000000       1.000000       1.000000       1.000000      0.0000000E+00
         8
  1.000000       1.000000       1.000000       1.000000       1.000000
  1.000000       1.000000       1.000000
        11
  1.000000       1.000000       1.000000       1.000000       1.000000
  1.000000       1.000000       1.000000       1.000000       1.000000
```

   In the above example, there are two representations with 9 and 10 states for spin up and 8 and 11 states for spin down.

   Caution: If there is an accidental or near degeneracy for a HOMO and LUMO in the same representation there can be charge oscillations that are akin to those observed when the Fermi Dirac distribution function is used. Sometimes this can be fixed by fractional occupations of the HOMO and LUMO states.

4. *I have started a calculation with occupied mode for methane. I have given the correct representations and occupancies from the EVALUES file. But my program crashes. Why?*

   EVALUES lists only the representations which have at least one states. The correct number of representations can be found in the screen file. If a representation has 0 number of states belonging to it, it still must be specified in the EVALUES file when you run in OCCU mode.

5. *How do I plot the density?*

   Create a file named POTGRID and rerun NRLMOL. IF the calculation is spin polarized then total density is written out in RHOTOT and spin density is written out in RHOSPN. These files have the Gaussian cubic format. Any plotting package that recognises the cubic format can be used to plot these files.

6. *Can I plot the HOMO density?*

   Create a file named WFGRID and rerun NRLMOL. By default the HOMO density is written out in WFHOMO00 file. The last three lines of WFGRID specifies the orbital to be plotted. The states above HOMO are indexed by positive numbers starting with +1 for LUMO and so on. The states below HOMO are indexed by negative numbers starting with -1 for HOMO-1 and so on. To plot LUMO density, open WFGRID and change the index number from 0 to 1. The output file names will be WFHOMO01 for unoccupied higher states and WFHOMO-1 for the occupied lower states. You can write out upto 10 states at a time.

7. How can I calculate the vibrational frequencies ? Later.

8. Is it possible to fix some atoms in the geometry optimization ?

   Yes, you can fix some atoms during the geometry optimization. The SYMBOL file contains the following lines 1.0 1 1 1 corresponding to each atom. The numbers 1(0) 1(0) 1(0) allow the atom to move(remain fixed) along x,y, and z directions according to the forces.

9. After convergence, when I looked at the RUNS file, its first line was "0 N+1" where N is the last geometry in the SYMBOL file. Does this mean that, it will first look at N+1st position info in SYMBOl, and if it cannot find it, it will do a new position calculation?

   If the geometry convergence criteria is reached in the Nth geometry, the program does not update the nuclear positions in SYMBOL file but the NCALC index in RUNS is changed by +1. If the code is run again, it will look for geometry number N+1 in SYMBOL file and when it does not find it , the program will stop.

10. Is it possible to force antiferromagntic spin ordering in some atoms ?

    Yes, you can specify the some atoms as spin up and some others as spin down in the SYMBOL file. Here is an example :

    ALL-MAN001 = 2.137000 -0.350000 0.003300 SUP ALL-MAN001 = 3.456900 2.109300 -0.093100 SDN ALL-OXY003 = -1.271400 0.035600 -0.012700 SUP ALL-CAR001 = 2.720100 -2.490500 0.106000 UPO The SUP, SDN and UPO signify spin up , spin down and unpolarized atoms. The default choice is UPO.

11. My screen file for the converged geometry got overwritten. Where can I find the spin moment ?

    The number of spin up and down electrons are recorded in the VIBINP file.

12. Where is the dipole moment written ?

    The dipole moment is written in the DIPOLE, VIBINP and the FRCOUT file. The second line from bottom in FRCOUT and VIBINP gives the x,y , and z components of the dipole vector.

13. How do I restart my SCF calculation ?

    The SCF calculation can be restarted from potential, wavefunction or from an earlier stored Hamiltonian. The user has to make the corresponding choice in the RUNS file. Before restarting a calculation, make sure that the NCALC parameter in RUNS corresponds to the correct geometry in SYMBOL file.

14. How do I tell NRLMOL to calculate the molecular properties ?

Some of the molecular properties are calculated automatically once the forces have dropped below the convergence limit. One can still tell the program to calculate properties for any geometry. Most often the user has to create a file with a particular name. Sometimes this file is empty, sometime the user has to write something in it. The following list shows which calculations are triggered by which file.

Property filename initial values

Charges in atomic sphere ATOMSPH

Charge density for plotting RHOGRID

Orbital density for plotting WFGRID

Density of states DOSOCCU

Joint density of states/ DOSJNT optical properties

Magnetic anisotropy energy SPNORB T F

Electron localization function ELF

About this document ... next up previous Back to HomePage. Next: About this document ... Rajendra Zope 2007-11-06