NWChem User Documentation

Release 4.0.1

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DISCLAIMER

LIMITED USE

ACKNOWLEDGMENT

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Contents

Chapter 1

Introduction

NWChem is a computational chemistry package designed to run on high-performance parallel supercomputers. Code capabilities include the calculation of molecular electronic energies and analytic gradients using Hartree-Fock self-consistent field (SCF) theory, Gaussian density function theory (DFT), and second-order perturbation theory. For all methods, geometry optimization is available to determine energy minima and transition states. Classical molecular dynamics capabilities provide for the simulation of macromolecules and solutions, including the computation of free energies using a variety of force fields.

NWChem is scalable, both in its ability to treat large problems efficiently, and in its utilization of available parallel computing resources. The code uses the parallel programming tools TCGMSG and the Global Array (GA) library developed at PNNL for the High Performance Computing and Communication (HPCC) grand-challenge software program and the Environmental Molecular Sciences Laboratory (EMSL) Project. NWChem has been optimized to perform calculations on large molecules using large parallel computers, and it is unique in this regard.

This document is intended as an aid to chemists using the code for their own applications. Users are not expected to have a detailed understanding of the code internals, but some familiarity with the overall structure of the code, how it handles information, and the nature of the algorithms it contains will generally be helpful. The following sections describe the structure of the input file, and give a brief overview of the code architecture. All input directives recognized by the code are described in detail, with options, defaults, and recommended usages, where applicable. The appendices present additional information on the molecular geometry and basis function libraries included in the code.

1.1 Citation

The EMSL Software Agreement stipulates that the use of NWChem will be acknowledged in any publications which use results obtained with NWChem. The acknowledgment should be of the form:

> NWChem Version 4.0.1, as developed and distributed by Pacific Northwest National Laboratory, P. O. Box 999, Richland, Washington 99352 USA, and funded by the U. S. Department of Energy, was used to obtain some of these results.

The words "A modified version of" should be added at the beginning, if appropriate. *Note: Your EMSL Software Agreement contains the complete specification of the required acknowledgment.*

Please use the following citation when publishing results obtained with NWChem:

High Performance Computational Chemistry Group, *NWChem, A Computational Chemistry Package for Parallel Computers, Version 4.0.1* (2001), Pacific Northwest National Laboratory, Richland, Washington 99352, USA.

1.2 User Feedback

This software comes without warranty or guarantee of support, but we do try to meet the needs of our user community. Please send bug reports, requests for enhancement, or other comments to

- `nwchem-support@emsl.pnl.gov`

When reporting problems, please provide as much information as possible, including:

- detailed description of problem
- site name (e.g., EMSL, NERSC, ...)
- platform you are running on, including
  - vendor name
  - computer model
  - operating system
  - compiler
- input file
- output file
- contact name and telephone number

Users can also subscribe to an electronic mailing list of other users of the code. This is intended as a general forum through which code users can contact one another and the developers, to share experience with the code and discuss problems. Announcements of new releases and bug fixes will also be made to this list.

To subscribe to the user list, send a message to

```
majordomo@emsl.pnl.gov
```

The body of the message must contain the line

```
subscribe nwchem-users
```

The automated list manager is capable of recognizing a number of commands, including ; "subscribe", "unsubscribe", "get", "index", "which", "who", "info" and "lists". The command "end" halts processing of commands. It will provide some help if the message includes the line `help` in the body.

Messages can be posted to the list by sending mail to `nwchem-users@emsl.pnl.gov`. Users are encouraged to report problems to the support address rather than the mailing list, since the support address (listed at the beginning of this section) interfaces to an automated bug tracking mechanism.

Chapter 2

Getting Started

This section provides an overview of NWChem input and program architecture, and the syntax used to describe the input. See Sections 2.2 and 2.3 for examples of NWChem input files with detailed explanation.

NWChem consists of independent modules that perform the various functions of the code. Examples of modules include the input parser, SCF energy, SCF analytic gradient, DFT energy, etc.. Data is passed between modules and saved for restart using a disk-resident database or dumpfile (see Section 3).

The input to NWChem is composed of commands, called directives, which define data (such as basis sets, geometries, and filenames) and the actions to be performed on that data. Directives are processed in the order presented in the input file, with the exception of certain start-up directives (see Section 2.1) which provide critical job control information, and are processed before all other input. Most directives are specific to a particular module and define data that is used by that module only. A few directives (see Section 5) potentially affect all modules, for instance by specifying the total electric charge on the system.

There are two types of directives. Simple directives consist of one line of input, which may contain multiple fields. Compound directives group together multiple simple directives that are in some way related and are terminated with an `END` directive. See the sample inputs (Sections 2.2, 2.3) and the input syntax specification (Section 2.4).

All input is free format and case is ignored except for actual data (e.g., names/tags of centers, titles). Directives or blocks of module-specific directives (i.e., compound directives) can appear in any order, with the exception of the `TASK` directive (see sections 2.1 and 5.10) which is used to invoke an NWChem module. All input for a given task must precede the `TASK` directive. This input specification rule allows the concatenation of multiple tasks in a single NWChem input file.

To make the input as short and simple as possible, most options have default values. The user needs to supply input only for those items that have no defaults, or for items that must be different from the defaults for the particular application. In the discussion of each directive, the defaults are noted, where applicable.

The input file structure is described in the following sections, and illustrated with two examples. The input format and syntax for directives is also described in detail.

2.1 Input File Structure

The structure of an input file reflects the internal structure of NWChem. At the beginning of a calculation, NWChem needs to determine how much memory to use, the name of the database, whether it is a new or restarted job, where to put scratch/permanent files, etc.. It is not necessary to put this information at the top of the input file, however. NWChem will read through the *entire* input file looking for the start-up directives. In this first pass, all other directives are ignored.

The start-up directives are

- `START`
- `RESTART`
- `SCRATCH_DIR`
- `PERMANENT_DIR`
- `MEMORY`
- `ECHO`

After the input file has been scanned for the start-up directives, it is rewound and read sequentially. Input is processed either by the top-level parser (for the directives listed in Section 5, such as `TITLE`, `SET`, ...) or by the parsers for specific computational modules (e.g., SCF, DFT, ...). Any directives that have already been processed (e.g., `MEMORY`) are ignored. Input is read until a `TASK` directive (see Section 5.10) is encountered. A `TASK` directive requests that a calculation be performed and specifies the level of theory and the operation to be performed. Input processing then stops and the specified task is executed. The position of the `TASK` directive in effect marks the end of the input for that task. Processing of the input resumes upon the successful completion of the task, and the results of that task are available to subsequent tasks in the same input file.

The name of the input file is usually provided as an argument to the execute command for NWChem. That is, the execute command looks something like the following;

```
nwchem input_file
```

The default name for the input file is `nwchem.nw`. If an input file name `input_file` is specified without an extension, the code assumes `.nw` as a default extension, and the input filename becomes `input_file.nw`. If the code cannot locate a file named either `input_file` or `input_file.nw` (or `nwchem.nw` if no file name is provided), an error is reported and execution terminates. The following section presents two input files to illustrate the directive syntax and input file format for NWChem applications.

2.2 Simple Input File — SCF geometry optimization

A simple example of an NWChem input file is an SCF geometry optimization of the nitrogen molecule, using a Dunning cc-pvdz basis set. This input file contains the bare minimum of information the user must specify to run this type of problem — fewer than ten lines of input, as follows:

```
title "Nitrogen cc-pvdz SCF geometry optimization"
geometry
  n 0 0 0
  n 0 0 1.08
end
basis
```

```
    n library cc-pvdz
  end
  task scf optimize
```

Examining the input line by line, it can be seen that it contains only four directives; `TITLE`, `GEOMETRY`, `BASIS`, and `TASK`. The `TITLE` directive is optional, and is provided as a means for the user to more easily identify outputs from different jobs. An initial geometry is specified in Cartesian coordinates and Angstrøms by means of the `GEOMETRY` directive. The Dunning cc-pvdz basis is obtained from the NWChem basis library, as specified by the `BASIS` directive input. The `TASK` directive requests an SCF geometry optimization.

The `GEOMETRY` directive (Section 6) defaults to Cartesian coordinates and Angstrøms (options include atomic units and Z-matrix format; see Section 6.4). The input blocks for the `BASIS` and `GEOMETRY` directives are structured in similar fashion, i.e., name, keyword, ..., end (In this simple example, there are no keywords). The `BASIS` input block *must* contain basis set information for every atom type in the geometry with which it will be used. Refer to Sections 7 and 8, and Appendix A for a description of available basis sets and a discussion of how to define new ones.

The last line of this sample input file (`task scf optimize`) tells the program to optimize the molecular geometry by minimizing the SCF energy. (For a description of possible tasks and the format of the `TASK` directive, refer to Section 5.10.)

If the input is stored in the file `n2.nw`, the command to run this job on a typical UNIX workstation is as follows:

```
  nwchem n2
```

NWChem output is to UNIX standard output, and error messages are sent to both standard output and standard error.

2.3 Water Molecule Sample Input File

A more complex sample problem is the optimization of a positively charged water molecule using second-order Møller-Plesset perturbation theory (MP2), followed by a computation of frequencies at the optimized geometry. A preliminary SCF geometry optimization is performed using a computationally inexpensive basis set (STO-3G). This yields a good starting guess for the optimal geometry, and any Hessian information generated will be used in the next optimization step. Then the optimization is finished using MP2 and a basis set with polarization functions. The final task is to calculate the MP2 vibrational frequencies. The input file to accomplish these three tasks is as follows:

```
start h2o_freq

charge 1

geometry units angstroms
  O       0.0  0.0  0.0
  H       0.0  0.0  1.0
  H       0.0  1.0  0.0
end

basis
```

```
  H library sto-3g
  O library sto-3g
end

scf
  uhf; doublet
  print low
end

title "H2O+ : STO-3G UHF geometry optimization"

task scf optimize

basis
  H library 6-31g**
  O library 6-31g**
end

title "H2O+ : 6-31g** UMP2 geometry optimization"

task mp2 optimize

mp2; print none; end
scf; print none; end

title "H2O+ : 6-31g** UMP2 frequencies"

task mp2 freq
```

The `START` directive (Section 5.1) tells NWChem that this run is to be started from the beginning. This directive need not be at the beginning of the input file, but it is commonly placed there. Existing database or vector files are to be ignored or overwritten. The entry `h2o_freq` on the `START` line is the prefix to be used for all files created by the calculation. This convention allows different jobs to run in the same directory or to share the same scratch directory (see Section 5.2), as long as they use different prefix names in this field.

As in the first sample problem, the geometry is given in Cartesian coordinates. In this case, the units are specified as Angstrøms. (Since this is the default, explicit specification of the units is not actually necessary, however.) The `CHARGE` directive defines the total charge of the system. This calculation is to be done on an ion with charge +1.

A small basis set (STO-3G) is specified for the intial geometry optimization. Next, the multiple lines of the first `SCF` directive in the `scf ...end` block specify details about the SCF calculation to be performed. Unrestricted Hartree-Fock is chosen here (by specifying the keyword `uhf`), rather than the default, restricted open-shell high-spin Hartree-Fock (ROHF). This is necessary for the subsequent MP2 calculation, because only UMP2 is currently available for open-shell systems (see Section 4). For open-shell systems, the spin multiplicity has to be specified (using `doublet` in this case), or it defaults to `singlet`. The print level is set to `low` to avoid verbose output for the starting basis calculations.

All input up to this point affects only the settings in the runtime database. The program takes its information from this database, so the sequence of directives up to the first `TASK` directive is irrelevant. An exchange of order of the different blocks or directives would not affect the result. The `TASK` directive, however, must be specified after all relevant input for a given problem. The `TASK` directive causes the code to perform the specified calculation using the parameters set in the preceding directives. In this case, the first task is an SCF calculation with geometry optimization, specified with the input `scf` and `optimize`. (See Section 5.10 for a list of available tasks and operations.)

After the completion of any task, settings in the database are used in subsequent tasks without change, unless they are overridden by new input directives. In this example, before the second task (`task mp2 optimize`), a better basis set (6-31G**) is defined and the title is changed. The second `TASK` directive invokes an MP2 geometry optimization.

Once the MP2 optimization is completed, the geometry obtained in the calculation is used to perform a frequency calculation. This task is invoked by the keyword `freq` in the final `TASK` directive, `task mp2 freq`. The second derivatives of the energy are calculated as numerical derivatives of analytical gradients. The intermediate energies and gradients are not of interest in this case, so output from the SCF and MP2 modules is disabled with the `PRINT` directives.

2.4 Input Format and Syntax for Directives

This section describes the input format and the syntax used in the rest of this documentation to describe the format of directives. The input format for the directives used in NWChem is similar to that of UNIX shells, which is also used in other chemistry packages, most notably GAMESS-UK. An input line is parsed into whitespace (blanks or tabs) separating tokens or fields. Any token that contains whitespace must be enclosed in double quotes in order to be processed correctly. For example, the basis set with the descriptive name `modified Dunning DZ` must appear in a directive as `"modified Dunning DZ"`, since the name consists of three separate words.

2.4.1 Input Format

A (physical) line in the input file is terminated with a newline character (also known as a 'return' or 'enter' character). A semicolon (`;`) can be also used to indicate the end of an input line, allowing a single physical line of input to contain multiple logical lines of input. For example, five lines of input for the `GEOMETRY` directive can be entered as follows;

```
geometry
 O 0  0     0
 H 0  1.430 1.107
 H 0 -1.430 1.107
end
```

These same five lines could be entered on a single line, as

```
geometry; O 0 0 0; H 0 1.430 1.107; H 0 -1.430 1.107; end
```

This one physical input line comprises five logical input lines. Each logical or physical input line must be no longer than 1023 characters.

In the input file:

- a string, token, or field is a sequence of ASCII characters (NOTE: if the string includes blanks or tabs (i.e., white space), the entire string must be enclosed in double quotes).

- \ (backslash) at the end of a line concatenates it with the next line. Note that a space character is automatically inserted at this point so that it is *not* possible to split tokens across lines. A backslash is also used to quote special characters such as whitespace, semi-colons, and hash symbols so as to avoid their special meaning (NOTE: these special symbols must be quoted with the backslash even when enclosed within double quotes).
- ; (semicolon) is used to mark the end of a logical input line within a physical line of input.
- # (the hash or pound symbol) is the comment character. All characters following # (up to the end of the physical line) are ignored.
- If *any* input line (excluding Python programs, Section 32) begins with the string INCLUDE (ignoring case) and is followed by a valid file name, then the data in that file are read as if they were included into the current input file at the current line. Up to three levels of nested include files are supported. The user should note that inputting a basis set from the standard basis library (Section 7) uses one level of include.
- Data is read from the input file until an end-of-file is detected, or until the string EOF (ignoring case) is encountered at the beginning of an input line.

2.4.2 Format and syntax of directives

Directives consist of a directive name, keywords, and optional input, and may contain one line or many. Simple directives consist of a single line of input with one or more fields. Compound directives can have multiple input lines, and can also include other optional simple and compound directives. A compound directive is terminated with an END directive. The directives START (see Section 5.1) and ECHO (see Section 5.4) are examples of simple directives. The directive GEOMETRY (see Section 6) is an example of a compound directive.

Some limited checking of the input for self-consistency is performed by the input module, but most defaults are imposed by the application modules at runtime. It is therefore usually impossible to determine beforehand whether or not all selected options are consistent with each other.

In the rest of this document, the following notation and syntax conventions are used in the generic descriptions of the NWChem input.

- a directive name always appears in all-capitals, and in computer typeface (e.g., GEOMETRY, BASIS, SCF). Note that the case of directives and keywords is ignored in the actual input.
- a keyword always appears in lower case, in computer typeface (e.g., swap, print, units, bqbq).
- variable names always appear in lower case, in computer typeface, and enclosed in angle brackets to distinguish them from keywords (e.g., <input_filename>, <basisname>, <tag>).
- $variable$ is used to indicate the substitution of the value of a variable.
- () is used to group items (the parentheses and other special symbols should not appear in the input).
- || separate exclusive options, parameters, or formats.
- [ ] enclose optional entries that have a default value.
- < > enclose a type, a name of a value to be specified, or a default value, if any.
- \ is used to concatenate lines in a description.

- ... is used to indicate indefinite continuation of a list.

An input parameter is identified in the description of the directive by prefacing the name of the item with the type of data expected, i.e.,

- **string** – an ASCII character string
- **integer** – integer value(s) for a variable or an array
- **logical** – true/false logical variable
- **real** – real floating point value(s) for a variable or an array
- **double** – synonymous with real

If an input item is not prefaced by one of these type names, it is assumed to be of type "string".

In addition, integer lists may be specified using Fortran triplet notation, which interprets lo:hi:inc as lo, lo+inc, lo+2*inc, ..., hi. For example, where a list of integers is expected in the input, the following two lines are equivalent

```
7 10 21:27:2 1:3 99
7 10 21 23 25 27 1 2 3 99
```

(In Fortran triplet notation, the increment, if unstated, is 1; e.g., 1:3 = 1:3:1.)

The directive VECTORS (Section 10.5) is presented here as an example of an NWChem input directive. The general form of the directive is as follows:

```
VECTORS [input (<string input_movecs default atomic>) || \
                (project <string basisname> <string filename>)] \
        [swap [(alpha||beta)] <integer vec1 vec2> ...] \
        [output <string output_movecs default $file_prefix$.movecs>]
```

This directive contains three optional keywords, as indicated by the three main sets of square brackets enclosing the keywords input, swap, and output. The keyword input allows the user to specify the source of the molecular orbital vectors. There are two mutually exclusive options for specifying the vectors, as indicated by the || symbol separating the option descriptions;

```
(<string input_movecs default atomic>) || \
               (project <string basisname> <string filename>) \
```

The first option, (<string input_movecs default atomic>), allows the user to specify an ASCII character string for the parameter input_movecs. If no entry is specified, the code uses the default atomic (i.e., atomic guess). The second option, (project <string basisname> <string filename>), contains the keyword project, which takes two string arguments. When this keyword is used, the vectors in file <filename> will be projected from the (smaller) basis <basisname> into the current atomic orbital (AO) basis.

The second keyword, swap, allows the user to re-order the starting vectors, specifying the pairs of vectors to be swapped. As many pairs as the user wishes to have swapped can be listed for <integer vec1 vec2 ... >. The optional keywords alpha and beta allow the user to swap the alpha or beta spin orbitals.

The third keyword, output, allows the user to tell the code where to store the vectors, by specifying an ASCII string for the parameter output_movecs. If no entry is specified for this parameter, the default is to write the vectors back into either the user- specified MO vectors input file or, if this is not available, the file `$file_prefix$.movecs`.

A particular example of the `VECTORS` directive is shown below. It specifies both the `input` and `output` keywords, but does not use the `swap` option.

```
  vectors input project "small basis" small_basis.movecs \
          output large_basis.movecs
```

This directive tells the code to generate input vectors by projecting from vectors in a smaller basis named `"small basis"`, which is stored in the file `small_basis.movecs`. The output vectors will be stored in the file `large_basis.movecs`.

The order of keyed optional entries within a directive should not matter, unless noted otherwise in the specific instructions for a particular directive.

Chapter 3

NWChem Architecture

As noted above, NWChem consists of independent modules that perform the various functions of the code. Examples include the input parser, self-consistent field (SCF) energy, SCF analytic gradient, and density functional theory (DFT) energy modules. The independent NWChem modules can share data only through a disk-resident database, which is similar to the GAMESS-UK dumpfile or the Gaussian checkpoint file. This allows the modules to share data, or to share access to files containing data.

It is not necessary for the user to be intimately familiar with the contents of the database in order to run NWChem. However, a nodding acquaintance with the design of the code will help in clarifying the logic behind the input requirements, especially when restarting jobs or performing multiple tasks within one job. Section 3.1 gives a general description of the database.

As described above (Section 2.1), all start-up directives are processed at the beginning of the job by the main program, and then the input module is invoked. Each input directive usually results in one or more entries being made in the database. When a `TASK` directive is encountered, control is passed to the appropriate module, which extracts relevant data from the database and any associated files. Upon completion of the task, the module will store significant results in the database, and may also modify other database entries in order to affect the behavior of subsequent computations.

3.1 Database Structure

Data is shared between modules of NWChem by means of the database. Three main types of information are stored in the data base: (1) arrays of data, (2) names of files that contain data, and (3) objects. Arrays are stored directly in the database, and contain the following information:

1. the name of the array, which is a string of ASCII characters (e.g., `"reference energies"`)
2. the type of the data in the array (i.e., real, integer, logical, or character)
3. the number (N) of data items in the array (Note: A scalar is stored as an array of unit length.)
4. the N items of data of the specified type

It is possible to enter data directly into the database using the `SET` directive (see Section 5.7). For example, to store a (64-bit precision) three-element real array with the name `"reference energies"` in the database, the directive is as follows:

```
set "reference energies" 0.0 1.0 -76.2
```

NWChem determines the data to be real (based on the type of the first element, `0.0`), counts the number of elements in the array, and enters the array into the database.

Much of the data stored in the database is internally managed by NWChem and should not be modified by the user. However, other data, including some NWChem input options, can be freely modified.

Objects are built in the database by storing associated data as multiple entries, using an internally consistent naming convention. This data is managed exclusively by the subroutines (or methods) that are associated with the object. Currently, the code has two main objects: basis sets and geometries. Sections 6 and 7 present a complete discussion of the input to describe these objects.

As an illustration of what comprises a geometry object, the following table contains a partial listing of the database contents for a water molecule geometry named `"test geom"`. Each entry contains the field `test geom`, which is the unique name of the object.

```
Contents of RTDB h2o.db
-----------------------

Entry                                  Type[nelem]
---------------------------  ----------------------
geometry:test geom:efield             double[3]
geometry:test geom:coords             double[9]
geometry:test geom:ncenter               int[1]
geometry:test geom:charges            double[3]
geometry:test geom:tags                 char[6]
...
```

Using this convention, multiple instances of objects may be stored with different names in the same database. For example, if a user needed to do calculations considering alternative geometries for the water molecule, an input file could be constructed containing all the geometries of interest by storing them in the database under different names.

The runtime database contents for the file `h2o.db` listed above were generated from the user-specified input directive,

```
geometry "test geom"
  O      0.00000000    0.00000000    0.00000000
  H      0.00000000    1.43042809   -1.10715266
  H      0.00000000   -1.43042809   -1.10715266
end
```

The `GEOMETRY` directive allows the user to specify the coordinates of the atoms (or centers), and identify the geometry with a unique name. (Refer to Section 6 for a complete description of the `GEOMETRY` directive.)

Unless a specific name is defined for the geometry, (such as the name `"test geom"` shown in the example), the default name of `geometry` is assigned. This is the geometry name that computational modules will look for when executing a calculation. The `SET` directive can be used in the input to force NWChem to look for a geometry with a name other than `geometry`. For example, to specify use of the geometry with the name `"test geom"` in the example above, the `SET` directive is as follows:

```
set geometry "test geom"
```

NWChem will automatically check for such indirections when loading geometries. Storage of data associated with basis sets, the other database resident object, functions in a similar fashion, using the default name `"ao basis"`.

3.2 Persistence of data and restart

The database is persistent, meaning that all input data and output data (calculation results) that are not destroyed in the course of execution are permanently stored. These data are therefore available to subsequent tasks or jobs. This makes the input for restart jobs very simple, since only new or changed data must be provided. It also makes the behavior of successive restart jobs *identical* to that of multiple tasks within one job.

Sometimes, however, this persistence is undesirable, and it is necessary to return an NWChem module to its default behavior by restoring the database to its input-free state. In such a case, the `UNSET` directive (see Section 5.8) can be used to delete all database entries associated with a given module (including both inputs and outputs).

Chapter 4

Functionality

NWChem provides many methods to compute the properties of molecular and periodic systems using standard quantum mechanical descriptions of the electronic wavefunction or density. In addition, NWChem has the capability to perform classical molecular dynamics and free energy simulations. These approaches may be combined to perform mixed quantum-mechanics and molecular-mechanics simulations.

NWChem is available on almost all high performance computing platforms, workstations, PCs running LINUX, as well as clusters of desktop platforms or workgroup servers. NWChem development has been devoted to providing maximum efficiency on massively parallel processors. It achieves this performance on the 512 node IBM SP system in the EMSL's MSCF and on the 512 node CRAY T3E-900 system in the National Energy Research Scientific Computing Center. It has not been optimized for high performance on single processor desktop systems.

4.1 Molecular electronic structure

The following quantum mechanical methods are available to calculate energies and analytic first derivatives with respect to atomic coordinates. Second derivatives are computed by finite difference of the first derivatives.

- Self Consistent Field (SCF) or Hartree Fock (RHF, UHF, high-spin ROHF).
- Gaussian Density Functional Theory (DFT), using many local and non-local exchange-correlation potentials (RHF or UHF) with formal N^3 and N^4 scaling.
- Spin-orbit DFT (SODFT), using many local and non-local exchange-correlation potentials (UHF).
- MP2 including semi-direct using frozen core and RHF and UHF reference.
- Complete active space SCF (CASSCF).

The following methods are available to compute energies only. First and second derivatives are computed by finite difference of the energies.

- CCSD, CCSD(T), CCSD+T(CCSD), with RHF reference.
- Selected-CI with second-order perturbation correction.

- MP2 fully-direct with RHF reference.
- Resolution of the identity integral approximation MP2 (RI-MP2), with RHF and UHF reference.

For all methods, the following operations may be performed:

- Single point energy
- Geometry optimization (minimization and transition state)
- Molecular dynamics on the fully *ab initio* potential energy surface
- Numerical first and second derivatives automatically computed if analytic derivatives are not available
- Normal mode vibrational analysis in cartesian coordinates
- ONIOM hybrid method of Morokuma and co-workers
- Generation of the electron density file for graphical display
- Evaluation of static, one-electron properties.
- Electrostatic potential fit of atomic partial charges (CHELPG method with optional RESP restraints or charge constraints)

For closed and open shell SCF and DFT:

- COSMO energies - the continuum solvation 'Conductor-Like Screening' Model of A. Klamt and G. Schuurmann to describe dielectric screening effects in solvents.

In addition, automatic interfaces are provided to

- The COLUMBUS multi-reference CI package
- The natural bond orbital (NBO) package
- Python

4.2 Relativistic effects

The following methods for including relativity in quantum chemistry calculations are available:

- The spin-free one-electron Douglas-Kroll approximation is available for all quantum mechanical methods and their gradients.
- Dyall's spin-free Modified Dirac Hamiltonian approximation is available for the Hartree-Fock method and its gradients.
- One-electron spin-orbit effects can be included via spin-orbit potentials. This option is available for DFT and its gradients, but has to be run without symmetry.

4.3 Pseudopotential plane-wave electronic structure

The following modules are available to compute the energy, minimize the geometry and perform ab initio molecular dynamics using pseudopotential plane-wave DFT.

- Fixed step length steepest descent
- Conuugate Gradient
- Car-Parrinello (extended Lagrangian dynamics)

With

- Vosko and PBE96 exchange-correlation potentials (restricted and unrestricted)
- (Gamma point) Periodic orthorhombic simulation cells for calculating molecules, liquids, crystals, and surfaces
- Aperiodic orthorhombic simulations cells for calculating molecules that are charged or highly polar
- Constant energy and constant temperature Car-Parrinello simulations
- Hamann and Troullier-Martins norm-conserving pseudopotentials with opt ional semicore corrections
- Modules to convert between small and large plane-wave expansions
- Interface to DRIVER, STEPPER, and VIB modules
- Mulliken analysis

4.4 Periodic system electronic structure

A module (Gaussian Approach to Polymers, Surfaces and Solids (GAPSS)) is available to compute energies by Gaussian Density Functional Theory (DFT) with many local and non-local exchange-correlation potentials.

4.5 Molecular dynamics

The following functionality is available for classical molecular simulations:

- Single configuration energy evaluation
- Energy minimization
- Molecular dynamics simulation
- Free energy simulation (multistep thermodynamic perturbation (MSTP) or multiconfiguration thermodynamic integration (MCTI) methods with options of single and/or dual topologies, double wide sampling, and separation-shifted scaling)

The classical force field includes:

- Effective pair potentials (functional form used in AMBER, GROMOS, CHARMM, etc.)
- First order polarization
- Self consistent polarization
- Smooth particle mesh Ewald (SPME)
- Twin range energy and force evaluation
- Periodic boundary conditions
- SHAKE constraints
- Consistent temperature and/or pressure ensembles

NWChem also has the capability to combine classical and quantum descriptions in order to perform:

- Mixed quantum-mechanics and molecular-mechanics (QM/MM) minimizations and molecular dynamics simulation , and
- Quantum molecular dynamics simulation by using any of the quantum mechanical methods capable of returning gradients.

4.6 Python

The Python programming language has been embedded within NWChem and many of the high level capabilities of NWChem can be easily combined and controlled by the user to perform complex operations.

4.7 Parallel tools and libraries (ParSoft)

- Global arrays (GA)
- Agregate Remote Memory Copy Interface (ARMCI)
- Linear Algebra (PeIGS) and FFT
- ParIO
- Memory allocation (MA)

Chapter 5

Top-level directives

Top-level directives are directives that can affect all modules in the code. Some specify molecular properties (e.g., total charge) or other data that should apply to all subsequent calculations with the current database. However, most top-level directives provide the user with the means to manage the resources for a calculation and to start computations. As the first step in the execution of a job, NWChem scans the entire input file looking for start-up directives, which NWChem must process before all other input. The input file is then rewound and processed sequentially, and each directive is processed in the order in which it is encountered. In this second pass, start-up directives are ignored.

The following sections describe each of the top-level directives in detail, noting all keywords, options, required input, and defaults.

5.1 START and RESTART — Start-up mode

A `START` or `RESTART` directive is optional. If one of these two directives is not specified explicitly, the code will infer one, based upon the name of the input file and the availability of the database. When allowing NWChem to infer the start-up directive, the user must be quite certain that the contents of the database will result in the desired action. It is usually more prudent to specify the directive explicitly, using the following format:

```
(RESTART || START)   \
            [<string file_prefix default $input_file_prefix$>] \
            [rtdb <string rtdb_file_name default $file_prefix$.db>]
```

The `START` directive indicates that the calculation is one in which a new database is to be created. Any relevant information that already exists in a previous database of the same name is destroyed. The string variable `<file_prefix>` will be used as the prefix to name any files created in the course of the calculation.

E.g., to start a new calculation on water, one might specify

```
  start water
```

which would result in all files beginning with `"water."`.

If the user does not specify an entry for `<file_prefix>` on the `START` directive (or omits the `START` directive altogether), the code uses the base-name of the input file as the file prefix. That is, the variable

<file_prefix> is assigned the name of the input file (not its full pathname), but without the last "dot-suffix". For example, the input file name `/home/dave/job.2.nw` yields `job.2` as the file prefix, if a name is not assigned explicitly using the `START` directive.

The user also has the option of specifying a unique name for the database, using the keyword `rtdb`. When this keyword is entered, the string entered for `rtdb_file_name` is used as the database name. If the keyword `rtbd` is omitted, the name of the database defaults to $<file_prefix>$.db in the directory for permanent files.

If a calculation is to start from a previous calculation and go on using the existing database, the `RESTART` directive must be used. In such a case, the previous database must already exist. The name specified for <file_prefix> usually should not be changed when restarting a calculation. If it is changed, NWChem will not be able to find needed files when going on with the calculation.

In the most common situation, the previous calculation was completed (with or without an error condition), and it is desired to perform a new task or restart the previous one, perhaps with some input changes. In these instances, the `RESTART` directive should be used. This reuses the previous database and associated files, and reads the input file for new input and task information.

The `RESTART` directive looks immediately for new input and task information, deleting information about previous incomplete tasks.

To summarize the default options for this start-up directive, if the input file does *not* contain a `START` or a `RESTART` directive, then

- the variable <file_prefix> is assigned the name of the input file for the job, without the suffix (which is usually `.nw`)
- the variable <rtdb_file_name> is assigned the default name, `$file_prefix$.db`

If the database with name `$file_prefix$.db` does *not* already exist, the calculation is carried out as if a `START` directive had been encountered. If the database with name `$file_prefix$.db` *does* exist, then the calculation is performed as if a `RESTART` directive had been encountered.

For example, NWChem can be run using an input file with the name `water.nw` by typing the UNIX command line,

```
nwchem water.nw
```

If the NWChem input file `water.nw` does not contain a `START` or `RESTART` directive, the code sets the variable <file_prefix> to `water`. Files created by the job will have this prefix, and the database will be named `water.db`. If the database `water.db` does *not* exist already, the code behaves as if the input file contains the directive,

```
start water
```

If the database `water.db` *does* exist, the code behaves as if the input file contained the directive,

```
restart water
```

5.2 SCRATCH_DIR and PERMANENT_DIR — File directories

These are start-up directives that allow the user to specify the directory location of scratch and permanent files created by NWChem. NWChem distinguishes between permanent (or persistent) files and scratch (or temporary) files, and allows the user the option of putting them in different locations. In most installations, however, permanent and scratch files are all written to the current directory by default. What constitutes "local" disk space may also differ from machine to machine.

The conventions for file storage are at the discretion of the specific installation, and are quite likely to be different on different machines. When assigning locations for permanent and scratch files, the user must be cognizant of the characteristics of the installation on a particular platform. To consider just a few examples, on the IBM SP and workstation clusters, machine-specific or process-specific names must be supplied for both local and shared file systems, while on the KSR it is useful to specify scratch file directories with automated striping across processors with round-robin allocation. On SMP clusters, both of these specifications are required.

The `SCRATCH_DIR` and `PERMANENT_DIR` directives are identical in format and capability, and enable the user to specify a single directory for all processes, or different directories for different processes. The general form of the directive is as follows:

```
(PERMANENT_DIR || SCRATCH_DIR) [(<string host>||<integer process>):] \
                                        <string directory> \
                               [...]
```

Directories are extracted from the user input by executing the following steps, in sequence:

1. Look for a directory qualified by the process ID number of the invoking process. Processes are numbered from zero. Else,
2. If there is a list of directories qualified by the name of the host machine[1], then use round-robin allocation from the list for processes executing on the given host. Else,
3. If there is a list of directories unqualified by any hostname or process ID, then use round-robin allocation from this list.

If directory allocation directive(s) are not specified in the input file, or if no match is found to the directory names specified by input using these directives, then the steps above are executed using the installation-specific defaults. If the code cannot find a valid directory name based on the input specified in either the directive(s) or the system defaults, files are automatically written to the current working directory (`"."`).

The following is a list of examples of specific allocations of scratch directory locations:

- Put scratch files from all processes in the local scratch directory (Warning: the definition of "local scratch directory" may change from machine to machine):

  ```
  scratch_dir /localscratch
  ```

- Put scratch files from Process 0 in `/piofs/rjh`, but put all other scratch files in `/scratch`:

  ```
  scratch_dir /scratch 0:/piofs/rjh
  ```

- Put scratch files from Process 0 in directory `scr1`, those from Process 1 in `scr2`, and so forth, in a round-robin fashion, using the given list of directories:

  ```
  scratch_dir /scr1 /scr2 /scr3 /scr4 /scr5
  ```

[1] As returned by `util_hostname()` which maps to the output of the command `hostname` on Unix workstations.

- Allocate files in a round-robin fashion from host-specific lists for processes distributed across two SGI multi-processor machines (node names *coho* and *bohr*):

```
scratch_dir coho:/xfs1/rjh coho:/xfs2/rjh coho:/xfs3/rjh \
   bohr:/disk01/rjh bohr:/disk02/rjh bohr:/disk13/rjh
```

5.3 MEMORY — Control of memory limits

This is a start-up directive that allows the user to specify the amount of memory that NWChem can use for the job. If this directive is not specified, memory is allocated according to installation-dependent defaults. *The defaults should generally suffice for most calculations, since the defaults usually correspond to the total amount of memory available on the machine. It should usually be unnecessary to provide a memory directive!!!*

The general form of the directive is as follows:

```
MEMORY [[total] <integer total_size>] \
       [stack <integer stack_size>] \
       [heap <integer heap_size>] \
       [global <integer global_size>] \
       [units <string units default real>] \
       [(verify||noverify)] \
       [(nohardfail||hardfail)] \
```

NWChem recognizes the following memory units:

- `real` and `double` (synonyms)
- `integer`
- `byte`
- `kb` (kilobytes)
- `mb` (megabytes)
- `mw` (megawords, 64-bit word)

In most cases, the user need specify only the total memory limit to adjust the amount of memory used by NWChem. The following specifications all provide for eight megabytes of total memory (assuming 64-bit floating point numbers), which will be distributed according to the default partitioning:

```
memory 1048576
memory 1048576 real
memory 1 mw
memory 8 mb
memory total 8 mb
memory total 1048576
```

In NWChem there are three distinct regions of memory: stack, heap, and global. Stack and heap are node-private, while the union of the global region on all processors is used to provide globally-shared memory.

The allowed limits on each category are determined from a default partitioning (currently 25Alternatively, the keywords **stack**, **heap**, and **global** can be used to define specific allocations for each of these categories. If the user sets only one of the stack, heap, or global limits by input, the limits for the other two categories are obtained by partitioning the remainder of the total memory available in proportion to the weight of those two categories in the default memory partitioning. If two of the category limits are given, the third is obtained by subtracting the two given limits from the total limit (which may have been specified or may be a default value). If all three category limits are specified, they determine the total memory allocated. However, if the total memory is also specified, it must be larger than the sum of all three categories. The code will abort if it detects an inconsistent memory specification.

The following memory directives also allocate 8 megabytes, but specify a complete partitioning as well:

```
memory total 8 stack 2 heap 2 global 4 mb
memory stack 2 heap 2 global 4 mb
```

The optional keywords **verify** and **noverify** in the directive give the user the option of enabling or disabling automatic detection of corruption of allocated memory. The default is **verify**, which enables the feature. This incurs a small overhead, which can be eliminated by specifying **noverify**.

The keywords **hardfail** and **nohardfail** give the user the option of forcing (or not forcing) the local memory management routines to generate an internal fatal error if any memory operation fails. The default is **nohardfail**, which allows the code to continue past any memory operation failure, and perhaps generate a more meaningful error message before terminating the calculation. Forcing a hard-fail can be useful when poorly coded applications do not check the return status of memory management routines.

When assigning the specific memory allocations using the keywords **stack**, **heap**, and **global** in the **MEMORY** directive, the user should be aware that some of the distinctions among these categories of memory have been blurred in their actual implementation in the code. The memory allocator (MA) allocates both the heap and the stack from a single memory region of size **heap+stack**, without enforcing the partition. The heap vs. stack partition is meaningful only to applications developers, and can be ignored by most users. Further complicating matters, the global array (GA) toolkit is allocated from within the MA space on distributed memory machines, while on shared-memory machines it is separate[2].

On distributed memory platforms, the MA region is actually the total size of

```
stack+heap+global
```

All three types of memory allocation compete for the same pool of memory, with no limits except on the total available memory. This relaxation of the memory category definitions usually benefits the user, since it can allow allocation requests to succeed where a stricter memory model would cause the directive to fail. These implementation characteristics must be kept in mind when reading program output that relates to memory usage.

Standard defaults for various platforms are listed in Table 5.3, though these are commonly overriden during installation at many sites.

5.4 ECHO — Print input file

This start-up directive is provided as a convenient way to include a listing of the input file in the output of a calculation. It causes the entire input file to be printed to Fortran unit six (standard output). It has no

[2] This is because on true shared-memory machines there is no choice but to allocate GAs from within a shared-memory segment, which is managed differently by the operating system.

Platform	Total Memory Limit (MBytes)
CRAY-T3E	83
DECOSF	200
IBM RS/6000	200
IBM SP-X	90
Linux	90
SGI	200
SGI Power Challenge	200
Sun	200

Table 5.1: Default total memory limits according to hardware platform.

keywords, arguments, or options, and consists of the single line:

```
ECHO
```

The `ECHO` directive is processed only once, by Process 0 when the input file is read.

5.5 TITLE — Specify job title

This top-level directive allows the user to identify a job or series of jobs that use a particular database. It is an optional directive, and if omitted, the character string containing the input title will be empty. Multiple `TITLE` directives may appear in the input file (e.g., the example file in Section 2.3) in which case a task will use the one most recently specified. The format for the directive is as follows:

```
TITLE <string title>
```

The character string `<title>` is assigned to the contents of the string following the `TITLE` directive. If the string contains white space, it must be surrounded by double quotes. For example,

```
title "This is the title of my NWChem job"
```

The title is stored in the database and will be used in all subsequent tasks/jobs until redefined in the input.

5.6 PRINT and NOPRINT — Print control

The `PRINT` and `NOPRINT` directives allow the user to control how much output NWChem generates. These two directives are special in that the compound directives for *all* modules are supposed to recognize them. Each module can control both the overall print level (general verbosity) and the printing of individual items which are identified by name (see below). The standard form of the `PRINT` directive is as follows:

```
PRINT [(none || low || medium || high || debug) default medium] \
      [<string list_of_names ... >]

NOPRINT <string list_of_names ... >
```

The default print level is medium.

Every output that is printed by NWChem has a print threshold associated with it. If this threshold is equal to or lower than the print level requested by the user, then the output is generated. For example, the threshold for printing the SCF energy at convergence is `low` (Section 10.17). This means that if the user-specified print level on the `PRINT` directive is `low`, `medium`, `high`, or `debug`, then the SCF energy will be printed at convergence.

The overall print level specified using the `PRINT` directive is a convenient tool for controlling the verbosity of NWChem. Setting the print level to `high` might be helpful in diagnosing convergence problems. The print level of `debug` might also be of use in evaluating problem cases, but the user should be aware that this can generate a huge amount of output. Setting the print level to `low` might be the preferable choice for geometry optimizations that will perform many steps which are in themselves of little interest to the user.

In addition, it is possible to enable the printing of specific items by naming them in the `PRINT` directive in the `<list_of_names>`. Items identified in this way will be printed, regardless of the overall print level specified. Similarly, the `NOPRINT` directive can be used to suppress the printing of specific items by naming them in its `<list_of_names>`. These items will *not* be printed, regardless of the overall print level, or the specific print level of the individual items.

The list of items that can be printed for each module is documented as part of the input instructions for that module. The items recognized by the top level of the code, and their thresholds, are:

Name	**Print Level**	**Description**
"total time"	medium	Print cpu and wall time at job end
"task time"	high	Print cpu and wall time for each task
"rtdb"	high	Print names of RTDB entries
"rtdbvalues"	high	Print name and values of RTDB entries
"ga summary"	medium	Summarize GA allocations at job end
"ga stats"	high	Print GA usage statistics at job end
"ma summary"	medium	Summarize MA allocations at job end
"ma stats"	high	Print MA usage statistics at job end
"version"	debug	Print version number of all compiled routines
"tcgmsg"	never	Print TCGMSG debug information

Table 5.2: Top Level Print Control Specifications

The following example shows how a `PRINT` directive for the top level process can be used to limit printout to only essential information. The directive is

```
print none "ma stats" rtdb
```

This directive instructs the NWChem main program to print nothing, except for the memory usage statistics (`ma stats`) and the names of all items stored in the database at the end of the job.

The print level within a module is inherited from the calling layer. For instance, by specifying the print to be low within the MP2 module will cause the SCF, CPHF and gradient modules when invoked from the MP2 to default to low print. Explicit user input of print thresholds overrides the inherited value.

5.7 SET — Enter data in the RTDB

This top-level directive allows the user to enter data directly into the database (see Section 3.1 for a description of the database). The format of the directive is as follows:

```
SET <string name> [<string type default automatic>] <$type$ data>
```

The entry for variable `<name>` is the name of data to be entered into the database. This must be specified; there is no default. The variable `<type>`, which is optional, allows the user to define a string specifying the type of data in the array `<name>`. The data type can be explicitly specified as `integer`, `real`, `double`, `logical`, or `string`. If no entry for `<type>` is specified on the directive, its value is inferred from the data type of the *first* datum. In such a case, floating-point data entered using this directive must include either an exponent or a decimal point, to ensure that the correct default type will be inferred. The correct default type will be inferred for logical values if logical-true values are specified as `.true.`, `true`, or `t`, and logical-false values are specified as `.false.`, `false`, or `f`. One exeception to the automatic detection of the data type is that the data type **must** be explicitly stated to input integer ranges, unless the first element in the list is an integer that is not a range (c.f., 2.4). For example,

```
set atomid 1 3:7 21
```

will be interpreted as a list of integers. However,

```
set atomid 3:7 21
```

will not work since the first element will be interpreted as a string and not an integer. To work around this feature, use instead

```
set atomid integer 3:7 21
```

The `SET` directive is useful for providing indirection by associating the name of a basis set or geometry with the standard object names (such as `"ao basis"` or `geometry`) used by NWChem. The following input file shows an example using the `SET` directive to direct different tasks to different geometries. The required input lines are as follows:

```
title "Ar dimer BSSE corrected MP2 interaction energy"
geometry "Ar+Ar"
  Ar1 0 0 0
  Ar2 0 0 2
end

geometry "Ar+ghost"
  Ar1 0 0 0
  Bq2 0 0 2
end

basis
  Ar1 library aug-cc-pvdz
  Ar2 library aug-cc-pvdz
  Bq2 library Ar aug-cc-pvdz
```

```
end

set geometry "Ar+Ar"
task mp2

scf; vectors atomic; end

set geometry "Ar+ghost"
task mp2
```

This input tells the code to perform MP2 energy calculations on an argon dimer in the first task, and then on the argon atom in the presence of the "ghost" basis of the other atom.

The `SET` directive can also be used as an indirect means of supplying input to a part of the code that does not have a separate input module (e.g., the atomic SCF, Section 10.5.2). Additional examples of applications of this directive can be found in the sample input files (see Section 2.3), and its usage with basis sets (Section 7) and geometries (Section 6).

5.8 UNSET — Delete data in the RTDB

This directive gives the user a way to delete simple entries from the database. The general form of the directive is as follows:

```
UNSET <string name>[*]
```

This directive cannot be used with complex objects such as geometries and basis sets[3]. A wild-card (*) specified at the end of the string `<name>` will cause *all* entries whose name begins with that string to be deleted. This is very useful as a way to reset modules to their default behavior, since modules typically store information in the database with names that begin with `module:`. For example, the SCF program can be restored to its default behavior by deleting all database entries beginning with `scf:`, using the directive

```
unset scf:*
```

The following example makes an entry in the database using the `SET` directive, and then immediately deletes it using the `UNSET` directive:

```
set mylist 1 2 3 4
unset mylist
```

5.9 STOP — Terminate processing

This top-level directive provides a convenient way of verifying an input file without actually running the calculation. It consists of the single line,

```
STOP
```

As soon as this directive is encountered, all processing ceases and the calculation terminates with an error condition.

[3] Complex objects are stored using a structured naming convention that is not matched by a simple wild card.

5.10 TASK — Perform a task

The `TASK` directive is used to tell the code what to do. The input directives are parsed sequentially until a `TASK` directive is encountered, as described in Section 2.1. At that point, the calculation or operation specified in the `TASK` directive is performed. When that task is completed, the code looks for additional input to process until the next `TASK` directive is encountered, which is then executed. This process continues to the end of the input file. NWChem expects the last directive before the end-of-file to be a `TASK` directive. If it is not, a warning message is printed. Since the database is persistent, multiple tasks within one job behave *exactly* the same as multiple restart jobs with the same sequence of input.

There are four main forms of the the `TASK` directive. The most common form is used to tell the code at what level of theory to perform an electronic structure calculation, and which specific calculations to perform. The second form is used to specify tasks that do not involve electronic structure calculations or tasks that have not been fully implemented at all theory levels in NWChem, such as simple property evaluations. The third form is used to execute UNIX commands on machines having a Bourne shell. The fourth form is specific to combined quantum-mechanics and molecular-mechanics (QM/MM) calculations.

By default, the program terminates when a task does not complete successfully. The keyword `ignore` can be used to prevent this termination, and is recognized by all forms of the `TASK` directive. When a `TASK` directive includes the keyword `ignore`, a warning message is printed if the task fails, and code execution continues with the next task.

The input options, keywords, and defaults for each of these four forms for the `TASK` directive are discussed in the following sections.

5.10.1 TASK Directive for Electronic Structure Calculations

This is the most commonly used version of the `TASK` directive, and it has the following form:

```
TASK <string theory> [<string operation default energy>] [ignore]
```

The string `<theory>` specifies the level of theory to be used in the calculations for this task. NWChem currently supports ten different options. These are listed below, with the corresponding entry for the variable `<theory>`:

- `scf` — Hartree-Fock
- `dft` — Density functional theory for molecules
- `sodft` — Spin-Orbit Density functional theory
- `gapss` — Density functional theory for periodic systems
- `mp2` — MP2 using a semi-direct algorithm
- `direct_mp2` — MP2 using a full-direct algorithm
- `rimp2` — MP2 using the RI approximation
- `ccsd` — Coupled-cluster single and double excitations
- `mcscf` — Multiconfiguration SCF
- `selci` — Selected configuration interaction with perturbation correction

- `md` — Classical molecular dynamics simulation using nwARGOS
- `cg\_pspw` — Pseudopotential Plane-Wave DFT (PSPW)

The string `<operation>` specifies the calculation that will be performed in the task. The default operation is a single point energy evaluation. The following list gives the selection of operations currently available in NWChem:

- `energy` — Evaluate the single point energy.
- `gradient` — Evaluate the derivative of the energy with respect to nuclear coordinates.
- `optimize` — Minimize the energy by varying the molecular structure. By default, this geometry optimization is presently driven by the Driver module (see Section 19), but the Stepper module (see Section 20) may also be used.
- `saddle` — Conduct a search for a transition state (or saddle point) using either Driver (Section 19, the default) or Stepper (Section 20).
- `frequencies` or `freq` — Compute second derivatives and print out an analysis of molecular vibrations.
- `dynamics` — Compute molecular dynamics using nwARGOS.
- `thermodynamics` — Perform multi-configuration thermodynamic integration using nwARGOS.

The user should be aware that some of these operations (gradient, optimize, dynamics, thermodynamics) require computation of derivatives of the energy with respect to the molecular coordinates. If analytical derivatives are not available (Section 4), they must be computed numerically, which can be very computationally intensive.

Here are some examples of the `TASK` directive, to illustrate the input needed to specify particular calculations with the code. To perform a single point energy evaluation using any level of theory, the directive is very simple, since the energy evaluation is the default for the string `operation`. For an SCF energy calculation, the input line is simply

```
task scf
```

Equivalently, the operation can be specified explicitly, using the directive

```
task scf energy
```

Similarly, to perform a geometry optimization using density functional theory, the `TASK` directive is

```
task dft optimize
```

The optional keyword `ignore` can be used to allow execution to continue even if the task fails, as discussed above.

5.10.2 TASK Directive for Special Operations

This form of the `TASK` directive is used in instances where the task to be performed does not fit the model of the previous version (such as execution of a Python program, Section 32), or if the operation has not yet been implemented in a fashion that applies to a wide range of theories (e.g., property evaluation). Instead of requiring `theory` and `operation` as input, the directive needs only a string identifying the task. The form of the directive in such cases is as follows:

```
TASK <string task> [ignore]
```

The supported tasks that can be accessed with this form of the TASK directive are listed below, with the corresponding entries for string variable <task>.

- python — Execute a Python program (Section 32).
- rtdbprint — Print the contents of the database.
- cphf — Invoke the CPHF module.
- property — Perform miscellaneous property calculations.
- dplot — Execute a DLOT run (Section 23)
- nbo — Execute a NBO run (Section 33.1)

This directive also recognizes the keyword ignore, which allows execution to continue after a task has failed.

5.10.3 TASK Directive for the Bourne Shell

This form of the TASK directive is supported only on machines with a fully UNIX-style operating system. This directive causes specified processes to be executed using the Bourne shell. This form of the task directive is:

```
TASK shell [(<integer-range process = 0>||all)] \
           <string command>
```

The keyword shell is required for this directive. It specifies that the given command will be executed in the Bourne shell. The user can also specify which process(es) will execute this command by entering values for process on the directive. The default is for only process zero to execute the command. A range of processes may be specified, using Fortran triplet notation[4]. Alternatively, all processes can be specified simply by entering the keyword all. The input entered for command must form a single string, and must consist of valid UNIX command(s). If the string includes white space, it must be enclosed in double quotes.

For example, the TASK directive to tell process zero to copy the molecular orbitals file to a backup location /piofs/save can be input as follows:

```
task shell "cp *.movecs /piofs/save"
```

The TASK directive to tell all processes to list the contents of their /scratch directories is as follows:

```
task shell all "ls -l /scratch"
```

The TASK directive to tell processes 0 to 10 to remove the contents of the current directory is as follows:

```
task shell 0:10:1 "/bin/rm -f *"
```

Note that NWChem's ability to quote special input characters is *very* limited when compared with that of the Bourne shell. To execute all but the simplest UNIX commands, it is usually much easier to put the shell script in a file and execute the file from within NWChem.

[4] The notation lo:hi:inc denotes the integers lo, lo+inc, lo+2*inc, ..., hi

5.10.4 TASK Directive for QM/MM simulations

This is very similar to the most commonly used version of the `TASK` directive described in Section 5.10.1, and it has the following form;

```
TASK QMMM <string theory> [<string operation default energy>] [ignore]
```

The string `<theory>` specifies the QM theory to be used in the QM/MM simulation[5]. The level of theory may be any QM method that can compute gradients but those algorithms in NWChem that do not support analytic gradients should be avoided (c.f., Section 4).

The string `<operation>` is used to specify the calculation that will be performed in the QM/MM task. The default operation is a single point energy evaluation. The following list gives the selection of operations currently available in the NWChem QM/MM module;

- `energy` — single point energy evaluation
- `optimize` — minimize the energy by variation of the molecular structure.
- `dynamics` — molecular dynamics using nwARGOS

Here are some examples of the `TASK` directive for QM/MM simulations. To perform a single point energy of a QM/MM system using any QM level of theory, the directive is very simple. As with the general task directive, the QM/MM energy evaluation is the default. For a DFT energy calculation the task directive input is,

```
task qmmm dft
```

or completely as

```
task qmmm dft energy
```

To do a molecular dynamics simulation of a QM/MM system using the SCF level of theory the task directive input would be

```
task qmmm scf dynamics
```

The optional keyword `ignore` can be used to allow execution to continue even if the task fails, as discussed above.

5.11 CHARGE — Total system charge

This is an optional top-level directive that allows the user to specify the total charge of the system. The form of the directive is as follows:

```
CHARGE <real charge default 0>
```

[5] If theory is "`md`" this is not a QM/MM simulation and will result in an appropriate error

The default charge[6] is zero if this directive is omitted. An example of a case where the directive would be needed is for a calculation on a doubly charged cation. In such a case, the directive is simply,

```
charge 2
```

If centers with fractional charge have been specified (Section 6) the net charge of the system should be adjusted to ensure that there are an integral number of electrons.

The charge may be changed between tasks, and is used by all wavefunction types. For instance, in order to compute the first two vertical ionization energies of LiH, one might optimize the geometry of LiH using a UHF SCF wavefunction, and then perform energy calculations at the optimized geometry on LiH^+ and LiH^{2+} in turn. This is accomplished with the following input:

```
geometry; Li 0 0 0; H  0 0 1.64; end
basis; Li library 3-21g; H library 3-21g; end

scf; uhf; singlet; end
task scf optimize

charge 1
scf; uhf; doublet; end
task scf

charge 2
scf; uhf; singlet; end
task scf
```

The `GEOMETRY`, `BASIS`, and `SCF` directives are described below (Sections 6, 7 and 10 respectively) but their intent should be clear. The `TASK` directive is described above (Section 5.10).

[6]The charge directive, in conjunction with the charges of atomic nuclei (which can be changed via the geometry input, cf. Section 6.3), determines the total number of electrons in the chemical system. Therefore, a `charge n` specification removes "n" electrons from the chemical system. Similarly, `charge -n` adds "n" electrons.

Chapter 6

Geometries

The GEOMETRY directive is a compound directive that allows the user to define the geometry to be used for a given calculation. The directive allows the user to specify the geometry with a relatively small amount of input, but there are a large number of optional keywords and additional subordinate directives that the user can specify, if needed. The directive therefore appears to be rather long and complicated when presented in its general form, as follows:

```
 GEOMETRY [<string name default geometry>] \
          [units <string units default angstroms>] \
          [(angstrom_to_au || ang2au) \
                <real angstrom_to_au default 1.8897265>] \
          [print [xyz] || noprint] \
          [center || nocenter] \
          [bqbq] \
          [autosym [real tol default 1d-2]] \
          [autoz || noautoz] \
          [adjust] \
          [(nuc || nucl || nucleus) <string nucmodel>]


   [SYMMETRY [group] <string group_name> [print] \
          [tol <real tol default 1d-2>]]



   <string tag> <real x y z> [vx vy vz] [charge <real charge>] \
          [mass <real mass>] \
          [(nuc || nucl || nucleus) <string nucmodel>]
   ... ]

   [ZMATRIX || ZMT || ZMAT
        <string tagn> <list_of_zmatrix_variables>
        ...

        [VARIABLES
             <string symbol> <real value>
```

```
          ... ]

      [CONSTANTS
          <string symbol> <real value>
          ... ]

   (END || ZEND)]

      [ZCOORD
          CVR_SCALING <real value>
          BOND    <integer i> <integer j> \
                  [<real value>] [<string name>] [constant]
          ANGLE   <integer i> <integer j> \
                  [<real value>] [<string name>] [constant]
          TORSION <integer i> <integer j> <integer k> <integer l> \
                  [<real value>] [<string name>] [constant]
       END]

       [SYSTEM surface  <molecule polymer surface crystal default molecule>
           lat_a <real lat_a> lat_b <real lat_b> lat_c <real lat_c>
           alpha <real alpha> beta <real beta> gamma <real gamma>
       END]

  END
```

The three main parts of the `GEOMETRY` directive are:

- keywords on the first line of the directive (to specify such optional input as the geometry name, input units, and print level for the output)
- symmetry information
- Cartesian coordinates or Z-matrix input to specify the locations of the atoms and centers
- lattice parameters (needed only for periodic systems)

The following sections present the input for this compound directive in detail, describing the options available and the usages of the various keywords in each of the three main parts.

6.1 Keywords on the GEOMETRY directive

This section presents the options that can be specified using the keywords and optional input on the main line of the `GEOMETRY` directive. As described above, the first line of the directive has the general form,

```
 GEOMETRY [<string name default geometry>] \
          [units <string units default angstroms>] \
          [bqbq] \
          [print [xyz] || noprint] \
```

```
[center || nocenter] \
[autosym [real tol default 1d-2]] \
[autoz || noautoz] \
[adjust] \
[(nuc || nucl || nucleus) <string nucmodel>]
```

All of the keywords and input on this line are optional. The following list describes all options and their defaults.

- `<name>` – user-supplied name for the geometry; the default name is `geometry`, and all NWChem modules look for a geometry with this name. However, multiple geometries may be specified by using a different name for each. Subsequently, the user can direct a module to a named geometry by by using the the `SET` directive (see the example in Section 5.7) to associate the default name of `geometry` with the alternate name.
- `units` – keyword specifying that a value will be entered by the user for the string variable `<units>`. The default units for the geometry input are Angstrøms (Note: atomic units or Bohr are used within the code, regardless of the option specified for the input units. The default conversion factor used in the code to convert from Angstrøms to Bohr is 1.8897265 which may be overidden with the `angstrom_to_au` keyword described below.). The code recognizes the following possible values for the string variable `<units>`:
  - `angstroms` or `an` — Angstroms ($\AA$), the default (converts to A.U. using the $\AA$ to A.U. conversion factor)
  - `au` or `atomic` or `bohr` — Atomic units (A.U.)
  - `nm` or `nanometers` — nanometers (converts to A.U. using a conversion factor computed as 10.0 times the Å to A.U. conversion factor)
  - `pm` or `picometers` — picometers (converts to A.U. using a conversion factor computed as 0.01 times the Å to A.U. conversion factor)
- `angstrom_to_au` – may also be specified as `ang2au`. This enables the user to modify the conversion factors used to convert between Å and A.U.. The default value is 1.8897265.
- `bqbq` – keyword to specify the treatment of interactions between dummy centers. The default in NWChem is to ignore such interactions when computing energies or energy derivatives. These interactions will be included if the keyword `bqbq` is specified.
- `print` and `noprint` – complementary keyword pair to enable or disable printing of the geometry. The default is to print the output associated with the geometry. In addition, the keyword `print` may be qualified by the additional keyword `xyz`, which specifies that the coordinates should be printed in the XYZ format of molecular graphics program XMol.
- `center` and `nocenter` – complementary keyword pair to enable or disable translation of the center of nuclear charge to the origin. With the origin at this position, all three components of the nuclear dipole are zero. The default is to move the center of nuclear charge to the origin.
- `autosym` – keyword to specify that the symmetry of the geometric system should be automatically determined. This option is off by default. Only groups up to and including O_h are recognized. Occasionally NWChem will be unable to determine the full symmetry of a molecular system, but will find a proper subgroup of the full symmetry. The default tolerance is set to work for most cases, but may need to be decreased to find the full symmetry of a geometry. Note that autosym will be turned off if the `SYMMETRY` group input is given (See section 6.2).

- `noautoz` – by default NWChem (release 3.3 and later) will generate redundant internal coordinates from user input Cartesian coordinates. The internal coordinates will be used in geometry optimizations. The `noautoz` keyword disables use of internal coordinates. The `autoz` keyword is provided only for backward compatibility. See Section 6.5 for a more detailed description of redundant internal coordinates, including how to force the definition of specific internal variables in combination with automatically generated variables.
- `adjust` – This indicates that an existing geometry is to be adjusted. Only new input for the redundant internal coordinates may be provided (Section 6.5). It is not possible to define new centers or to modify the point group using this keyword. See Section 6.5 for an example of its usage.
- `nucleus` – keyword to specify the default model for the nuclear charge distribution. The following values are recognized:
  - `point` or `pt` — point nuclear charge distribution. This is the default.
  - `finite` or `fi` — finite nuclear charge distribution with a Gaussian shape. The RMS radius of the Gaussian is determined from the nuclear mass number A by the expression $r_{\mathrm{RMS}} = 0.836 * A^{1/3} + 0.57$ fm.

  NOTE: If you specify a finite nuclear size, you should ensure that the basis set you use is contracted for a finite nuclear size. See the Section 7 for more information.

The following examples illustrate some of the various options that the user can specify on the first input line of the `GEOMETRY` directive, using the keywords and input options described above.

The following directives all specify the same geometry for H_2 (a bond length of 0.732556 Å):

```
geometry                             geometry units nm
  h 0 0 0                              h 0 0 0
  h 0 0 0.732556                       h 0 0 0.0732556
end                                  end

geometry units pm                    geometry units atomic
  h 0 0 0                              h 0 0 0
  h 0 0 73.2556                        h 0 0 1.3843305
end                                  end
```

6.2 Symmetry Group Input

The `SYMMETRY` directive is used (optionally) within the compound `GEOMETRY` directive to specify the point group for the molecular geometry. The general form of the directive, as described above within the general form of the `GEOMETRY` directive, is as follows:

```
[SYMMETRY [group] <string group_name> [print] \
       [tol <real tol default 1d-2>]]
```

The keyword `group` is optional, and can be omitted without affecting how the input for this directive is processed[1]. However, if the `SYMMETRY` directive is used, a group name must be specified by supplying an entry for the string variable `<group_name>`. The group name should be specified as the standard Schöflies symbol. Examples of expected input for the variable `group_name` include such entries as:

[1]For periodic systems, there are additional keywords within this directive (not yet documented), so having a keyword for the group name is useful.

- `c2v` – for molecular symmetry C_{2v}
- `d2h` – for molecular symmetry D_{2h}
- `Td` – for molecular symmetry T_d
- `d6h` – for molecular symmetry D_{6h}

The `SYMMETRY` directive is optional. The default is no symmetry (i.e., C_1 point group). Automatic detection of point group symmetry is available through the use of `autosym` in the `GEOMETRY` directive main line (discussed in Section 6.1). Note: if the `SYMMETRY` directive is present the `autosym` keyword is ignored.

If only symmetry-unique atoms are specified, the others will be generated through the action of the point group operators, but the user if free to specify all atoms. The user must know the symmetry of the molecule being modeled, and be able to specify the coordinates of the atoms in a suitable orientation relative to the rotation axes and planes of symmetry. Appendix C lists a number of examples of the `GEOMETRY` directive input for specific molecules having symmetry patterns recognized by NWChem. The exact point group symmetry will be forced upon the molecule, and atoms within 10^{-3} A.U. of a symmetry element (e.g., a mirror plane or rotation axis) will be forced onto that element. Thus, it is not necessary to specify to a high precision those coordinates that are determined solely by symmetry.

The keyword `print` gives information concerning the point group generation, including the group generators, a character table, the mapping of centers, and the group operations.

The keyword `tol` relates to the accuracy with which the symmetry-unique atoms should be specified. When the atoms are generated, those that are within the tolerance, `tol`, are considered the same.

6.3 Cartesian coordinate input

The default in NWChem is to specify the geometry information entirely in Cartesian coordinates, and examples of this format have appeared above (e.g, Section 2.3). Each center (usually an atom) is identified on a line of the following form:

```
<string tag> <real x y z> [vx vy vz] \
    [charge <real charge>] [mass <real mass>] \
    [(nuc || nucl || nucleus) <string nucmodel>]
```

The string `<tag>` is the name of the atom or center, and its case (upper or lower) is important. The tag is limited to 16 characters and is interpreted as follows:

- If the entry for `<tag>` begins with either the symbol or name of an element (regardless of case), then the center is treated as an atom of that type. The default charge is the atomic number (adjusted for the presence of ECPs by the ECP `NELEC` directive ; see Section 8). Additional characters can be added to the string, to distinguish between atoms of the same element (For example, the tags `oxygen`, `O`, `o34`, `olonepair`, and `Oxygen-ether`, will all be interpreted as oxygen atoms.).
- If the entry for `<tag>` begins with the characters `bq` or `x` (regardless of case), then the center is treated as a dummy center with a default zero charge (Note: a tag beginning with the characters `xe` will be interpreted as a xenon atom rather than as a dummy center.). Dummy centers may optionally have basis functions or non-zero charge. See Section B.2 for a sample input using dummy centers with charges.

It is *important* to be aware of the following points regarding the definitions and usage of the values specified for the variable `<tag>` to describe the centers in a system:

- If the tag begins with characters that cannot be matched against an atom, and those characters are not `BQ` or `X`, then a fatal error is generated.
- The tag of a center is used in the `BASIS` (Section 7) and `ECP` (Section 8) directives to associate functions with centers.
- All centers with the same tag will have the same basis functions.
- When using automatic symmetry detection, only centers with the same tag will be candidates for testing for symmetry equivalence.
- The user-specified charges (of all centers, atomic and dummy) and any net total charge of the system (Section 5.11) are used to determine the number of electrons in the system.

The Cartesian coordinates of the atom in the molecule are specified as real numbers supplied for the variables `x`, `y`, and `z` following the characters entered for the tag. The values supplied for the coordinates must be in the units specified by the value of the variable `<units>` on the first line of the `GEOMETRY` directive input.

After the Cartesian coordinate input, optional velocities may be entered as real numbers for the variables `vx`, `vy`, and `vz`. The velocities should be given in atomic units and are used in QMD and PSPW calculations.

The Cartesian coordinate input line also contains the optional keywords `charge`, `mass` and `nucleus`, which allow the user to specify the charge of the atom (or center) and its mass (in atomic mass units), and the nuclear model. The default charge for an atom is its atomic number, adjusted for the presence of ECPs (see Section 8). In order to specify a different value for the charge on a particular atom, the user must enter the keyword `charge`, followed by the desired value for the variable `<charge>`.

The default mass for an atom is taken to be the mass of its most abundant naturally occurring isotope or of the isotope with the longest half-life. To model some other isotope of the element, its mass must be defined explicitly by specifying the keyword `mass`, followed by the value (in atomic mass units) for the variable `<mass>`.

The default nuclear model is a point nucleus. The keyword `nucleus` (or `nucl` or `nuc`) followed by the model name `<nucmodel>` overrides this default. Allowed values of `<nucmodel>` are `point` or `pt` and `finite` or `fi`. The `finite` option is a nuclear model with a Gaussian shape. The RMS radius of the Gaussian is determined by the atomic mass number via the formula $r_{\mathrm{RMS}} = 0.836 * A^{1/3} + 0.57$ fm. The mass number A is derived from the variable `<mass>`.

The geometry of the system can be specified entirely in Cartesian coordinates by supplying a `<tag>` line of the type described above for each atom or center. The user has the option, however, of supplying the geometry of some or all of the atoms or centers using a Z-matrix description. In such a case, the user supplies the input tag line described above for any centers to be described by Cartesian coordinates, and then specifies the remainder of the system using the optional `ZMATRIX` directive described below in Section 6.4.

6.4 Z-matrix input

The `ZMATRIX` directive is an optional directive that can be used within the compound `GEOMETRY` directive to specify the structure of the system with a Z-matrix, which can include both internal and Cartesian coordinates. The ZMATRIX directive is itself a compound directive that can include the VARIABLES and CONSTANTS directives, depending on the options selected. The general form of the compound ZMATRIX directive is as follows:

```
[ZMATRIX || ZMT || ZMAT
     <string tagn> <list_of_zmatrix_variables>
     ...

     [VARIABLES
          <string symbol> <real value>
          ... ]

     [CONSTANTS
          <string symbol> <real value>
          ... ]

(END || ZEND)]
```

The input module recognizes three possible spellings of this directive name. It can be invoked with ZMATRIX, ZMT, or ZMAT. The user can specify the molecular structure using either Cartesian coordinates or internal coordinates (bond lengths, bond angles and dihedral angles. The Z-matrix input for a center defines connectivity, bond length, and bond or torsion angles. Cartesian coordinate input for a center consists of three real numbers defining the x,y,z coordinates of the atom.

Within the Z-matrix input, bond lengths and Cartesian coordinates must be input in the user-specified units, as defined by the value specified for the variable <units> on the first line of the GEOMETRY directive. All angles are specified in degrees.

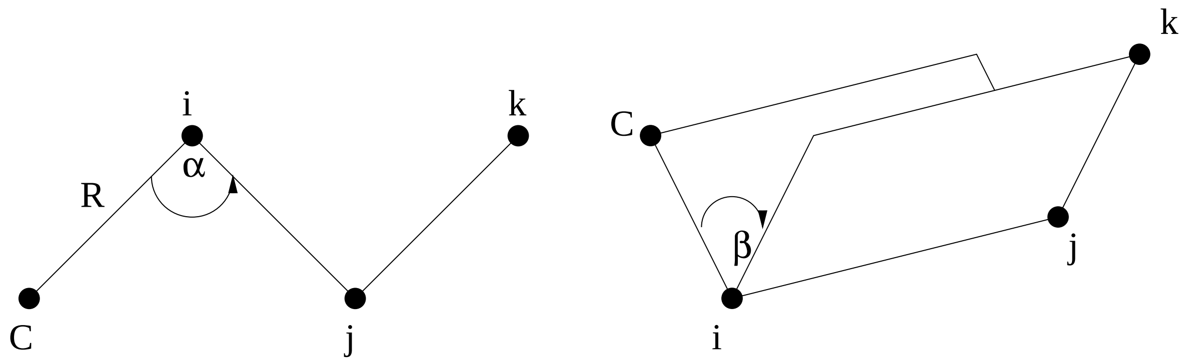
The individual centers (denoted as i, j, and k below) used to specify Z-matrix connectivity may be designated either as integers (identifying each center by number) or as tags (*If tags are used, the tag must be unique for each center.*) The use of "dummy" atoms is possible, by using X or BQ at the start of the tag.

Bond lengths, bond angles and dihedral angles (denoted below as R, alpha, and beta, respectively) may be specified either as numerical values or as symbolic strings that must be subsequently defined using the VARIABLES or CONSTANTS directives. The numerical values of the symbolic strings labeled VARIABLES may be subject to changes during a geometry optimization say, while the numerical values of the symbolic strings labeled —verb+CONSTANTS+ will stay frozen to the value given in the input. The same symbolic string can be used more than once, and any mixture of numeric data and symbols is acceptable. Bond angles (α) must be in the range $0 < \alpha < 180$.

The Z-matrix input is specified sequentially as follows:

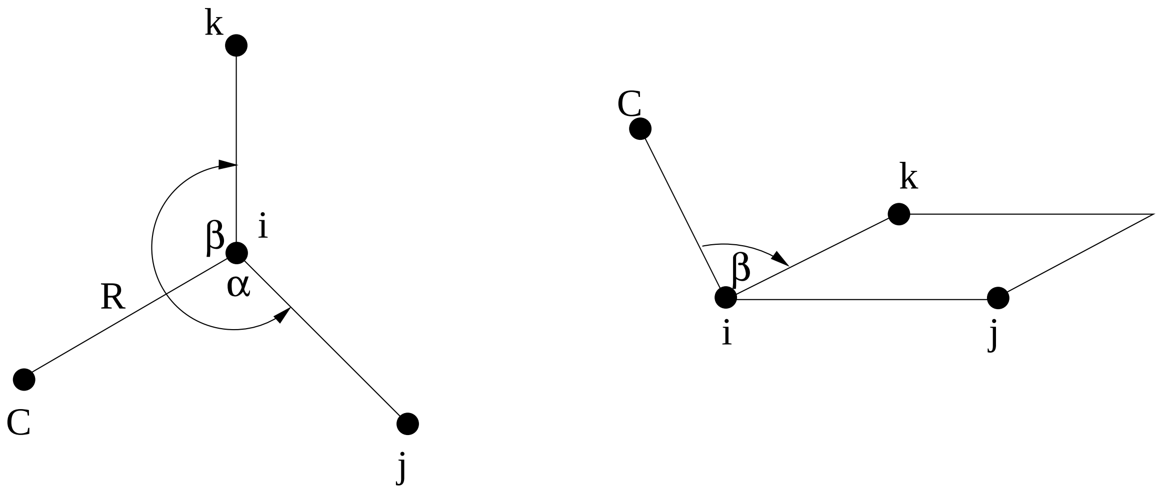
```
tag1
tag2 i R
tag3 i R j alpha
tag4 i R j alpha k beta [orient]
...
```

The structure of this input is described in more detail below. In the following discussion, the tag or number of the center being currently defined is labeled as C ("C" for current). The values entered for these tags for centers defined in the Z-matrix input are interpreted in the same way as the <tag> entries for Cartesian coordinates described above (see Section 6.3). Figures 6.1, 6.2 and 6.3 display the relationships between the input data and the definitions of centers and angles.



Input line: C i R j alpha k beta

Figure 6.1: Relationships between the centers, bond angle and dihedral angle in Z-matrix input.



Input line: C i R j alpha k beta +1

Figure 6.2: Relationships between the centers and two bond angles in Z-matrix input with optional parameter specified as +1.

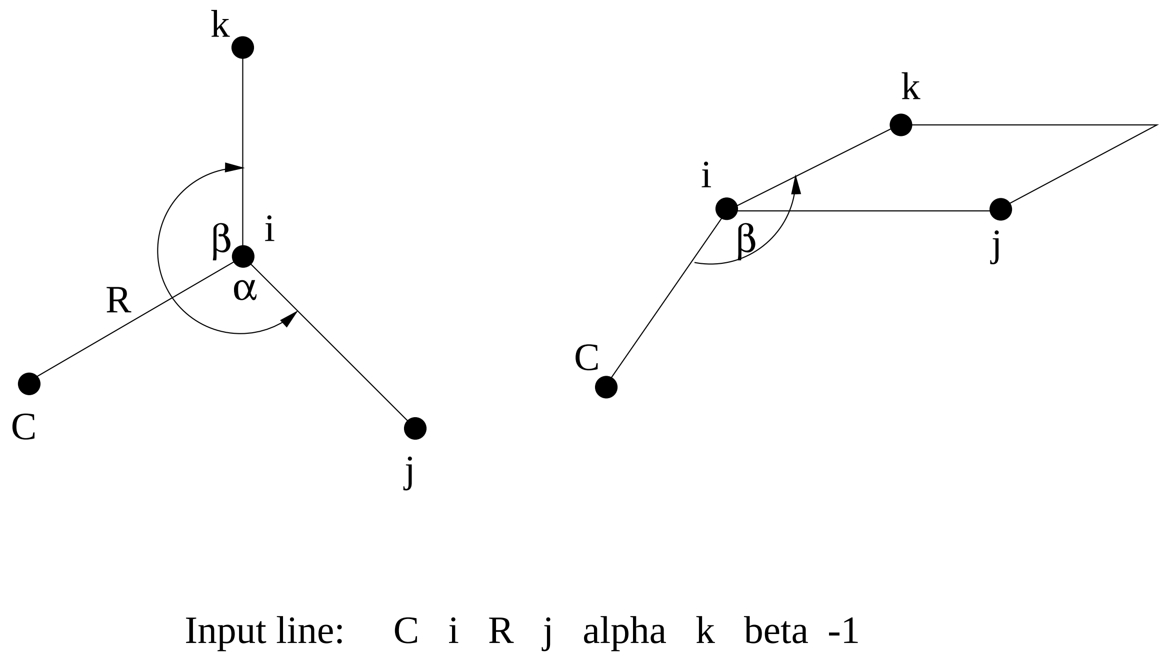


Figure 6.3: Relationships between the centers and two bond angles in Z-matrix input with optional parameter specified as -1.

The Z-matrix input shown above is interpreted as follows:

1. `tag1`

   Only a tag is required for the first center.

2. `tag2 i R`

   The second center requires specification of its tag and the bond length (R_{Ci}) distance to a previous atom, which is identified by `i`.

3. `tag3 i R j alpha`

   The third center requires specification of its tag, its bond length distance (R_{Ci}) to one of the two previous centers (identified by the value of `i`), and the bond angle $\alpha = \widehat{Cij}$.

4. `tag i R j alpha k beta [<integer orient default 0>]`

   The fourth, and all subsequent centers, require the tag, a bond length (R_{Ci}) relative to center `i`, the bond angle with centers `i` and `j` ($\alpha = \widehat{Cij}$), and *either*

   (a) the dihedral angle (β) between the current center and centers `i`, `j`, and `k` (Figure 6.1), or

   (b) a second bond angle $\beta = \widehat{Cik}$ and an orientation to the plane containing the other three centers (Figure 6.2 and 6.3).

   By default, β is interpreted as a dihedral angle (see Figure 6.1), but if the optional final parameter (`<orient>`) is specified with the value ± 1, then β is interpreted as the angle $\widehat{Cik}$. The sign of `<orient>` specifies the direction of the bond angle relative to the plane containing the three reference atoms. If `<orient>` is $+1$, then the new center (`C`) is above the plane (Figure 6.2); and if `<orient>` is -1, then `C` is below the plane (Figure 6.3).

Following the Z-matrix center definitions described above, the user can specify initial values for any symbolic variables used to define the Z-matrix tags. This is done using the optional `VARIABLES` directive, which has the general form:

```
VARIABLES
  <string symbol>  <real value>
  ...
```

Each line contains the name of a variable followed by its value. Optionally, an equals sign (`=`) can be included between the symbol and its value, for clarity in reading the input file.

Following the `VARIABLES` directive, the `CONSTANTS` directive may be used to define any Z-matrix symbolic variables that remain unchanged during geometry optimizations. To freeze the Cartesian coordinates of an atom, refer to Section 6.6. The general form of this directive is as follows:

```
CONSTANTS
  <string symbol>  <real value>
  ...
```

Each line contains the name of a variable followed by its value. As with the `VARIABLES` directive, an equals sign (`=`) can be included between the symbol and its value.

The end of the Z-matrix input using the compound `ZMATRIX` directive is signaled by a line containing either `END` or `ZEND`, following all input for the directive itself and its associated optional directives.

A simple example is presented for water. All Z-matrix parameters are specified numerically, and symbolic tags are used to specify connectivity information. This requires that all tags be unique, and therefore different tags are used for the two hydrogen atoms, which may or may not be identical.

```
geometry
  zmatrix
    O
    H1 O 0.95
    H2 O 0.95 H1 108.0
  end
end
```

The following example illustrates the Z-matrix input for the molecule CH_3CF_3. This input uses the numbers of centers to specify the connectivity information (`i`, `j`, and `k`), and uses symbolic variables for the Z-matrix parameters `R`, `alpha`, and `beta`, which are defined in the inputs for the `VARIABLES` and `CONSTANTS` directives.

```
geometry
 zmatrix
   C
   C 1 CC
   H 1 CH1 2 HCH1
   H 1 CH2 2 HCH2 3  TOR1  0
   H 1 CH3 2 HCH3 3 -TOR2  0
   F 2 CF1 1 CCF1 3  TOR3  0
   F 2 CF2 1 CCF2 6  FCH1  1
```

```
   F 2 CF3 1 CCF3 6  FCH2 -1
   variables
     CC    1.4888
     CH1   1.0790
     CH2   1.0789
     CH3   1.0789
     CF1   1.3667
     CF2   1.3669
     CF3   1.3669
   constants
     HCH1  104.28
     HCH2  104.74
     HCH3  104.7
     CCF1  112.0713
     CCF2  112.0341
     CCF3  112.0340
     TOR1  109.3996
     TOR2  109.3997
     TOR3  180.0000
     FCH1  106.7846
     FCH2  106.7842
 end
end
```

The input for any centers specified with Cartesian coordinates must be specified using the format of the `<tag>` lines described in Section 6.3 above. However, in order to correctly specify these Cartesian coordinates within the Z-matrix, the user must understand the orientation of centers specified using internal coordinates. These are arranged as follows:

- The first center is placed at the origin.
- The second center is placed along the positive z-axis.
- The third center is placed in the z-x plane.

6.5 ZCOORD — Forcing internal coordinates

By default redundant internal coordinates are generated for use in geometry optimizations. Connectivity is inferred by comparing inter-atomic distances with the sum of the van der Waals radii of the two atoms involved in a possible bond, times a scaling factor. The scaling factor is an input parameter of `ZCOORD` which maybe changed from its default value of 1.3. Under some circumstances (unusual bonding, bond dissociation, ...) it will be necessary to augment the automatically generated list of internal coordinates to force some specific internal coordinates to be included in among the internal coordinates. This is accomplished by including the optional directive `ZCOORD` within the geometry directive. The general form of the `ZCOORD` directive is as follows:

```
  ZCOORD
     CVR_SCALING <real value>
     BOND    <integer i> <integer j> \
             [<real value>] [<string name>] [constant]
```

```
    ANGLE   <integer i> <integer j> <integer k> \
            [<real value>] [<string name>] [constant]
    TORSION <integer i> <integer j> <integer k> <integer l> \
            [<real value>] [<string name>] [constant]
 END
```

The centers `i`, `j`, `k` and `l` *must* be specified using the numbers of the centers, as supplied in the input for the Cartesian coordinates. The `ZCOORD` input parameters are defined as follows:

- `cvr_scaling` — scaling factor applied to van der Waals radii.
- `bond` — a bond between the two centers.
- `angle` — a bond angle $\widehat{ijk}$.
- `torsion` — a torsion (or dihedral) angle. The angle between the planes `i-j-k` and `j-k-l`.

A value may be specified for a user-defined internal coordinate, in which case it is forced upon the input Cartesian coordinates while attempting to make only small changes in the other internal coordinates. If no value is provided the value implicit in the input coordinates is kept. If the keyword `constant` is specified, then that internal variable is not modified during a geometry optimization with DRIVER (Section 19). Each internal coordinate may also be named either for easy identification in the output, or for the application of constraints (Section 6.6).

If the keyword `adjust` is specified on the main `GEOMETRY` directive, only `ZCOORD` data may be specified and it can be used to change the user-defined internal coordinates, including adding/removing constraints and changing their values.

6.6 Applying constraints in geometry optimizations

Internal coordinates specified as constant in a `ZCOORD` directive or in the constants section of a `ZMATRIX` directive, will be frozen at their initial values if a geometry optimization is performed with DRIVER (Section 19).

If internal coordinates have the same name (give or take an optional sign for torsions) then they are forced to have the same value. This may be used to force bonds or angles to be equal even if they are not related by symmetry.

When atoms have been specified by their cartesian coordinates, *and* internal coordinates are not being used, it is possible to freeze the cartesian position of selected atoms. This is useful for such purposes as optimizing a molecule absorbed on the surface of a cluster with fixed geometry. Only the gradients associated with the active atoms are computed. This can result in a big computational saving, since gradients associated with frozen atoms are forced to zero (Note, however, that this destroys the translational and rotational invariance of the gradient. This is not yet fully accommodated by the STEPPER geometry optimization software, and can sometimes result in slower convergence of the optimization. The DRIVER optimization package does not suffer from this problem).

The `SET` directive (Section 5.7) is used to freeze atoms, by specifying a directive of the form:

```
 set geometry:actlist <integer list_of_center_numbers>
```

This defines only the centers in the list as active. All other centers will have zero force assigned to them, and will remain frozen at their starting coordinates during a geometry optimization.

For example, the following directive specifies that atoms numbered 1, 5, 6, 7, 8, and 15 are active and all other atoms are frozen:

```
set geometry:actlist 1 5:8 15
```

or equivalently,

```
set geometry:actlist 1 5 6 7 8 15
```

If this option is not specified by entering a `SET` directive, the default behavior in the code is to treat all atoms as active. To revert to this default behavior after the option to define frozen atoms has been invoked, the `UNSET` directive must be used (since the database is persistent, see Section 3.2). The form of the `UNSET` directive is as follows:

```
unset geometry:actlist
```

6.7 SYSTEM — Lattice parameters for periodic systems

This keyword is needed only for for 1-, 2-, and 3-dimensional periodic systems.

The `system` keyword can assume the following values

- `polymer` — system with 1-d translational symmetry.
- `surface` — system with 2-d translational symmetry.
- `crystal` — system with 3-d translational symmetry.
- `molecule` — no translational symmetry (this is the default)

When the system possess translational symmetry, **fractional** coordinates are used in the directions where translational symmetry exists. This means that for crystals x, y and z are fractional, for surfaces x and y are fractional, whereas for polymers only z is fractional. For example, in the following H_2O layer input (a 2-d periodic system), x and y coordinates are fractionay, whereas z is expressed in Å.

```
geometry units angstrom
  O     0.353553    0.353553         2.100000000
  H     0.263094    0.353553         2.663590000
  H     0.444007    0.353553         2.663590000
```

Since no space group symmetry is available yet other than $P1$, input of cell parameters is relative to the primitive cell. For example, this is the input required for the cubic face-centered type structure of bulk MgO.

```
system crystal
 lat_a 2.97692 lat_b 2.97692 lat_c 2.97692
 alpha 60.00 beta 60.00 gamma 60.00
end
```

Chapter 7

Basis sets

NWChem currently supports basis sets consisting of generally contracted[1] Cartesian Gaussian functions up to a maximum angular momentum of seven (*i* functions), and also *sp* (or L) functions[2] . The `BASIS` directive is used to define these, and also to specify use of an effective core potential (ECP) that is associated with a basis set; see Section 8.)

The basis functions to be used for a given calculation can be drawn from a standard set in the EMSL basis set library that is included in the release of NWChem (See Appendix A for a list of the standard basis sets currently supplied with the release of the code). Alternatively, the user can specify particular functions explicitly in the input, to define a particular basis set.

The general form of the `BASIS` directive is as follows:

```
BASIS [<string name default "ao basis">] \
      [(spherical || cartesian) default cartesian] \
      [(segment || nosegment) default segment] \
      [(print || noprint) default print]
      [rel]

   <string tag> library [<string tag_in_lib>] \
                <string standard_set> [file <filename>] [rel]

      ...

   <string tag> <string shell_type> [rel]
      <real exponent> <real list_of_coefficients>
      ...

END
```

Examining the keywords on the first line of the `BASIS` directive:

- `name`

[1] Generally contracted meaning that the same primitive, Gaussian functions are contracted into multiple contracted functions using different contraction coefficients. Reuse of the radial functions increases the efficiency of integral generation.

[2] An *sp* shell is two-component general contraction. However, the first component specifies an *s* shell and the second a *p* shell. Again, reuse of the radial functions increases the efficiency of integral generation.

By default, the basis set is stored in the database with the name `"ao basis"`. Another name may be specified in the `BASIS` directive, thus, multiple basis sets may be stored simultaneously in the database. Also, the DFT (Section 11), RI-SCF (Section 10.9) and RIMP2 (Section 15) modules and the Dyall-modified-Dirac relativistic method (Section 9.2) require multiple basis sets with specific names.

The user can associate the `"ao basis"` with another named basis using the `SET` directive (see Section 5.7).

- `SPHERICAL` or `CARTESIAN`

  The keywords `spherical` and `cartesian` offer the option of using either spherical-harmonic (5 d, 7 f, 9 g, ...) or Cartesian (6 d, 10 f, 15 g, ...) angular functions. The default is Cartesian.

  Note that the correlation-consistent basis sets were designed using spherical harmonics and to use these, the `spherical` keyword should be present in the `BASIS` directive. The use of spherical functions also helps eliminate problems with linear dependence.

- `SEGMENT` or `NOSEGMENT`

  By default, NWChem forces all basis sets to be segmented, even if they are input with general contractions or L or sp shells. This is because the current derivative integral program cannot handle general contractions. If a calculation is computing energies only, a performance gain can result from exploiting generally contracted basis sets, in which case `NOSEGMENT` should be specified.

- `PRINT` or `NOPRINT`

  The default is for the input module to print all basis sets encountered. Specifying the keyword `noprint` allows the user to suppress this output.

- `REL`

  This keyword marks the entire basis as a relativistic basis for the purposes of the Dyall-modified-Dirac relativistic integral code. The marking of the basis set is necessary for the code to make the proper association between the relativistic shells in the ao basis and the shells in the large and/or small component basis. This is only necessary for basis sets which are to be used as the ao basis. The user is referred to Section 9.2 for more details.

Basis sets are associated with centers by using the tag of a center in a geometry that has either been input by the user (Section 6) or is available elsewhere. Each atom or center with the same `tag` will have the same basis set. All atoms must have basis functions assigned to them — only dummy centers may have no basis functions. To facilitate the specification of the geometry and the basis set for any chemical system, the matching process of a basis set tag to a geometry tag first looks for an exact match. If no match is found, NWChem will attempt to match, ignoring case, the name or symbol of the element. E.g., all hydrogen atoms in asystem could be labeled "H1", "H2", ..., in the geometry but only one basis set specification for "H" or "hydrogen" is necessary. If desired, a special basis may be added to one or more centers (e.g., "H1") by providing a basis for that tag. If the matching mechanism fails then NWChem stops with an appropriate error message.

Examined next is how to reference standard basis sets in the basis set library, and finally, how to define a basis set using exponents and coefficients.

7.1 Basis set library

The keyword `library` associated with each specific `tag` entry specifies that the calculation will use the standard basis set in NWChem for that center. The variable `<standard_set>` is the name that identifies the functions in the library. The names of standard basis sets are not case sensitive. See Appendix A for a complete list of the basis sets in the NWChem library and their specifications.

For example, the NWChem basis set library contains the Dunning cc-pvdz basis set. These may be used as follows

```
basis
  oxygen library cc-pvdz
  hydrogen library cc-pvdz
end
```

A default path to the basis set library is provided on installation of the code, but a different path can be defined by specifying the keyword `file` and then explicitly naming the file to be accessed for the basis functions. For example,

```
basis
  o  library 3-21g file /usr/d3g681/nwchem/library
  si library 3-21g file /usr/d3g681/nwchem/library
end
```

This directive tells the code to use the basis sets `3-21g` in the file `/usr/d3g681/nwchem/library` for atoms `o` and `si`, rather than look for them in the default library.

If standard basis sets are to be placed upon a dummy center, the variable `<tag_in_lib>` must also be entered on this line, to identify the correct atom type to use from the basis function library (see the ghost atom example in Section 5.7 and below). For example: To specify the cc-pvdz basis for a calculation on the water monomer in the dimer basis, where the dummy oxygen and dummy hydrogen centers have been identified as `bqo` and `bqh` respectively, the `BASIS` directive is as follows:

```
basis
  o   library cc-pvdz
  h   library cc-pvdz
  bqo library o cc-pvdz
  bqh library h cc-pvdz
end
```

The library basis sets can also be marked as relativistic by adding the `rel` keyword to the tag line. See Section 9.2 for more details. The correlation consistent basis sets have been contracted for relativistic effects and are included in the standard library.

There are also contractions in the standard library for both a point nucleus and a finite nucleus of Gaussian shape. These are usually distinguished by the suffixex `_pt` and `_fi`. It is the user's responsibility to ensure that the contraction matches the nuclear type specified in the geometry object. The specification of a finite nucleus basis set does NOT automagically set the nuclear type for that atom to be finite. See Section 6 for information.

7.2 Explicit basis set definition

If the basis sets in the library or available in other external files are not suitable for a given calculation, the basis set may be explicitly defined. A generally contracted Gaussian basis function is associated with a center using an input line of the following form:

```
  <string tag> <string shell_type> [rel]
     <real exponent> <real list_of_coefficients>
     ...
```

The variable `<shell_type>` identifies the angular momentum of the shell, s, p, d, ... NWChem is configured to handle up to i shells. The keyword `rel` marks the shell as relativistic — see Section 9.2 for more details. Subsequent lines define the primitive function exponents and contraction coefficients. General contractions are specified by including multiple columns of coefficients.

For example, the following `BASIS` directive augments the Dunning cc-pvdz basis set for the water molecule with a diffuse s-shell on oxygen:

```
basis spherical nosegment
  oxygen library cc-pvdz
  hydrogen library cc-pvdz
  oxygen s
    0.01 1.0
end
```

This is equivalent to the following explicit specification:

```
basis spherical nosegment
  oxygen s
    11720.0000    0.000710  -0.000160
     1759.0000    0.005470  -0.001263
      400.8000    0.027837  -0.006267
      113.7000    0.104800  -0.025716
       37.0300    0.283062  -0.070924
       13.2700    0.448719  -0.165411
        5.0250    0.270952  -0.116955
        1.0130    0.015458   0.557368
        0.3023   -0.002585   0.572759
  oxygen s
        0.3023    1.000000
  oxygen p
       17.7000    0.043018
        3.8540    0.228913
        1.0460    0.508728
        0.2753    0.460531
  oxygen p
        0.2753    1.000000
  oxygen d
        1.1850    1.000000
  hydrogen s
       13.0100    0.019685
        1.9620    0.137977
        0.4446    0.478148
        0.1220    0.501240
  hydrogen s
        0.1220    1.000000
  hydrogen p
```

```
        0.7270     1.000000
  oxygen s
        0.01       1.0
end
```

Chapter 8

Effective Core Potentials

Effective core potentials (ECPs) are a useful means of replacing the core electrons in a calculation with an effective potential, thereby eliminating the need for the core basis functions, which usually require a large set of Gaussians to describe them. In addition to replacing the core, they may be used to represent relativistic effects, which are largely confined to the core. In this context, both the scalar (spin-free) relativistic effects and spin-orbit (spin-dependent) relativistic effects may be included in effective potentials. NWChem has the facility to use both, and these are described in the next two sections.

A brief recapitulation of the development of RECPs is given here, following Pacios and Christiansen[1]. The process can be viewed as starting from an atomic Dirac-Hartree-Fock calculation, done in jj coupling, and producing relativistic effective potentials (REPs) for each l and j value, $U_{lj}^{\rm REP}$. From these, a local potential is extracted, which for example contains the Coulomb potential of the core electrons balanced by the part of the nuclear attraction which cancels the core electron charge. The residue is expressed in a semi-local form,

$$U^{\rm REP} = U_{LJ}^{\rm REP}(r) + \sum_{l=0}^{L-1} \sum_{j=|l-1/2}^{l+1/2} \left[U_{lj}^{\rm REP}(r) - U_{LJ}^{\rm REP}(r)\right] \sum_m |ljm\rangle\langle ljm| \tag{8.1}$$

where L is one larger than the maximum angular momentum in the atom. The scalar potential is obtained by averaging the REPs for each j for a given l to give an averaged relativistic effective potential, or AREP,

$$U_l^{\rm AREP}(r) = \frac{1}{2l+1}\left[lU_{l-1/2}^{\rm REP}(r) + (l+1)U_{l+1/2}^{\rm REP}(r)\right]. \tag{8.2}$$

These are summed into the full potential.

The spin-orbit potential is obtained from the difference between the REPs for the two j values for a given l, and may be represented in terms of an effective spin-orbit operator,

$$H^{\rm SO} = \mathbf{s}\cdot\sum_{l=1}^{L-1} \frac{2}{2l+1}\Delta U_l^{\rm REP} \sum_{mm'} |lm\rangle\langle lm|\hat{l}|lm'\rangle\langle lm'|. \tag{8.3}$$

where

$$\Delta U_l^{\rm REP} = U_{l+1/2}^{\rm REP}(r) - U_{l-1/2}^{\rm REP}(r). \tag{8.4}$$

[1] L. F. Pacios and P. A. Christiansen, J. Chem. Phys. **82**, 2664 (1985)

The spin-orbit integrals generated by NWChem are the integrals over the sum, including the factor of $2/(2l+1)$, so that they may be treated as an effective spin-orbit operator without further factors introduced.

The effective potentials, both scalar and spin-orbit, are fitted to Gaussians with the form

$$r^2 U_l(r) = \sum_k A_{lk} r^{n_{lk}} e^{-B_{lk} r^2}$$

where A_{lk} is the contraction coefficient, n_{lk} is the exponent of the "r" term (r-exponent), and B_{lk} is the Gaussian exponent. The n_{lk} is shifted by 2, in accordance with most of the ECP literature and implementations, i.e., an $n_{lk} = 0$ implies r^{-2}. The current implementation allows n_{lk} values of only 0, 1, or 2.

8.1 Scalar ECPs

The optional directive `ECP` allows the user to describe an effective core potential (ECP) in terms of contracted Gaussian functions as given above. Potentials using these functions must be specified explicitly by user input in the `ECP` directive. This directive has essentially the same form and properties as the standard `BASIS` directive, except for essential differences required for ECPs. Because of this, the ECP is treated internally as a basis set. The form of the input for the `ECP` directive is as follows:

```
ECP [<string name default "ecp basis">] \
      [print || noprint default print]

   <string tag> library [<string tag_in_lib>] \
                <string standard_set> [file <filename>]

   <string tag> [nelec] <integer number_of_electrons_replaced>

      ...

   <string tag> <string shell_type>
   <real r-exponent> <real Gaussian-exponent> <real list_of_coefficients>
      ...

END
```

ECPs are automatically segmented, even if general contractions are input. The projection operators defined in an ECP are spherical by default, so there is no need to include the `CARTESIAN` or `SPHERICAL` keyword as there is for a standard basis set. ECPs are associated with centers in geometries through tags or names of centers. These tags must match in the same manner as for basis sets the tags in a `GEOMETRY` and `ECP` directives, and are limited to sixteen (16) characters. Each center with the same tag will have the same ECP. By default, the input module prints each ECP that it encounters. The `NOPRINT` option can be used to disable printing. There can be only one active ECP, even though several may exist in the input deck. The ECP modules load "ecp basis" inputs along with any "ao basis" inputs present. ECPs may be used in both energy and gradient calculations.

ECPs are named in the same fashion as geometries or regular basis sets, with the default name being `"ecp basis"`. It should be clear from the above discussion on geometries and database entries how indirection is supported. All directives that are in common with the standard Gaussian basis set input have the same function and syntax.

As for regular basis sets, ECPs may be obtained from the standard library. The names of the sets of ECPs available in the standard library (their coverage is described in Appendix A) are

- "Hay-Wadt MB (n+1) ECP"
- "Hay-Wadt VDZ (n+1) ECP"
- "LANL2DZ ECP"
- "SBKJC VDZ ECP"
- "Stuttgart RLC ECP"
- "Stuttgart RSC ECP"
- "CRENBL ECP"
- "CRENBS ECP"

The keyword `nelec` allows the user to specify the number of core electrons replaced by the ECP. Additional input lines define the specific coefficients and exponents. The variable `<shell_type>` is used to specify the components of the ECP. The keyword `ul` entered for `<shell_type>` denotes the local part of the ECP. This is equivalent to the highest angular momentum functions specified in the literature for most ECPs. The standard entries (`s, p, d`, etc.) for `shell_type` specify the angular momentum projector onto the local function. The shell type label of `s` indicates the `ul-s` projector input, `p` indicates the `ul-p`, etc.

For example, the Christiansen, Ross and Ermler ARECPs are available in the standard basis set libary named `{crenbl_ecp}`. To perform a calculation on uranyl (UO_2^{2+}) with all-electron oxygen (aug-cc-pvdz basis), and uranium with an ARECP and using the corresponding basis the following input can be used

```
geometry
  U 0 0  0
  O 0 0  1.65
  O 0 0 -1.65
end
basis
  U library crenbl_ecp
  O library aug-cc-pvdz
end
ecp
  U library crenbl_ecp
end
```

The following is an example of explicit input of an ECP for H_2CO. It defines an ECP for the carbon and oxygen atoms in the molecule.

```
ecp
  C nelec 2 # ecp replaces 2 electrons on C
  C ul      # d
          1      80.0000000      -1.60000000
          1      30.0000000      -0.40000000
          2       0.5498205      -0.03990210
 C s        # s - d
```

```
          0        0.7374760         0.63810832
          0      135.2354832        11.00916230
          2        8.5605569        20.13797020
  C p       # p - d
          2       10.6863587        -3.24684280
          2       23.4979897         0.78505765
  O nelec 2 # ecp replaces 2 electrons on O
  O ul      # d
          1       80.0000000        -1.60000000
          1       30.0000000        -0.40000000
          2        1.0953760        -0.06623814
  O s       # s - d
          0        0.9212952         0.39552179
          0       28.6481971         2.51654843
          2        9.3033500        17.04478500
  O p       # p - s
          2       52.3427019        27.97790770
          2       30.7220233       -16.49630500
end
```

8.2 Spin-orbit ECPs

The Spin-orbit ECPs can be used with the Density Functional Approach, but one has to run the calculations without symmetry. Note: when a Hartree-Fock method is specified the spin-orbit input will be ignored.

Spin-orbit ECPs are fitted in precisely the same functional form as the scalar RECPs and have the same properties, with the exception that there is no local potential ul, no s potential and no effective charge has to be defined. Spin-orbit potentials are specified in the same way as ECPs except that the directive `SO` is used instead of `ECP`. Note that there currently are no spin-orbit ECPs defined in the standard NWChem library. The `SO` directive is as follows:

```
SO [<string name default "so basis">] \
      [print || noprint default print]

   <string tag> <string shell_type>
   <real r-exponent> <real Gaussian-exponent> <real list_of_coefficients>
      ...

END
```

Note: in the literature the coefficients of the spin-orbit potentials are NOT always defined in the same manner. The NWChem code assumes that the spin-orbit potential defined in the input is of the form:

$$\Delta U_l^{\mathrm{NWChem}} = \frac{2}{2l+1} \Delta U_l \tag{8.5}$$

For example, in the literature the Stuttgart potentials are defined as ΔU_l and, hence, have to be multiplied by $2/(2l+1)$. On the other hand, the CRENBL potentials in the published papers are defined as $\frac{l}{2l+1}\Delta U_l$ and, hence, have to be multiplied by $2/l$ (Warning: on the CRENBL website the spin-orbit potentials already have been corrected with the $2/l$ factor).

Chapter 9

Relativistic All-electron Approximations

All methods which include treatment of relativistic effects are ultimately based on the Dirac equation, which has a four component wave function. The solutions to the Dirac equation describe both positrons (the "negative energy" states) and electrons (the "positive energy" states), as well as both spin orientations, hence the four components. The wave function may be broken down into two-component functions traditionally known as the large and small components; these may further be broken down into the spin components.

The implementation of approximate all-electron relativistic methods in quantum chemical codes requires the removal of the negative energy states and the factoring out of the spin-free terms. Both of these may be achieved using a transformation of the Dirac Hamiltonian known in general as a Foldy-Wouthuysen transformation. Unfortunately this transformation cannot be represented in closed form for a general potential, and must be approximated. One popular approach is that originally formulated by Douglas and Kroll[1] and developed by Hess[2]. This approach decouples the positive and negative energy parts to second order in the external potential (and also fourth order in the fine structure constant, α). Another approach is based on a modification of the Dirac equation by Dyall[3], and involves an exact FW transformation on the atomic basis set level[4].

Since these approximations only modify the integrals, they can in principle be used at all levels of theory. At present the Douglas-Kroll implementation can be used at all levels of theory whereas Dyall's approach is currently available at the Hartree-Fock level. The derivatives have been implemented, allowing both methods to be used in geometry optimizations and frequency calculations.

The `RELATIVISTIC` directive provides input for the implemented relativistic approximations and is a compound directive that encloses additional directives specific to the approximations:

```
RELATIVISTIC
 [DOUGLAS-KROLL [<string (ON||OFF) default ON> \
              <string (FPP||DKH||DKFULL) default DKH>]  ||
  DYALL-MOD-DIRAC [ (ON || OFF) default ON ]
               [ (NESC1E || NESC2E) default NESC1E ] ]
 [CLIGHT <real clight default 137.0359895>]
```

[1] M. Douglas and N. M. Kroll, Ann. Phys. (N.Y.) **82**, 89 (1974)
[2] B.A. Hess, Phys. Rev. A **32**, 756 (1985); **33**, 3742 (1986)
[3] K. G. Dyall, J. Chem. Phys. **100**, 2118 (1994)
[4] K. G. Dyall, J. Chem. Phys. **106**, 9618 (1997); K. G. Dyall and T. Enevoldsen, J. Chem. Phys. **111**, 10000 (1999).

```
END
```

Only one of the methods may be chosen at a time. If both methods are found to be on in the input block, NWChem will stop and print an error message. There is one general option for both methods, the definition of the speed of light in atomic units:

```
CLIGHT <real clight default 137.0359895>
```

The following sections describe the optional sub-directives that can be specified within the `RELATIVISTIC` block.

9.1 Douglas-Kroll approximation

The (spin-free) one-electron Douglas-Kroll approximation has been implemented. The use of relativistic effects from this Douglas-Kroll approximation can be invoked by specifying:

```
DOUGLAS-KROLL [<string (ON||OFF) default ON> \
               <string (FPP||DKH||DKFULL) default DKH>]
```

The `ON|OFF` string is used to turn on or off the Douglas-Kroll approximation. By default, if the `DOUGLAS-KROLL` keyword is found, the approximation will be used in the calculation. If the user wishes to calculate a non-relativistic quantity after turning on Douglas-Kroll, the user will need to define a new `RELATIVISTIC` block and turn the approximation `OFF`. The user could also simply put a blank `RELATIVISTIC` block in the input file and all options will be turned off.

The `FPP` is the approximation based on free-particle projection operators[5] whereas the `DKH` and `DKFULL` approximations are based on external-field projection operators[6]. The latter two are considerably better approximations than the former. `DKH` is the Douglas-Kroll-Hess approach and is the approach that is generally implemented in quantum chemistry codes. `DKFULL` includes certain cross-product integral terms ignored in the `DKH` approach (see for example Häberlen and Rösch[7]).

The contracted basis sets used in the calculations should reflect the relativistic effects, i.e. one should use contracted basis sets which were generated using the Douglas-Kroll Hamiltonian. Basis sets that were contracted using the non-relativistic (Schödinger) Hamiltonian WILL PRODUCE ERRONEOUS RESULTS for elements beyond the first row. See appendix A for available basis sets and their naming convention.

NOTE: we suggest that spherical basis sets are used in the calculation. The use of high quality cartesian basis sets can lead to numerical inaccuracies.

In order to compute the integrals needed for the Douglas-Kroll approximation the implementation makes use of a fitting basis set (see literature given above for details). The current code will create this fitting basis set based on the given `"ao basis"` by simply uncontracting that basis. This again is what is commonly implemented in quantum chemistry codes that include the Douglas-Kroll method. Additional flexibility is available to the user by explicitly specifying a Douglas-Kroll fitting basis set. This basis set must be named `"D-K basis"` (see Chapter 7).

[5] B.A. Hess, Phys. Rev. A **32**, 756 (1985)
[6] B.A. Hess, Phys. Rev. A **33**, 3742 (1986)
[7] O.D. Häberlen, N. Rösch, Chem. Phys. Lett. **199**, 491 (1992)

9.2 Dyall's Modified Dirac Hamitonian approximation

The approximate methods described in this section are all based on Dyall's modified Dirac Hamiltonian. This Hamiltonian is entirely equivalent to the original Dirac Hamiltonian, and its solutions have the same properties. The modification is achieved by a transformation on the small component, extracting out $\sigma \cdot \mathbf{p}/2mc$. This gives the modified small component the same symmetry as the large component, and in fact it differs from the large component only at order α^2. The advantage of the modification is that the operators now resemble the operators of the Breit-Pauli Hamiltonian, and can be classified in a similar fashion into spin-free, spin-orbit and spin-spin terms. It is the spin-free terms which have been implemented in NWChem, with a number of further approximations.

The first is that the negative energy states are removed by a normalized elimination of the small component (NESC), which is equivalent to an exact Foldy-Wouthuysen (EFW) transformation. The number of components in the wave function is thereby effectively reduced from 4 to 2. NESC on its own does not provide any advantages, and in fact complicates things because the transformation is energy-dependent. The second approximation therefore performs the elimination on an atom-by-atom basis, which is equivalent to neglecting blocks which couple different atoms in the EFW transformation. The advantage of this approximation is that all the energy dependence can be included in the contraction coefficients of the basis set. The tests which have been done show that this approximation gives results well within chemical accuracy. The third approximation neglects the commutator of the EFW transformation with the two-electron Coulomb interaction, so that the only corrections that need to be made are in the one-electron integrals. This is the equivalent of the Douglas-Kroll(-Hess) approximation as it is usually applied.

The use of these approximations can be invoked with the use of the `DYALL-MOD-DIRAC` directive in the `RELATIVISTIC` directive block. The syntax is as follows.

```
DYALL-MOD-DIRAC [ (ON || OFF) default ON ]
                [ (NESC1E || NESC2E) default NESC1E ]
```

The `ON|OFF` string is used to turn on or off the Dyall's modified Dirac approximation. By default, if the `DYALL-MOD-DIRAC` keyword is found, the approximation will be used in the calculation. If the user wishes to calculate a non-relativistic quantity after turning on Dyall's modified Dirac, the user will need to define a new `RELATIVISTIC` block and turn the approximation `OFF`. The user could also simply put a blank `RELATIVISTIC` block in the input file and all options will be turned off.

Both one- and two-electron approximations are available `NESC1E || NESC2E`, and both have analytic gradients. The one-electron approximation is the default. The two-electron approximation specified by `NESC2E` has some sub options which are placed on the same logical line as the `DYALL-MOD-DIRAC` directive, with the following syntax:

```
NESC2E [ (SS1CENT [ (ON || OFF) default ON ] || SSALL) default SSALL ]
       [ (SSSS [ (ON || OFF) default ON ] || NOSSSS) default SSSS ]
```

The first sub-option gives the capability to limit the two-electron corrections to those in which the small components in any density must be on the same center. This reduces the $(LL|SS)$ contributions to at most three-center integrals and the $(SS|SS)$ contributions to two centers. For a case with only one relativistic atom this option is redundant. The second controls the inclusion of the $(SS|SS)$ integrals which are of order α^4. For light atoms they may safely be neglected, but for heavy atoms they should be included.

In addition to the selection of this keyword in the `RELATIVISTIC` directive block, it is necessary to supply basis sets in addition to the `ao basis`. For the one-electron approximation, three basis sets are needed: the atomic FW basis set, the large component basis set and the small component basis set. The atomic

FW basis set should be included in the `ao basis`. The large and small components should similarly be incorporated in basis sets named `large component` and `small component`, respectively. For the two-electron approximation, only two basis sets are needed. These are the large component and the small component. The large component should be included in the `ao basis` and the small component is specified separately as `small component`, as for the one-electron approximation. This means that the two approximations can *not* be run correctly without changing the `ao basis`, and it is up to the user to ensure that the basis sets are correctly specified.

There is one further requirement in the specification of the basis sets. In the `ao basis`, it is necessary to add the `rel` keyword either to the `basis` directive or the library tag line (See below for examples). The former marks the basis functions specified by the tag as relativistic, the latter marks the whole basis as relativistic. The marking is actually done at the unique shell level, so that it is possible not only to have relativistic and nonrelativistic atoms, it is also possible to have relativistic and nonrelativistic shells on a given atom. This would be useful, for example, for diffuse functions or for high angular momentum correlating functions, where the influence of relativity was small. The marking of shells as relativistic is necessary to set up a mapping between the ao basis and the large and/or small component basis sets. For the one-electron approximation the large and small component basis sets MUST be of the same size and construction, i.e. differing only in the contraction coefficients.

It should also be noted that the relativistic code will NOT work with basis sets that contain sp shells, nor will it work with ECPs. Both of these are tested and flagged as an error.

Some examples follow. The first example sets up the data for relativistic calculations on water with the one-electron approximation and the two-electron approximation, using the library basis sets.

```
start h2o-dmd

geometry units bohr
symmetry c2v
  O       0.000000000    0.000000000   -0.009000000
  H       1.515260000    0.000000000   -1.058900000
  H      -1.515260000    0.000000000   -1.058900000
end

basis "fw" rel
  oxygen library cc-pvdz_pt_sf_fw
  hydrogen library cc-pvdz_pt_sf_fw
end

basis "large"
  oxygen library cc-pvdz_pt_sf_lc
  hydrogen library cc-pvdz_pt_sf_lc
end

basis "large2" rel
  oxygen library cc-pvdz_pt_sf_lc
  hydrogen library cc-pvdz_pt_sf_lc
end

basis "small"
  oxygen library cc-pvdz_pt_sf_sc
  hydrogen library cc-pvdz_pt_sf_sc
```

```
end

set "ao basis" fw
set "large component" large
set "small component" small

relativistic
  dyall-mod-dirac
end

task scf

set "ao basis" large2
unset "large component"
set "small component" small

relativistic
  dyall-mod-dirac nesc2e
end

task scf
```

The second example has oxygen as a relativistic atom and hydrogen nonrelativistic.

```
start h2o-dmd2

geometry units bohr
symmetry c2v
  O       0.000000000    0.000000000   -0.009000000
  H       1.515260000    0.000000000   -1.058900000
  H      -1.515260000    0.000000000   -1.058900000
end

basis "ao basis"
  oxygen library cc-pvdz_pt_sf_fw rel
  hydrogen library cc-pvdz
end

basis "large component"
  oxygen library cc-pvdz_pt_sf_lc
end

basis "small component"
  oxygen library cc-pvdz_pt_sf_sc
end

relativistic
  dyall-mod-dirac
end

task scf
```

Chapter 10

Hartree-Fock or Self-consistent Field

The NWChem self-consistent field (SCF) module computes closed-shell restricted Hartree-Fock (RHF) wavefunctions, restricted high-spin open-shell Hartree-Fock (ROHF) wavefunctions, and spin-unrestricted Hartree-Fock (UHF) wavefunctions.

The `SCF` directive provides input to the SCF module and is a compound directive that encloses additional directives specific to the SCF module:

```
SCF
  ...
END
```

10.1 Wavefunction type

A spin-restricted, closed shell RHF calculation is performed by default. An error results if the number of electrons is inconsistent with this assumption. The number of electrons is inferred from the total charge on the system and the sum of the effective nuclear charges of all centers (atoms and dummy atoms, Section 6). The total charge on the system is zero by default, unless specified at some value by input on the `CHARGE` directive (Section 5).

The options available to define the SCF wavefunction and multiplicity are as follows:

```
SINGLET
DOUBLET
TRIPLET
QUARTET
QUINTET
SEXTET
SEPTET
OCTET
NOPEN <integer nopen default 0>
RHF
ROHF
UHF
```

The optional keywords SINGLET, DOUBLET, ..., OCTET and NOPEN allow the user to specify the number of singly occupied orbitals for a particular calculation. SINGLET is the default, and specifies a closed shell; DOUBLET specifies one singly occupied orbital; TRIPLET specifies two singly occupied orbitals; and so forth. If there are more than seven singly occupied orbitals, the keyword NOPEN must be used, with the integer nopen defining the number of singly occupied orbitals (sometimes referred to as open shells).

If the multiplicity is any value other than SINGLET, the default calculation will be a spin-restricted, high-spin, open-shell SCF calculation (keyword ROHF). The open-shell orbitals must be the highest occupied orbitals. If necessary, any starting vectors may be rearranged through the use of the SWAP keyword on the VECTORS directive (see Section 10.5) to accomplish this.

A spin-unrestricted solution can also be performed by specifying the keyword UHF. In UHF calculations, it is assumed that the number of singly occupied orbitals corresponds to the difference between the number of alpha-spin and beta-spin orbitals. For example, a UHF calculation with 2 more alpha-spin orbitals than beta-spin orbitals can be obtained by specifying

```
scf
   triplet ; uhf    # (Note: two logical lines of input)
   ...
end
```

The user should be aware that, by default, molecular orbitals are symmetry adapted in NWChem. This may not be desirable for fully unrestricted wavefunctions. In such cases, the user has the option of defeating the defaults by specifying the keywords ADAPT OFF (see Section 10.3) and SYM OFF (see Section 10.2).

The keywords RHF and ROHF are provided in the code for completeness. It may be necessary to specify these in order to modify the behavior of a previous calculation (see Section 3.2 for restart behavior).

10.2 SYM — use of symmetry

```
SYM <string (ON||OFF) default ON>
```

This directive enables/disables the use of symmetry to speed up Fock matrix construction (via the petite-list or skeleton algorithm) in the SCF, if symmetry was used in the specification of the geometry. Symmetry adaptation of the molecular orbitals is not affected by this option. The default is to use symmetry if it is specified in the geometry directive (Section 6).

For example, to disable use of symmetry in Fock matrix construction:

```
sym off
```

10.3 ADAPT – symmetry adaptation of MOs

```
ADAPT <string (ON||OFF) default ON>
```

The default in the SCF module calculation is to force symmetry adaption of the molecular orbitals. This does not affect the speed of the calculation, but without explicit adaption the resulting orbitals may be symmetry contaminated for some problems. This is especially likely if the calculation is started using orbitals from a distorted geometry.

The underlying assumption in the use of symmetry in Fock matrix construction is that the density is totally symmetric. If the orbitals are symmetry contaminated, this assumption may not be valid — which could result in incorrect energies and poor convergence of the calculation. It is thus advisable when specifying `ADAPT OFF` to also specify `SYM OFF` (Section 10.2).

10.4 TOL2E — integral screening threshold

```
TOL2E <real tol2e default min(10^-7 , 0.01*$thresh$)>
```

The variable `tol2e` is used in determining the integral screening threshold for the evaluation of the energy and related Fock-like matrices. The Schwarz inequality is used to screen the product of integrals and density matrices in a manner that results in an accuracy in the energy and Fock matrices that approximates the value specified for `tol2e`.

It is generally not necessary to set this parameter directly. Specify instead the required precision in the wavefunction, using the `THRESH` directive (Section 10.7). The default threshold is the minimum of 10^{-7} and 0.01 times the requested convergence threshold for the SCF calculation (Section 10.7).

The input to specify the threshold explicitly within the `SCF` directive is, for example:

```
tol2e 1e-9
```

For very diffuse basis sets, or for high-accuracy calculations it might be necessary to set this parameter. A value of 10^{-12} is sufficient for nearly all such purposes.

10.5 VECTORS — input/output of MO vectors

```
VECTORS [[input] (<string input_movecs default atomic>) || \
                 (project <string basisname> <string filename>) || \
                 (fragment <string file1> [<string file2> ...])] \
        [swap [alpha||beta] <integer vec1 vec2> ...] \
        [output <string output_filename default input_movecs>] \
        [lock]
```

The `VECTORS` directive allows the user to specify the source and destination of the molecular orbital vectors. In a startup calculation (see Section 5.1), the default source for guess vectors is a diagonalized Fock matrix constructed from a superposition of the atomic density matrices for the particular problem. This is usually a very good guess. For a restarted calculation, the default is to use the previous MO vectors.

The optional keyword `INPUT` allows the user to specify the source of the input molecular orbital vectors as any of the following:

- `ATOMIC` — eigenvectors of a Fock-like matrix formed from a superposition of the atomic densities (the default guess). See Sections 10.5.2 and 10.6.
- `HCORE` — eigenvectors of the bare-nucleus Hamiltonian or the one-electron Hamiltonian.

- `filename` — the name of a file containing the MO vectors from a previous calculation. Note that unless the path is fully qualified, or begins with a dot ("."), then it is assumed to reside in the directory for permanent files (see Section 5.2).
- `PROJECT basisname filename` — projects the existing MO vectors in the file `filename` from the smaller basis with name `basisname` into the current basis. The definition of the basis `basisname` must be available in the current database, and the basis must be smaller than the current basis. In addition, the geometry used for the previous calculations must have the atoms in the same order and in the same orientation as the current geometry.
- `FRAGMENT file1 ...` — assembles starting MO vectors from previously performed calculations on fragments of the system and is described in more detail in Section 10.5.1. Even though there are some significant restrictions in the use of the initial implementation of this method (see Section 10.5.1), this is the most powerful initial guess option within the code. It is particularly indispensible for open shell metallic systems.

The molecular orbitals are saved every iteration if more than 600 seconds have elapsed, and also at the end of the calculation. At completion (converged or not), the SCF module always canonically transforms the molecular orbitals by *separately* diagonalizing the closed–closed, open–open, and virtual–virtual blocks of the Fock matrix.

The name of the file used to store the MO vectors is determined as follows:

- if the `OUTPUT` keyword was specified on the `VECTORS` directive, then the filename that follows this keyword is used, or
- if the input vectors were read from a file, this file is reused for the output vectors (overwriting the input vectors); else,
- a default file name is generated in the directory for permanent files (Section 5.2) by prepending `".movecs"` with the file prefix, i.e., "<file_prefix>.movecs".

The name of this file is stored in the database so that a subsequent SCF calculation will automatically restart from these MO vectors.

Applications of this directive are illustrated in the following examples.

Example 1:

```
vectors output h2o.movecs
```

Assuming a start-up calculation, this directive will result in use of the default atomic density guess, and will output the vectors to the file `h2o.movecs`.

Example 2:

```
vectors input initial.movecs output final.movecs
```

This directive will result in the initial vectors being read from the file `"initial.movecs"`. The results will be written to the file `final.movecs`. The contents of `"initial.movecs"` will not be changed.

Example 3:

```
vectors input project "small basis" small.movecs
```

This directive will cause the calculation to start from vectors in the file `"small.movecs"` which are in a basis named `"small basis"`. The output vectors will be written to the default file `"<file_prefix.movecs>"`.

Once starting vectors have been obtained using any of the possible options, they may be reordered through use of the `SWAP` keyword. This optional keyword requires a list of orbital pairs that will be swapped. For UHF calculations, separate `SWAP` keywords may be provided for the alpha and beta orbitals, as necessary.

An example of use of the `SWAP` directive:

```
vectors input try1.movecs swap 173 175 174 176 output try2.movecs
```

This directive will cause the initial orbitals to be read from the file `"try1.movecs"`. The vectors for the orbitals within the pairs 173–175 will be swapped with those within 174–176, so the resulting order is 175, 176, 173, 174. The final orbitals obtained in the calculation will be written to the file `"try2.movecs"`.

The swapping of orbitals occurs as a sequential process in the order (left to right) input by the user. Thus, regarding each pair as an elementary transposition it is possible to construct arbitrary permutations of the orbitals. For instance, to apply the permutation (6789)[1] we note that this permutation is equal to (67)(78)(89), and thus may be specified as

```
vectors swap 8 9  7 8  6 7
```

Another example, now illustrating this feature for a UHF calculation, is the directive

```
vectors swap beta 4 5 swap alpha 5 6
```

This input will result in the swapping of the 5–6 alpha orbital pair and the 4–5 beta orbital pair. (All other items in the input use the default values.)

The `LOCK` keyword allows the user to specify that the ordering of orbitals will be locked to that of the initial vectors, insofar as possible. The default is to order by ascending orbital energies within each orbital space. One application where locking might be desirable is a calculation where it is necessary to preserve the ordering of a previous geometry, despite flipping of the orbital energies. For such a case, the `LOCK` directive can be used to prevent the SCF calculation from changing the ordering, even if the orbital energies change.

10.5.1 Superposition of fragment molecular orbitals

The fragment initial guess is particularly useful in the following instances:

- The system naturally decomposes into molecules that can be treated individually, e.g., a cluster.
- One or more fragments are particularly hard to converge and therefore much time can be saved by converging them independently.
- A fragment (e.g., a metal atom) must be prepared with a specific occupation. This can often be readily accomplished with a calculation on the fragment using dummy charges to model a ligand field.
- The molecular occupation predicted by the atomic initial guess is often wrong for systems with heavy metals which may have partially occupied orbitals with lower energy than some doubly occupied orbitals. The fragment initial guess avoids this problem.

[1] The cyclic permutation (6789) maps the ordered list `6 7 8 9` into `9 6 7 8`.

```
VECTORS [input] fragment <string file1> [<string file2> ...]
```

The molecular orbitals are formed by superimposing the previously generated orbitals of fragments of the molecule being studied. These fragment molecular orbitals must be in the same basis as the current calculation. The input specifies the files containing the fragment molecular orbitals. For instance, in a calculation on the water dimer, one might specify

```
vectors fragment h2o1.movecs h2o2.movecs
```

where `h2o1.movecs` contains the orbitals for the first fragment, and `h2o2.movecs` contains the orbitals for the second fragment.

A complete example of the input for a calculation on the water dimer using the fragment guess is as follows:

```
start dimer

title "Water dimer SCF using fragment initial guess"

geometry dimer
  O   -0.595   1.165  -0.048
  H    0.110   1.812  -0.170
  H   -1.452   1.598  -0.154
  O    0.724  -1.284   0.034
  H    0.175  -2.013   0.348
  H    0.177  -0.480   0.010
end

geometry h2o1
  O   -0.595   1.165  -0.048
  H    0.110   1.812  -0.170
  H   -1.452   1.598  -0.154
end

geometry h2o2
  O    0.724  -1.284   0.034
  H    0.175  -2.013   0.348
  H    0.177  -0.480   0.010
end

basis
  o library 3-21g
  h library 3-21g
end

set geometry h2o1
scf; vectors input atomic output h2o1.movecs; end
task scf

set geometry h2o2
scf; vectors input atomic output h2o2.movecs; end
```

```
task scf

set geometry dimer
scf
vectors input fragment h2o1.movecs h2o2.movecs \
        output dimer.movecs
end
task scf
```

First, the geometry of the dimer and the two monomers are specified and given names. Then, after the basis specification, calculations are performed on the fragments by setting the geometry to the appropriate fragment (Section 5.7) and redirecting the output molecular orbitals to an appropriately named file. Note also that use of the atomic initial guess is forced, since the default initial guess is to use any existing MOs which would not be appropriate for the second fragment calculation. Finally, the dimer calculation is performed by specifying the dimer geometry, indicating use of the fragment guess, and redirecting the output MOs.

The following points are important in using the fragment initial guess:

1. The fragment calculations must be in the same basis set as the full calculation.
2. The order of atoms in the fragments and the order in which the fragment files are specified must be such that when the fragment basis sets are concatentated all the basis functions are in the same order as in the full system. This is readily accomplished by first generating the full geometry with atoms for each fragment contiguous, splitting this into numbered fragments and specifying the fragment MO files in the correct order on the `VECTORS` directive.
3. The occupation of orbitals is preserved when they are merged from the fragments to the full molecule and the resulting occupation must match the requested occupation for the full molecule. E.g., a triplet ROHF calculation must be comprised of fragments that have a total of exactly two open-shell orbtials.
4. Because of these restrictions, it is not possible to introduce additional atoms (or basis functions) into fragments for the purpose of cleanly breaking real bonds. However, it is possible, and highly recommended, to introduce additional point charges to simulate the presence of other fragments.
5. MO vectors of partially occupied or strongly polarized systems are very sensitive to orientation. While it is possible to specify the same fragment MO vector file multiple times in the `VECTORS` directive, it is usually much better to do a separate calculation for each fragment.

A more involved example is now presented. We wish to model the sextet state of Fe(III) complexed with water, imidazole and a heme with a net unit positive charge. The default atomic guess does not give the correct d^5 occupation for the metal and also gives an incorrect state for the double anion of the heme. The following performs calculations on all of the fragments. Things to note are:

1. The use of a dummy +2 charge in the initial guess on the heme which in part simulates the presence of the metal ion, and also automatically forces an additional two electrons to be added to the system (the default net charge being zero).
2. The iron fragment calculation (charge +3, d^5, sextet) will yield the correct open-shell occupation for the full system. If, instead, the d-orbitals were partially occupied (e.g., the doublet state) it would be useful to introduce dummy charges around the iron to model the ligand field and thereby lift the degeneracy to obtain the correct occupation.
3. C_s symmetry is used for all of the calculations. It is not necessary that the same symmetry be used in all of the calculations, provided that the order and orientation of the atoms is preserved.

4. The `unset scf:*` directive is used immediately before the calculation on the full system so that the default name for the output MO vector file can be used, rather than having to specify it explicitly.

```
start heme6a1
title  "heme-H2O (6A1) from M.Dupuis"

#############################################################
# Define the geometry of the full system and the fragments #
#############################################################

geometry full-system
   symmetry cs

   H     0.438   -0.002    4.549
   C     0.443   -0.001    3.457
   C     0.451   -1.251    2.828
   C     0.452    1.250    2.828
   H     0.455    2.652    4.586
   H     0.461   -2.649    4.586
   N1    0.455   -1.461    1.441
   N1    0.458    1.458    1.443
   C     0.460    2.530    3.505
   C     0.462   -2.530    3.506
   C     0.478    2.844    1.249
   C     0.478    3.510    2.534
   C     0.478   -2.848    1.248
   C     0.480   -3.513    2.536
   C     0.484    3.480    0.000
   C     0.485   -3.484    0.000
   H     0.489    4.590    2.664
   H     0.496   -4.592    2.669

   H     0.498    4.573    0.000
   H     0.503   -4.577    0.000
   H    -4.925    1.235    0.000
   H    -4.729   -1.338    0.000
   C    -3.987    0.685    0.000
   N    -3.930   -0.703    0.000
   C    -2.678    1.111    0.000
   C    -2.622   -1.076    0.000
   H    -2.284    2.126    0.000
   H    -2.277   -2.108    0.000
   N    -1.838    0.007    0.000

   Fe    0.307    0.000    0.000

   O     2.673   -0.009    0.000
   H     3.238   -0.804    0.000
   H     3.254    0.777    0.000
end
```

```
geometry ring-only
   symmetry cs
   H     0.438   -0.002    4.549
   C     0.443   -0.001    3.457
   C     0.451   -1.251    2.828
   C     0.452    1.250    2.828
   H     0.455    2.652    4.586
   H     0.461   -2.649    4.586
   N1    0.455   -1.461    1.441
   N1    0.458    1.458    1.443
   C     0.460    2.530    3.505
   C     0.462   -2.530    3.506
   C     0.478    2.844    1.249
   C     0.478    3.510    2.534
   C     0.478   -2.848    1.248
   C     0.480   -3.513    2.536
   C     0.484    3.480    0.000
   C     0.485   -3.484    0.000
   H     0.489    4.590    2.664
   H     0.496   -4.592    2.669

   Bq    0.307    0.0       0.0    charge 2  # simulate the iron
end

geometry imid-only
   symmetry cs
   H     0.498    4.573    0.000
   H     0.503   -4.577    0.000
   H    -4.925    1.235    0.000
   H    -4.729   -1.338    0.000
   C    -3.987    0.685    0.000
   N    -3.930   -0.703    0.000
   C    -2.678    1.111    0.000
   C    -2.622   -1.076    0.000
   H    -2.284    2.126    0.000
   H    -2.277   -2.108    0.000
   N    -1.838    0.007    0.000
end

geometry fe-only
   symmetry cs
   Fe    .307    0.000    0.000
end

geometry water-only
   symmetry cs
   O     2.673   -0.009    0.000
   H     3.238   -0.804    0.000
   H     3.254    0.777    0.000
end
```

```
############################
# Basis set for everything #
############################

basis nosegment
  O  library 6-31g*
  N  library 6-31g*
  C  library 6-31g*
  H  library 6-31g*
 Fe  library "Ahlrichs pVDZ"
end

##########################################################
# SCF on the fragments for initial guess for full system #
##########################################################

scf; thresh 1e-2; end

set geometry ring-only
scf; vectors atomic swap 80 81 output ring.mo; end
task scf

set geometry water-only
scf; vectors atomic output water.mo; end
task scf

set geometry imid-only
scf; vectors atomic output imid.mo; end
task scf

charge 3
set geometry fe-only
scf; sextet; vectors atomic output fe.mo; end
task scf

##########################
# SCF on the full system #
##########################

unset scf:*     # This restores the defaults

charge 1

set geometry full-system

scf
 sextet
 vectors fragment ring.mo imid.mo fe.mo water.mo
 maxiter 50
end
```

```
task scf
```

10.5.2 Atomic guess orbitals with charged atoms

As noted above, the default guess vectors are based on superimposing the density matrices of the neutral atoms. If some atoms are significantly charged, this default guess may be improved upon by modifying the atomic densities. This is done by setting parameters that add fractional charges to the occupation of the valence atomic orbitals. Since the atomic SCF program does not have its own input block, the `SET` directive (Section 5.7) must be used to set these parameters.

The input specifies a list of tags (i.e., names of atoms in a geometry, see Section 6) and the charges to be added to those centers. Two parameters must be set as follows:

```
set atomscf:tags_z <string list_of_tags>
set atomscf:z      <real list_of_charges>
```

The array of strings `atomscf:tags_z` should be set to the list of tags, and the array `atomscf:z` should be set to the list of charges which must be real numbers (not integers). All atoms that have a tag specified in the list of tags will be assigned the corresponding charge from the list of charges.

For example, the following specifies that all oxygen atoms with tag `O` be assigned a charge of `-1` and all iron atoms with tag `Fe` be assigned a charge of `+2`

```
set atomscf:z        -1  2.0
set atomscf:tags_z    O  Fe
```

There are some limitations to this feature. It is not possible to add electrons to closed shell atoms, nor is it possible to remove all electrons from a given atom. Attempts to do so will cause the code to report an error, and it will not report further errors in the input for modifying the charge even when they are detected.

Finally, recall that the database is persistent (Section 3.2) and that the modified settings will be used in subsequent atomic guess calculations unless the data is deleted from the database with the `UNSET` directive (Section 5.8).

10.6 Accuracy of initial guess

For SCF, the initial Fock-matrix construction from the atomic guess is now (staring from version 3.3) performed to a default precision of 1e-7. However, other wavefunctions, notably DFT, use a lower precision. In charged, or diffuse basis sets, this precision may not be sufficient and could result in incorrect ordering of the initial orbitals. The accuracy may be increased with the following directive which should be inserted in the top-level of input (i.e., outside of the SCF input block) and before the `TASK` directive.

```
set tolguess 1e-7
```

10.7 THRESH — convergence threshold

```
THRESH  <real thresh default 1.0e-4>
```

This directive specifies the convergence threshold for the calculation. The convergence threshold is the norm of the orbital gradient, and has a default value in the code of 10^{-4}.

The norm of the orbital gradient corresponds roughly to the precision available in the wavefunction, and the energy should be converged to approximately the square of this number. It should be noted, however, that the precision in the energy will not exceed that of the integral screening tolerance. This tolerance (Section 10.4) is automatically set from the convergence threshold, so that sufficient precision is usually available by default.

The default convergence threshold suffices for most SCF energy and geometry optimization calculations, providing about 6–8 decimal places in the energy, and about four significant figures in the density and energy derivative with respect to nuclear coordinates. However, greater precision may be required for calculations involving weakly interacting systems, floppy molecules, finite-difference of gradients to compute the Hessian, and for post-Hartree-Fock calculations. A threshold of 10^{-6} is adequate for most such purposes, and a threshold of 10^{-8} might be necessary for very high accuracy or very weak interactions. A threshold of 10^{-10} should be regarded as the best that can be attained in most circumstances.

10.8 MAXITER — iteration limit

```
MAXITER <integer maxiter default 8>
```

The maximum number of iterations for the SCF calculation defaults to 20 for both ROHF/RHF and UHF calculations. For most molecules, this number of iterations is more than sufficient for the quadratically convergent SCF algorithm to obtain a solution converged to the default threshold (see Section 10.7 above). If the SCF program detects that the quadratically convergent algorithm is not efficient, then it will resort to a linearly convergent algorithm and increase the maximum number of iterations by 10.

Convergence may not be reached in the maximum number of iterations for many reasons, including input error (e.g., an incorrect geometry or a linearly dependent basis), a very low convergence threshold, a poor initial guess, or the fact that the system is intrinsically hard to converge due to the presence of many states with similar energies.

The following sets the maximum number of SCF iterations to 50:

```
maxiter 50
```

10.9 RI-SCF — resolution of the identity approximation

The resolution of the identity (RI) approximation (using the V-approximation of Almlöf and Vahtras) is automatically invoked if a basis set named `"riscf basis"` is present in the database. This basis will be used as the fitting basis. The RISCF method provides the most computational speedup with the least loss of accuracy when applied to relatively small molecules in large basis sets. Calculations on large molecules in modest basis sets will not realize a significant performance gain from RISCF.

The full RISCF approximation will be applied by default, and the `RI-SCF` directive serves to modify the extent of the approximation and the computational strategy.

```
 RI-SCF [<string (hessian || preconverge || full) default full>] \
        [<string (disk || memory || auto) default auto>]
```

The first three parameters determine the extent of the approximation:

- `FULL` — is the default and specifies that the RI approximation will be used for all Fock builds in the calculation. This is the fastest of the three options (perhaps 3–10 times faster than direct SCF), but will result in only an approximate value for the energy.
- `HESSIAN` — only the orbital Hessian will be calculated with an approximated Fock matrix. This will yield an exact energy and wavefunction and, using the quadratically convergent SCF algorithm, should result in a 1.5–2-fold speedup over direct SCF.
- `PRECONVERGE` — specifies a two-part calculation. First, the SCF calculation is performed with the full RI approximation. Then an "exact" direct SCF calculation is performed, using the RI approximated Hessian (the same as the `HESSIAN` option above). An exact energy and wavefunction will be obtained.

The next three parameters determine the computational strategy:

- `AUTO` — This is the default option, and allows the code to make its own decision on where to store the 3-center integrals. If there is enough memory available, it will use the in-core (memory) option; otherwise, the disk-based algorithm will be used, if available.
- `MEMORY` — This forces storage of the 3-center integrals in memory. If insufficient memory is available, an error results.
- `DISK` — If the "Disk Resident Array" library is implemented in the local installation of NWChem, the keyword `DISK` can be used to specify that the 3-center integrals will be stored on disk. Otherwise, an error results.

10.10 PROFILE — performance profile

This directive allows the user to obtain timing and parallel execution information about the SCF module. It is specified by the simple keyword

```
PROFILE
```

This option can be helpful in understanding the computational performance of an SCF calculation. However, it can introduce a significant overhead on machines that have expensive timing routines, such as the SUN.

10.11 DIIS — DIIS convergence

This directive allows the user to specify DIIS convergence rather than second-order convergence for the SCF calculation. The form of the directive is as follows:

```
DIIS
```

The implementation of this option is currently fairly rudimentary. It does not have level-shifting and damping, and does not support open shells or UHF. It is provided on an "as is" basis, and should be used with caution.

When the `DIIS` directive is specified in the input, the user has the additional option of specifying the size of the subspace for the DIIS extrapolation. This is accomplished with the `DIISBAS` directive, which is of the form:

```
DIISBAS <integer diisbas default 5>
```

The default of 5 should be adequate for most applications, but may be increased if convergence is poor. On large systems, it may be necessary to specify a lower value for `diisbas`, to conserve memory.

10.12 DIRECT and SEMIDIRECT — recomputation of integrals

In the context of SCF calculations direct means that all integrals are recomputed as required and none are stored. The other extreme are disk- or memory-resident (sometimes termed conventional) calculations in which all integrals are computed once and stored. Semi-direct calculations are between these two extremes with some integrals being precomputed and stored, and all other integrals being recomputed as necessary.

The default behavior of the SCF module is

- If enough memory is available, the integrals are computed once and are cached in memory.
- If there is not enough memory to store all the integrals at once, then 95% of the available disk space in the scratch directory (see Section 5.2) is assumed to be available for this purpose, and as many integrals as possible are cached on disk (with no memory being used for caching). Some attempt is made to store the most expensive integrals in the cache.
- If there is not enough room in memory or on disk for all the integrals, then the ones that are not cached are recomputed in a semidirect fashion.

The integral file is deleted at the end of a calculation, so it is not possible to restart a semidirect calculation when the integrals are cached in memory or on disk. Many computer systems (e.g., the EMSL IBM SP) clear the fast scratch space at the end of each job, adding a further complication to the problem of restarting a *parallel* semidirect calculation.

On the IBM SP or any other computer with fast disks local to each processor, semidirect calculation offers the best behavior. It can result in *quadratic speedup* as more processors are added.

A fully direct calculation (with recomputation of the integrals at each iteration) is forced by specifying the directive

```
DIRECT
```

Alternatively, the `SEMIDIRECT` directive can be used to control the default semidirect calculation by defining the amount of disk space and the cache memory size. The form of this directive is as follows:

```
SEMIDIRECT [filesize <integer filesize default disksize>]
           [memsize  <integer memsize default available>]
           [filename <string filename default $file_prefix.aoints$>]
```

The keyword `FILESIZE` allows the user to specify the amount of disk space to be used per process for storing the integrals in 64-bit words. Similarly, the keyword `MEMSIZE` allows the user to specify the number of 64-bit words to be used per process for caching integrals in memory. (Note: If the amount of storage space specified by the entry for `memsize` is not available, the code cuts the value in half and checks again for available space. This process is repeated until the request is satisfied.)

By default, the integral files are placed into the scratch directory (see Section 5.2). Specifying the keyword `FILENAME` overrides this default. The user-specified name entered in the string `filename` has the process number appended to it, so that each process has a distinct file but with a common base-name and directory. Therefore, it is not possible to use this keyword to specify different disks for different processes. The `SCRATCH_DIR` directive (see Section 5.2) can be used for this purpose.

For example, to force full recomputation of all integrals:

```
direct
```

Exactly the same result could be obtained by entering the directive:

```
semidirect filesize 0 memsize 0
```

To disable the use of memory for caching integrals and limit disk usage by each process to 100 megawords (MW):

```
semidirect memsize 0 filesize 100000000
```

The integral records are typically 32769 words long and any non-zero value for `filesize` or `memsize` should be enough to hold at least one record.

10.12.1 Integral File Size and Format for the SCF Module

The file format is rather complex, since it accommodates a variety of packing and compression options and the distribution of data. This section presents some information that may help the user understand the output, and illustrates how to use the output information to estimate file sizes.

If integrals are stored with a threshold of greater than 10^{-10}, then the integrals are stored in a 32-bit fixed-point format (with appropriate treatment for large values to retain precision). If integrals are stored with a threshold less than 10^{-10}, however, the values are stored in 64-bit floating-point format. If a replicated-data calculation is being run, then 8 bits are used for each basis function label, unless there are more than 256 functions, in which case 16 bits are used. If distributed data is being used, then the labels are always packed to 8 bits (the distributed blocks always being less than 256; labels are relative to the start of the block).

Thus, the number (W) of 64-bit words required to store N integrals, may be computed as

$$W = \begin{cases} N \text{ , 8-bit labels and 32-bit values} \\ \frac{3}{2}N \text{ , 16-bit labels and 32-bit values} \\ \frac{3}{2}N \text{ , 8-bit labels and 64-bit values} \\ 2N \text{ , 16-bit labels and 64-bit values} \end{cases}$$

The actual number of words required can exceed this computed value by up to one percent, due to bookkeeping overhead, and because the file itself is organized into fixed-size records.

With at least the default print level, all semidirect (not direct) calculations will print out information about the integral file and the number of integrals computed. The form of this output is as follows:

```
 Integral file          = ./c6h6.aoints.0
 Record size in doubles =  32769        No. of integs per rec  =  32768
 Max. records in memory =      3        Max. records in file   =      5
 No. of bits per label  =      8        No. of bits per value  =     32

 #quartets = 2.0D+04  #integrals = 7.9D+05  direct = 63.6%  cached = 36.4%
```

The file information above relates only to process 0. The line of information about the number of quartets, integrals, etc., is a sum over all processes.

When the integral file is closed, additional information of the following form is printed:

```
------------------------------------------------------------
EAF file 0: "./c6h6.aoints.0" size=262152 bytes
------------------------------------------------------------
               write      read    awrite     aread      wait
               -----      ----    ------     -----      ----
     calls:        6        12         0         0         0
   data(b): 1.57e+06  3.15e+06  0.00e+00  0.00e+00
   time(s): 1.09e-01  3.12e-02                      0.00e+00
rate(mb/s): 1.44e+01  1.01e+02
------------------------------------------------------------

 Parallel integral file used       4 records with       0 large values
```

Again, the detailed file information relates just to process 0, but the final line indicates the total number of integral records stored by all processes.

This information may be used to optimize subsequent calculations, for instance by assigning more memory or disk space.

10.13 SCF Convergence Control Options

Note to users: It is desired that the SCF program converge reliably with the default options for a wide variety of molecules. In addition, it should be guaranteed to converge for any system, with sufficient iterations. Please report significant convergence problems to `nwchem-support@emsl.pnl.gov`, and include the input file.

The SCF program uses a preconditioned conjugate gradient (PCG) method that is unconditionally convergent. Basically, a search direction is generated by multiplying the orbital gradient (the derivative of the energy with respect to the orbital rotations) by an approximation to the inverse of the level-shifted orbital Hessian. In the initial iterations (see Section 10.14), an inexpensive one-electron approximation to the inverse orbital Hessian is used. Closer to convergence, the full orbital Hessian is used, which should provide quadratic convergence. For both the full or one-electron orbital Hessians, the inverse-Hessian matrix-vector product is formed iteratively. Subsequently, an approximate line search is performed along the new search direction. If the exact Hessian is being employed, then the line search should require a single step (of unity). Preconditioning with approximate Hessians may require additional steps, especially in the initial iterations. It is the (approximate) line search that provides the convergence guarantee. The iterations required to solve the linear equations are referred to as micro-iterations. A macro-iteration comprises both the iterative solution and a line search.

Level-shifting plays the same role in this algorithm as it does in the conventional iterative solution of the SCF equations. The approximate Hessian used for preconditioning should be positive definite. If this is not the case, then level-shifting by a positive constant (Δ) serves to make the preconditioning matrix positive definite, by adding Δ to all of its eigenvalues. The level-shifts employed for the RHF orbital Hessian should be approximately four times (only twice for UHF) the value that one would employ in a conventional SCF[2]. Level-shifting is automatically enabled in the early iterations, and the default options suffice for most test cases.

So why do things go wrong and what can be done to fix convergence problems? Most problems encountered so far arise either poor initial guesses or from small or negative eigenvalues of the orbital Hessian. The atomic orbital guess is usually very good. However, in calculations on charged systems, especially with open shells, incorrect initial occupations may result. The SCF might then converge very slowly since very large orbital rotations might be required to achieve the correct occupation or move charge large distances in the molecule. Possible actions are

- Modify the atomic guess by assigning charges to the atoms known to carry substantial charges (Section 10.5.2)
- Examining an analysis of the initial orbitals (Section 10.17) and then swapping them to attain the desired occupation (Section 10.5).
- Converging the calculation in a minimial basis set, which is usually easier, and then projecting into a larger basis set (Section 10.5).
- Using the fragment orbital initial guess (Section 10.5.1).

Small or negative Hessian eigenvalues can occur even though the calculation seem to be close to convergence (as measured by the gradient norm, or the off-diagonal Fock matrix elements). Small eigenvalues will cause the iterative linear equation solver to converge slowly, resulting in an excessive number of micro-iterations. This makes the SCF expensive in terms of computation time, and it is possible to exceed the maximum number of iterations without achieving the accuracy required for quadratic convergence — which causes more macro-iterations to be performed.

Two main options are available when a problem will not converge: Newton-Raphson can be disabled temporarily or permanently (see Section 10.14), and level-shifting can be applied to the matrix (see Section 10.15). In some cases, both options may be necessary to achieve final convergence.

If there is reason to suspect a negative eigenvalue, the first course is to disable the Newton-Raphson iteration until the solution is closer to convergence. It may be necessary to disable it completely. At some point close to convergence, the Hessian will be positive definite, so disabling Newton-Raphson should yield a solution with approximately the same convergence rate as DIIS.

If temporarily disabling Newton-Raphson is not sufficient to achieve convergence, it may be necessary to disable it entirely and apply a small level-shift to the approximate Hessian. This should improve the convergence rate of the micro-iterations and stabilize the macro-iterations. The level-shifting will destroy exact quadratic convergence, but the optimization process is automatically adjusted to reflect this by enforcing conjugacy and reducing the accuracy to which the linear equations are solved. The net result of this is that the solution will do more macro-iterations, but each one should take less time than it would with the unshifted Hessian.

The following sections describe the directives needed to disable the Newton-Raphson iteration and specify level-shifting.

[2] This can be seen by considering a one-electron approximation to the closed-shell RHF Hessian in canonical orbitals, $A_{ia,jb} = 4\delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i)$. Similarly, the level shift should be twice as large for UHF.

10.14 NR — controlling the Newton-Raphson

```
NR <real nr_switch default 0.1>
```

The exact orbital Hessian is adopted as the preconditioner when the maximum element of the orbital gradient is below the value specified for `nr_switch`. The default value is 0.1, which means that Newton-Raphson will be disabled until the maximum value of the orbital gradient (twice the largest off-diagonal Fock matrix element) is less than 0.1. To disable the Newton-Raphson entirely, the value of `nr_switch` must be set to zero. The directive to accomplish this is as follows:

```
nr 0
```

10.15 LEVEL — level-shifting the orbital Hessian

This directive allows the user to specify level-shifting to obtain a positive-definite preconditioning matrix for the SCF solution procedure. Separate level shifts can be set for the first-order convergent one-electron approximation to the Hessian used with the preconditioned conjugate gradient (PCG) method, and for the full Hessian used with the Newton-Raphson (NR) approach. It is also possible to change the level-shift automatically as the solution attains some specified accuracy. The form of the directive is as follows:

```
LEVEL [pcg <real initial default 20.0> \
        [<real tol default 0.5> <real final default 0.0>]] \
      [nr <real initial default 0.0> \
        [<real tol default 0.0> <real final default 0.0>]]
```

This directive contains only two keywords: one for the PCG method and the other for the exact Hessian (Newton Raphson, or NR). Use of PCG or NR is determined by the input specified for `nr_switch` on the `NR` directive, Section 10.14 above.

Specifying the keyword `pcg` on the `LEVEL` directive allows the user to define the level shifting for the approximate (i.e., PCG) method. Specifying the keyword `nr` allows the user to define the level shifting for the exact Hessians. In both options, the initial level shift is defined by the value specified for the variable `initial`. Optionally, `tol` can be specified independently with each keyword to define the level of accuracy that must be attained in the solution before the level shifting is changed to the value specified by input in the real variable `final`. Level shifts and gradient thresholds are specified in atomic units.

For the PCG method (as specified using the keyword `pcg`), the defaults for this input are 20.0 for `initial`, 0.5 for `tol`, and 0.0 for `final`. This means that the approximate Hessian will be shifted by 20.0 until the maximum element of the gradient falls below 0.5, at which point the shift will be set to zero.

For the exact Hessian (as specified using the keyword `nr`), the defaults are all zero. The exact Hessian is usually not shifted since this destroys quadratic convergence. An example of an input directive that applies a shift of 0.2 to the exact Hessian is as follows:

```
level nr 0.2
```

To apply this shift to the exact Hessian only until the maximum element of the gradient falls below 0.005, the required input directive is as follows:

```
level nr 0.2 0.005 0
```

Note that in both of these examples, the parameters for the PCG method are at the default values. To obtain values different from the defaults, the keyword `pcg` must also be specified. For example, to specify the level shifting in the above example for the exact Hessian *and* non-default shifting for the PCG method, the directive would be something like the following:

```
level pcg 20 0.3 0.0 nr 0.2 0.005 0.0
```

This input will cause the PCG method to be level-shifted by 20.0 until the maximum element of the gradient falls below 0.3, then the shift will be zero. For the exact Hessian, the level shifting is initially 0.2, until the maximum element falls below 0.005, after which the shift is zero.

The default options correspond to

```
level pcg 20 0.5 0 nr 0 0 0
```

10.16 Orbtial Localization

The SCF module includes an *experimental* implementation of orbital localization, including Foster-Boys and Pipek-Mezey which only works for closed-shell (RHF) wavefunctions. There is currently no input in the SCF block to control this so the `SET` directive (Section 5.7) must be used.

The directive

```
set scf:localize t
```

will separately localize the core, valence, and virtual orbital spaces using the Pipek-Mezey algorithm. If the additional directive

```
set scf:loctype FB
```

is included, then the Foster-boys algorithm is used. The partitioning of core-orbitals is performed using the atomic information described in Section 15.1.1.

In the next release, this functionality will be extended to included all wavefunctions using molecular orbitals.

10.17 Printing Information from the SCF Module

All output from the SCF module is controlled using the `PRINT` directive described in Section 5.6. The following list describes the items from SCF that are currently under direct print control, along with the print level for each one.

Name	Print Level	Description
"atomic guess density"	debug	guess density matrix
"atomic scf"	debug	details of atomic SCF
"mo guess"	default	brief info from mo guess
"information"	low	results
"initial vectors"	debug	
"intermediate vectors"	debug	
"final vectors"	debug	
"final vectors analysis"	default	
"initial vectors analysis"	never	
"intermediate evals"	debug	
"final evals"	default	
"schwarz"	high	integral screening info & stats at completion
"screening statistics"	debug	display stats after every Fock build
"geometry"	high	
"symmetry"	debug	detailed symmetry info
"basis"	high	
"geombas"	debug	detailed basis map info
"vectors i/o"	default	report vectors I/O
"parameters"	default	convergence parameters
"convergence"	default	info each iteration

Table 10.1: SCF Print Control Specifications

10.18 Hartree-Fock or SCF, MCSCF and MP2 Gradients

The input for this directive allows the user to adjust the print control for the SCF, UHF, ROHF, MCSCF and MP2 gradients. The form of the directive is as follows:

```
GRADIENTS
  [print || noprint] ...
END
```

The complementary keyword pair `print` and `noprint` allows the user some additional control on the information that can be included in the print output from the SCF calculation. Currently, only a few items can be explicitly invoked via print control. These are as follows:

Name	Print Level	Description
"information"	low	calculation info
"geometry"	high	geometry information
"basis"	high	basis set(s) used
"forces"	low	details of force components
"timing"	default	timing for each phase

Table 10.2: Gradient Print Control Specifications

Chapter 11

DFT for Molecules (DFT)

The NWChem density functional theory (DFT) module uses the Gaussian basis set approach to compute closed shell and open shell densities and Kohn-Sham orbitals in the:

- local density approximation (LDA),
- non-local density approximation (NLDA),
- local spin-density approximation (LSD),
- non-local spin-density approximation (NLSD), and
- any empirical mixture of local and non-local approximations (including exact exchange).

The formal scaling of the DFT computation can be reduced by choosing to use auxiliary Gaussian basis sets to fit the charge density (CD) and/or fit the exchange-correlation (XC) potential.

DFT input is provided using the compound `DFT` directive

```
DFT
  ...
END
```

The actual DFT calculation will be performed when the input module encounters the `TASK` directive (Section 5.10).

```
TASK DFT
```

Once a user has specified a geometry and a Kohn-Sham orbital basis set the DFT module can be invoked with no input directives (defaults invoked throughout). There are sub-directives which allow for customized application; those currently provided as options for the DFT module are:

```
VECTORS [[input] (<string input_movecs default atomic>) || \
                 (project <string basisname> <string filename>)] \
        [swap [alpha||beta] <integer vec1 vec2> ...] \
        [output <string output_filename default input_movecs>] \
        [lock]
```

```
XC [[acm] [b3lyp] [beckehandh] [pbe0]\
   [becke97]  [becke97-1] [becke98] [hcth] [h120] [h147]\
    [h402] [becke97gga1] \
    [HFexch <real prefactor default 1.0>] \
    [becke88 [nonlocal] <real prefactor default 1.0>] \
    [xperdew91 [nonlocal] <real prefactor default 1.0>] \
    [xpbe96 [nonlocal] <real prefactor default 1.0>] \
    [gill96 [nonlocal] <real prefactor default 1.0>] \
    [xhcth  <real prefactor default 1.0>] \
    [lyp <real prefactor default 1.0>] \
    [perdew81 <real prefactor default 1.0>] \
    [perdew86 [nonlocal] <real prefactor default 1.0>] \
    [perdew91 [nonlocal] <real prefactor default 1.0>] \
    [cpbe96 [nonlocal] <real prefactor default 1.0>] \
    [chcth  <real prefactor default 1.0>] \
    [pw91lda <real prefactor default 1.0>] \
    [slater <real prefactor default 1.0>] \
    [vwn_1 <real prefactor default 1.0>] \
    [vwn_2 <real prefactor default 1.0>] \
    [vwn_3 <real prefactor default 1.0>] \
    [vwn_4 <real prefactor default 1.0>] \
    [vwn_5 <real prefactor default 1.0>] \
    [vwn_1_rpa <real prefactor default 1.0>]]


CONVERGENCE [[energy <real energy default 1e-7>] \
             [density <real density default 1e-5>] \
             [gradient <real gradient default 5e-4>] \
             [dampon <real dampon default 0.0>] \
             [dampoff <real dampoff default 0.0>] \
             [diison <real diison default 0.0>] \
             [diisoff <real diisoff default 0.0>] \
             [levlon <real levlon default 0.0>] \
             [levloff <real levloff default 0.0>] \
             [ncydp <integer ncydp default 2>] \
             [ncyds <integer ncyds default 30>] \
             [ncysh <integer ncysh default 30>] \
             [damp <integer ndamp default 70>] [nodamping] \
             [diis [nfock <integer nfock default 10>]] \
             [nodiis] [lshift <real lshift default 0.5>] \
             [nolevelshifting] \
             [hl_tol <real hl_tol default 0.1>]]


GRID [(xcoarse||coarse||medium||fine||xfine) default medium] \
     [(gausleg||lebedev ) default lebedev ] \
     [(old||new) default new ] \
     [(becke||erf1||erf2||ssf) default erf1] \
     [(euler||mura||treutler||lindh) default mura] \
```

```
     [rm <real rm default 2.0>]


  TOLERANCES [[tight] [tol_rho <real tol_rho default 1e-10>] \
             [accCoul <integer accCoul default 10>] \
             [radius <real radius default 25.0>]]


  DECOMP
  DFT||ODFT
  DIRECT
  INCORE
  ITERATIONS <integer iterations default 30>
  MAX_OVL
  MULLIKEN
  MULT <integer mult default 1>
  NOIO
  PRINT||NOPRINT
```

The following sections describe these keywords and optional sub-directives that can be specified for a `DFT` calculation in NWChem.

11.1 Specification of Basis Sets for the DFT Module

The DFT module requires at a minimum the basis set for the Kohn-Sham molecular orbitals. This basis set must be in the default basis set named `"ao basis"`, or it must be assigned to this default name using the `SET` directive (see Section 5.7).

In addition to the basis set for the Kohn-Sham orbitals, the charge density fitting basis set can also be specified in the input directives for the DFT module. This basis set is used for the evaluation of the Coulomb potential in the Dunlap scheme[1]. The charge density fitting basis set must have the name `"cd basis"`. This can be the actual name of a basis set, or a basis set can be assigned this name using the `SET` directive, as described in Section 5.7. If this basis set is not defined by input, the $O(N^4)$y exact Coulomb contribution is computed.

The user also has the option of specifying a third basis set for the evaluation of the exchange-correlation potential. This basis set must have the name `"xc basis"`. If this basis set is not specified by input, the exchange contribution (XC) is evaluated by numerical quadrature. In most applications, this approach is efficient enough, so the `"xc basis"` basis set is not generally required.

For the DFT module, the input options for defining the basis sets in a given calculation can be summarized as follows;

- `"ao basis"` – Kohn-Sham molecular orbitals; required for all calculations
- `"cd basis"` – charge density fitting basis set; optional, but recommended for evaluation of the Coulomb potential
- `"xc basis"` – exchange-correlation (XC) fitting basis set; optional, and usually not recommended

[1] B.I. Dunlap, J.W.D. Connolly and J.R. Sabin, J. Chem. Phys. **71**, 4993 (1979)

11.2 VECTORS and MAX_OVL — KS-MO Vectors

The VECTORS directive is the same as that in the SCF module (Section 10.5). Currently, the LOCK keyword is not supported by the DFT module, however the directive

```
MAX_OVL
```

has the same effect.

11.3 XC and DECOMP — Exchange-Correlation Potentials

```
XC [[acm] [b3lyp] [beckehandh] [pbe0]\
   [becke97]  [becke97-1] [becke98] [hcth] [h120] [h147] \
    [h402] [becke97gga1] \
    [HFexch <real prefactor default 1.0>] \
    [becke88 [nonlocal] <real prefactor default 1.0>] \
    [xperdew91 [nonlocal] <real prefactor default 1.0>] \
    [xpbe96 [nonlocal] <real prefactor default 1.0>] \
    [gill96 [nonlocal] <real prefactor default 1.0>] \
    [xhcth  <real prefactor default 1.0>] \
    [lyp <real prefactor default 1.0>] \
    [perdew81 <real prefactor default 1.0>] \
    [perdew86 [nonlocal] <real prefactor default 1.0>] \
    [perdew91 [nonlocal] <real prefactor default 1.0>] \
    [cpbe96 [nonlocal] <real prefactor default 1.0>] \
    [chcth  <real prefactor default 1.0>] \
    [pw91lda <real prefactor default 1.0>] \
    [slater <real prefactor default 1.0>] \
    [vwn_1 <real prefactor default 1.0>] \
    [vwn_2 <real prefactor default 1.0>] \
    [vwn_3 <real prefactor default 1.0>] \
    [vwn_4 <real prefactor default 1.0>] \
    [vwn_5 <real prefactor default 1.0>] \
    [vwn_1_rpa <real prefactor default 1.0>]]
```

The user has the option of specifying the exchange-correlation treatment in the DFT Module. The default exchange-correlation functional is defined as the local density approximation (LDA) for closed shell systems and its counterpart the local spin-density (LSD) approximation for open shell systems. Within this approximation the exchange functional is the Slater $\rho^{1/3}$ functional (from J.C. Slater, *Quantum Theory of Molecules and Solids, Vol. 4: The Self-Consistent Field for Molecules and Solids* (McGraw-Hill, New York, 1974)), and the correlation functional is the Vosko-Wilk-Nusair (VWN) functional (functional V) (S.J. Vosko, L. Wilk and M. Nusair, Can. J. Phys. **58**, 1200 (1980)). The parameters used in this formula are obtained by fitting to the Ceperley and Alder[2] Quantum Monte-Carlo solution of the *homogeneous electron gas*.

These defaults can be invoked explicitly by specifying the following keywords within the DFT module input directive,

```
XC slater vwn_5
```

[2]D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

The DECOMP directive causes the components of the energy corresponding to each functional to be printed, rather than just the total exchange-correlation energy which is the default.

Many alternative exchange and correlation functionals are available to the user. The following sections describe these options.

11.3.1 Optional Exchange Functionals

There are six exchange functionals in addition to the default exchange functional. These are

- the Becke 1998 gradient-corrected functional (see A.D. Becke, J. Chem. Phys. **88**, 3098 (1988)), is invoked by specifying

  ```
  XC becke88
  ```

- the Perdew 1991 gradient-corrected exchange functional (J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992)), is invoked by specifying

  ```
  XC xperdew91
  ```

- the Perdew-Burke-Ernzerhof gradient-corrected exchange functional (J.P. Perdew, K. Burke and M. Ernzerhof, Physical Review Letters **77**, 3865 (1996); **78**, 1396 (1997))), is invoked by specifying

  ```
  XC xpbe96
  ```

- the Gill 1996 gradient-corrected exchange functional (P.W.Gill , Mol. Phys. **89**, 433 (1996)), is invoked by specifying

  ```
  XC gill96
  ```

- the Hamprecht-Cohen-Tozer-Handy gradient-corrected exchange functional (F.A.Hamprecht, A.J.Cohen, D.J.Tozer and N.C.Handy, J. Chem. Phys. **109**, 6264 (1998))

  ```
  XC xhcth
  ```

- The Hartree-Fock exact exchange functional, (which has $O(N^4)$ computation expense), is invoked by specifying

  ```
  XC HFexch
  ```

Note that the user also has the ability to include only the local or nonlocal contributions of a given functional. In addition the user can specify a multiplicative prefactor (the variable `<prefactor>` in the input) for the local/nonlocal component or total. An example of this might be,

```
XC becke88 nonlocal 0.72
```

The user should be aware that the Becke88 local component is simply the Slater exchange and should be input as such.

Any combination of the supported exchange functional options can be used. For example the popular Gaussian B3 exchange could be specified as:

```
XC slater 0.8 becke88 nonlocal 0.72 HFexch 0.2
```

11.3.2 Optional Correlation Functionals

In addition to the default `vwn_5` correlation functional, the user has 10 alternative correlation functionals to choose from: lyp, perdew81, perdew86, perdew91, pw91lda, `vwn_1`, `vwn_2`, `vwn_3`, `vwn_4`, and `vwn_1_rpa`.

As in the exchange functional input, individual local/nonlocal components as well as multiplicative prefactors can be invoked where appropriate. Each of the correlation functionals is listed below along with appropriate citation.

- VWN local density functionals; S.J. Vosko, L. Wilk and M. Nusair, Can. J. Phys. **58**, 1200 (1980); all five (5) functionals as described in this paper (addressed in the paper as I - V) have been implemented. These functionals can be invoked with the keywords:

```
XC vwn_1
XC vwn_2
XC vwn_3
XC vwn_4
XC vwn_5
```

  Note that functionals; `vwn_2`, `vwn_3`, and `vwn_4` require both sets of parameters (the Monte Carlo parameters of Ceperley and Alder and VWN's RPA parameters) used in fitting the homogeneous electron gas correlation energy. Functionals `vwn_1` and `vwn_5` require only the Monte Carlo fitting parameters. In order to reproduce results in the literature another functional was added; the `vwn_1_rpa`. This is the original `vwn_1` functional with RPA parameters as opposed to the prescribed Monte Carlo parameters. This functional can be invoked with the keyword,

```
XC vwn_1_rpa
```

- Perdew81 local density functional; J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981). This functional can be invoked with the keyword,

```
XC perdew81
```

- Perdew & Wang 1991 local density functional; J.P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992). The parameters used in this formula are obtained by fitting to the Ceperley and Alder Quantum Monte Carlo solution of the *homogeneous electron gas*. This functional can be invoked with the keyword,

```
XC pw91lda
```

- Perdew86 gradient-corrected functional; J. P. Perdew, Phys. Rev. B **33**, 8822 (1986). Note that this is a nonlocal functional and in the absence of any local functional specification the local component is defaulted to the perdew81 local correlation functional. This functional can be invoked with the keyword,

```
XC perdew86
```

- Perdew91 gradient-corrected functional; J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992). Note that this is a nonlocal functional and in the absence of any local functional specification the local component is defaulted to the `pw91lda` local correlation functional. This functional can be invoked with the keyword,

```
XC perdew91
```

- the Perdew-Burke-Ernzerhof gradient-corrected correlation functional (J.P. Perdew, K. Burke and M. Ernzerhof, Physical Review Letters **77**, 3865 (1996); **78**, 1396 (1997))), is invoked by specifying

  ```
  XC cpbe96
  ```

- the Hamprecht-Cohen-Tozer-Handy gradient-corrected correlation functional (F.A.Hamprecht, A.J.Cohen, D.J.Tozer and N.C.Handy, J. Chem. Phys. **109**, 6264 (1998))

  ```
  XC chcth
  ```

- LYP gradient-corrected functional; C. Lee, W. Yang and R. G. Parr, Phys. Rev. B **37**, 785 (1988). Note that this is a local and nonlocal functional but cannot be conveniently split into the individual components. The option to scale the total remains. This functional can be invoked with the keyword,

  ```
  XC lyp
  ```

Any combination of the supported correlation functional options can be used. For example B3LYP could be specified as:

```
XC vwn_1_rpa 0.19 lyp 0.81 HFexch 0.20  slater 0.80 becke88 nonlocal 0.72
```

11.3.3 Combined Exchange and Correlation Functionals

In addition to the options listed above for the exchange and correlation functionals, the user has the alternative of specifying combined exchange and correlation functionals. The available hybrid functionals consist of the Becke *"half and half"* (see A.D. Becke, J. Chem. Phys. 98, 1372 (1992)), the adiabatic connection method (see A.D. Becke, J. Chem. Phys. 98, 5648 (1993)), b3lyp (popularized by Gaussian9X), Becke 1997 ("Becke V" paper: A.D.Becke, J. Chem. Phys., **107**, 8554 (1997)

These options can be invoked by specifying any of the following input lines,

```
XC beckehandh
XC acm
XC b3lyp
XC becke97
Xc becke97-1
xc becke98
xc pbe0
xc hcth
xc h120
xc h147
xc h402
xc becke97gga1
```

The keyword `beckehandh` specifies that the exchange-correlation energy will be computed as

$$E_{XC} \approx \frac{1}{2}E_X^{\mathrm{HF}} + \frac{1}{2}E_X^{\mathrm{Slater}} + \frac{1}{2}E_C^{\mathrm{PW91LDA}}$$

We know this is NOT the correct Becke prescribed implementation which requires the XC potential in the energy expression. But this is what is currently implemented as an approximation to it.

The keyword **acm** specifies that the exchange-correlation energy is computed as

$$\begin{aligned} E_{XC} &= a_0 E_X^{\mathrm{HF}} + (1-a_0) E_X^{\mathrm{Slater}} + a_X \Delta E_X^{\mathrm{Becke88}} + E_C^{\mathrm{VWN}} + a_C \Delta E_C^{Perdew91} \\ & \quad \text{where} \\ a_0 &= 0.20,\ a_X = 0.72,\ a_C = 0.81 \end{aligned}$$

and Δ stands for a non-local component.

The keyword **b3lyp** specifies that the exchange-correlation energy is computed as

$$\begin{aligned} E_{XC} &= a_0 E_X^{\mathrm{HF}} + (1-a_0) E_X^{\mathrm{Slater}} + a_X \Delta E_X^{\mathrm{Becke88}} + (1-a_C) E_C^{\mathtt{VWN\_1\_RPA}} + a_C E_C^{LYP} \\ & \quad \text{where} \\ a_0 &= 0.20,\ a_X = 0.72,\ a_C = 0.81 \end{aligned}$$

The keyword **becke97-1** specifies the hybrid exchange-correlation energy derived by Handy et al by re-fitting the Becke 1997 functional (F.A.Hamprecht, A.J.Cohen, D.J.Tozer and N.C.Handy, J. Chem. Phys. **109**, 6264 (1998))

The keyword **hcth** specifies the exchange-correlation energy functional derived by Hamprecht-Cohen-Tozer-Handy (this is not a hybrid functional) (F.A.Hamprecht, A.J.Cohen, D.J.Tozer and N.C.Handy, J. Chem. Phys. **109**, 6264 (1998))

Keyword	X	C	GCA	Hybrid	Ref.
slater	⋆				[1]
vwn_1		⋆			[2]
vwn_2		⋆			[2]
vwn_3		⋆			[2]
vwn_4		⋆			[2]
vwn_5		⋆			[2]
vwn_1_rpa		⋆			[2]
perdew81		⋆			[3]
pw91lda		⋆			[4]
becke88	⋆		⋆		[5]
xperdew91	⋆		⋆		[6]
xpbe96	⋆		⋆		[7]
gill96	⋆		⋆		[8]
perdew86		⋆	⋆		[9]
lyp		⋆	⋆		[10]
perdew91		⋆	⋆		[6]
cpbe96		⋆	⋆		[7]
hcth	⋆	⋆	⋆		[11]
h120	⋆	⋆	⋆		[12]
h147	⋆	⋆	⋆		[12]
h402	⋆	⋆	⋆		[19]
beckehandh	⋆	⋆		⋆	[13]
b3lyp	⋆	⋆	⋆	⋆	[14]
acm	⋆	⋆	⋆	⋆	[14]
becke97	⋆	⋆	⋆	⋆	[15]
becke97-1	⋆	⋆	⋆	⋆	[15]
becke97gga1	⋆	⋆	⋆	⋆	[18]
becke98	⋆	⋆	⋆	⋆	[16]
pbe0	⋆	⋆	⋆	⋆	[17]

Table 11.1: Table of available Exchange (X) and Correlation (C) functionals

1. C. Slater, *Quantum Theory of Molecules and Solids, Vol. 4* (McGraw-Hill, New York, 1974)
2. S.J. Vosko, L. Wilk and M. Nusair, Can. J. Phys. **58**, 1200 (1980).
3. J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
4. J.P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).
5. A.D. Becke, J. Chem. Phys. **88**, 3098 (1988).
6. J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).
7. J.P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996); **78** , 1396 (1997).
8. P.W.Gill , Mol. Phys. **89**, 433 (1996).
9. J. P. Perdew, Phys. Rev. B **33**, 8822 (1986).
10. C. Lee, W. Yang and R. G. Parr, Phys. Rev. B **37**, 785 (1988).
11. F.A.Hamprecht, A.J.Cohen, D.J.Tozer and N.C. Handy, J. Chem. Phys. **109**, 6264 (1998).
12. A.D.Boese, N.L.Doltsinis, N.C.Handy and M.Sprik. J. Chem. Phys. **112**, 1670 (2000).
13. A.D. Becke, J. Chem. Phys. **98**, 1372 (1992).
14. A.D. Becke, J. Chem. Phys. **98**, 5648 (1993).
15. A.D.Becke, J. Chem. Phys. **107**, 8554 (1997).
16. H.L.Schmider and A.D. Becke, J. Chem. Phys. **108**, 9624 1998).
17. C.Adamo and V.Barone, J. Chem. Phys. **110**, 6158 (1998).
18. A.J.Cohen and N.C. Handy, Chem. Phys. Lett. **316**, 160 (2000).
19. A.D.Boese, N.C.Handy J. Chem. Phys., submitted (2000).

11.4 ITERATIONS — Number of SCF iterations

```
ITERATIONS <integer iterations default 30>
```

The default optimization in the DFT module is to iterate on the Kohn-Sham (SCF) equations for a specified number of iterations (default 30). The keyword that controls this optimization is `ITERATIONS`, and has the following general form,

```
 iterations <integer iterations default 30>
```

The optimization procedure will stop when the specified number of iterations is reached or convergence is met.

11.5 CONVERGENCE — SCF Convergence Control

```
CONVERGENCE [energy <real energy default 1e-6>] \
            [density <real density default 1e-5>] \
            [gradient <real gradient default 5e-4>] \
            [hl_tol <real hl_tol default 0.1>]
            [dampon <real dampon default 0.0>] \
            [dampoff <real dampoff default 0.0>] \
            [ncydp <integer ncydp default 2>] \
            [ncyds <integer ncyds default 30>] \
            [ncysh <integer ncysh default 30>] \
            [damp <integer ndamp default 70>] [nodamping] \
            [diison <real diison default 0.0>] \
            [diisoff <real diisoff default 0.0>] \
            [(diis [nfock <integer nfock default 10>]) || nodiis] \
            [levlon <real levlon default 0.0>] \
            [levloff <real levloff default 0.0>] \
            [(lshift <real lshift default 0.5>) || nolevelshifting] \
```

Convergence is satisfied by meeting any or all of three criteria;

- convergence of the total energy; this is defined to be when the total DFT energy at iteration N and at iteration N-1 differ by a value less than some value (the default is 1e-6). This value can be modified using the key word,

  ```
  CONVERGENCE energy <real energy default 1e-6>
  ```

- convergence of the total density; this is defined to be when the total DFT density matrix at iteration N and at iteration N-1 have a RMS difference less than some value (the default is 1e-5). This value can be modified using the key word,

  ```
  CONVERGENCE density <real density default 1e-5>
  ```

- convergence of the orbital gradient; this is defined to be when the DIIS error vector becomes less than some value (the default is 5e-4). This value can be modified using the key word,

```
CONVERGENCE gradient <real gradient default 5e-4>
```

The default optimization strategy is to immediately begin direct inversion of the iterative subspace[3]. Damping is also initiated (using 70% of the previous density) for the first 2 iteration. In addition, if the HOMO - LUMO gap is small and the Fock matrix somewhat diagonally dominant, then level-shifting is automatically initiated. There are a variety of ways to customize this procedure to whatever is desired.

An alternative optimization strategy is to specify, by using the change in total energy (from iterations when N and N-1), when to turn damping, level-shifting, and/or DIIS on/off. Start and stop keywords for each of these is available as,

```
CONVERGENCE  [dampon <real dampon default 0.0>] \
             [dampoff <real dampoff default 0.0>] \
             [diison <real diison default 0.0>] \
             [diisoff <real diisoff default 0.0>] \
             [levlon <real levlon default 0.0>] \
             [levloff <real levloff default 0.0>]
```

So, for example, damping, DIIS, and/or level-shifting can be turned on/off as desired.

Another strategy can be to simply specify how many iterations (cycles) you wish each type of procedure to be used. The necessary keywords to control the number of damping cycles (ncydp), the number of DIIS cycles (ncyds), and the number of level-shifting cycles (ncysh) are input as,

```
CONVERGENCE  [ncydp <integer ncydp default 2>] \
             [ncyds <integer ncyds default 30>] \
             [ncysh <integer ncysh default 0>]
```

The amount of damping, level-shifting, time at which level-shifting is automatically imposed, and Fock matrices used in the DIIS extrapolation can be modified by the following keywords

```
CONVERGENCE  [damp <integer ndamp default 70>] \
             [diis [nfock <integer nfock default 10>]] \
             [lshift <real lshift default 0.5>] \
             [hl_tol <real hl_tol default 0.1>]]
```

Damping is defined to be the percentage of the previous iterations density mixed with the current iterations density. So, for example

```
CONVERGENCE damp 70
```

would mix 30% of the current iteration density with 70% of the previous iteration density.

Level-Shifting[4] is defined as the amount of shift applied to the diagonal elements of the unoccupied block of the Fock matrix. The shift is specified by the keyword `lshift`. For example the directive,

```
CONVERGENCE lshift 0.5
```

causes the diagonal elements of the Fock matrix corresponding to the virtual orbitals to be shifted by 0.5 au. By default, this level-shifting procedure is switched on whenever the HOMO-LUMO gap is small. Small

[3] P. Pulay, Chem. Phys. Lett. **73**, 393 (1980) and P. Pulay, J. Comp. Chem. **3**, 566 (1982)

[4] M.F. Guest and V.R. Saunders, Mol. Phys. **28**, 819 (1974)

is defined by default to be 0.05 au but can be modified by the directive `hl_tol`. An example of changing the HOMO-LUMO gap tolerance to 0.01 would be,

```
CONVERGENCE hl_tol 0.01
```

Direct inversion of the iterative subspace with extrapolation of up to 10 Fock matrices is a default optimization procedure. For large molecular systems the amount of available memory may preclude the ability to store this number of N**2 arrays in global memory. The user may then specify the number of Fock matrices to be used in the extrapolation (must be greater than three (3) to be effective). To set the number of Fock matrices stored and used in the extrapolation procedure to 3 would take the form,

```
CONVERGENCE diis 3
```

Finally, the user has the ability to simply turn off any optimization procedures deemed undesirable with the obvious keywords,

```
CONVERGENCE [nodamping] [nodiis] [nolevelshifting]
```

11.6 GRID — Numerical Integration of the XC Potential

```
GRID [(xcoarse||coarse||medium||fine||xfine) default medium] \
     [(gausleg||lebedev ) default lebedev ] \
     [(old||new) default new ] \
     [(becke||erf1||erf2||ssf) default erf1] \
     [(euler||mura||treutler) default mura] \
     [rm <real rm default 2.0>]
```

A numerical integration is necessary for the evaluation of the exchange-correlation contribution to the density functional. The default quadrature used for the numerical integration is an Euler-MacLaurin scheme for the radial components (with a modified Mura-Knowles transformation) and a Lebedev scheme for the angular components. Within this numerical integration procedure various levels of accuracy have been defined and are available to the user. The user can specify the level of accuracy with the keywords; xcoarse, coarse, medium, fine, and xfine. The default is medium.

```
GRID [xcoarse||coarse||medium||fine||xfine]
```

Our intent is to have a numerical integration scheme which would give us approximately the accuracy defined below regardless of molecular composition.

Keyword	`Total Energy Target Accuracy`
`xcoarse`	$1x10^{-4}$
`coarse`	$1x10^{-5}$
`medium`	$1x10^{-6}$
`fine`	$1x10^{-7}$
`xfine`	$1x10^{-8}$

In order to determine the level of radial and angular quadrature needed to give us the target accuracy we computed total DFT energies at the LDA level of theory for many homonuclear atomic, diatomic and triatomic systems in rows 1-4 of the periodic table. In each case all bond lengths were set to twice the Bragg-Slater radius. The total DFT energy of the system was computed using the converged SCF density with atoms having radial shells ranging from 35-235 (at fixed 48/96 angular quadratures) and angular quadratures of 12/24-48/96 (at fixed 235 radial shells). The error of the numerical integration was determined by comparison to a "best" or most accurate calculation in which a grid of 235 radial points 48 theta and 96 phi angular points on each atom was used. This corresponds to approximately 1 million points per atom. The following tables were empirically determined to give the desired target accuracy for DFT total energies. These tables below show the number of radial and angular shells which the DFT module will use for for a given atom depending on the row it is in (in the periodic table) and the desired accuracy. Note, differing atom types in a given molecular system will most likely have differing associated numerical grids. The intent is to generate the desired energy accuracy (with utter disregard for speed).

Table 11.2: Program default number of radial and angular shells empirically determined for Row 1 atoms (Li $\rightarrow$ F) to reach the desired accuracies.

Keyword	`Radial`	`Theta`	`phi`
`xcoarse`	30	12	24
`coarse`	50	15	30
`medium`	70	18	36
`fine`	100	24	48
`xfine`	140	34	68

Table 11.3: Program default number of radial and angular shells empirically determined for Row 2 atoms (Na $\rightarrow$ Cl) to reach the desired accuracies.

Keyword	`Radial`	`Theta`	`phi`
`xcoarse`	45	12	24
`coarse`	75	18	36
`medium`	95	24	48
`fine`	125	30	60
`xfine`	175	44	88

Table 11.4: Program default number of radial and angular shells empirically determined for Row 3 atoms (K $\rightarrow$ Br) to reach the desired accuracies.

Keyword	`Radial`	`Theta`	`phi`
`xcoarse`	75	14	28
`coarse`	95	22	44
`medium`	110	30	60
`fine`	160	34	68
`xfine`	210	38	76

Table 11.5: Program default number of radial and angular shells empirically determined for Row 4 atoms (Rb $\rightarrow$ I) to reach the desired accuracies.

Keyword	`Radial`	`Theta`	`phi`
`xcoarse`	105	16	32
`coarse`	130	20	40
`medium`	155	32	64
`fine`	205	44	88
`xfine`	235	48	96

11.6.1 Angular grids

In addition to the simple keyword specifying the desired accuracy as described above, the user has the option of specifying a custom quadrature of this type in which ALL atoms have the same grid specification. This is accomplished by using the `gausleg` keyword.

Gauss-Legendre angular grid

```
GRID gausleg <integer nradpts default 50> <integer nagrid default 10>
```

In this type of grid, the number of phi points is twice the number of theta points. So, for example, a specification of,

```
GRID gausleg 80 20
```

would be interpreted as 80 radial points, 20 theta points, and 40 phi points per center (or 64000 points per center before pruning).

Lebedev angular grid A second quadrature is the Lebedev scheme for the angular components[5]. Within this numerical integration procedure various levels of accuracy have also been defined and are available to the user. The input for this type of grid takes the form,

```
GRID lebedev <integer radpts > <integer iangquad >
```

In this context the variable iangquad specifies a certain number of angular points as indicated by the table below.[6] Therefore the user can specify any number of radial points along with the level of angular quadrature (1-29).

The user can also specify grid parameters specific for a given atom type: parameters that must be supplied are: atom tag, number of radial points, number of angular points and `accQrad` (all three parameters must be given). As an example, here is a grid input line for the water molecule

```
grid lebedev 80 11 H 70 8 12 O 90 11 15
```

[5] The subroutine for the Lebedev grid was derived from a routine supplied by M. Causà of the University of Torino and from the grid points supplied by D.N. Laikov from Moscow State University.

[6] V.I. Lebedev and D.N. Laikov, Doklady Mathematics **366**, 741 (1999).

$IANGQUAD$	$N_{angular}$	l
1	38	9
2	50	11
3	74	13
4	86	15
5	110	17
6	146	19
7	170	21
8	194	23
9	230	25
10	266	27
11	302	29
12	350	31
13	434	35
14	590	41
15	770	47
16	974	53
17	1202	59
18	1454	65
19	1730	71
20	2030	77
21	2354	83
22	2702	89
23	3074	95
24	3470	101
25	3890	107
26	4334	113
27	4802	119
28	5294	125
29	5810	131

Table 11.6: List of Lebedev quadratures

11.6.2 Partitioning functions

```
GRID [(becke||erf1||erf2||ssf) default erf1]
```

`becke` A. D. Becke, J. Chem. Phys. **88**, 1053 (1988).

`ssf` R.E.Stratmann, G.Scuseria and M.J.Frisch, Chem. Phys. Lett. **257**, 213 (1996).

`erf1` modified ssf

`erf2` modified ssf

Erf$n$ partionioning functions

$$
\begin{aligned}
w_A(r) &= \prod_{B\neq A} \frac{1}{2}[1 \; - \; erf(\mu'_{AB})] \\
\mu'_{AB} &= \frac{1}{\alpha}\,\frac{\mu_{AB}}{(1-\mu_{AB}^2)^n} \\
\mu_{AB} &= \frac{\mathbf{r}_A - \mathbf{r}_B}{|\mathbf{r}_A - \mathbf{r}_B|}
\end{aligned}
$$

11.6.3 Radial grids

```
GRID [[euler||mura||treutler]  default mura]
```

`euler` Euler-McLaurin quadrature wih the transformation devised by C.W. Murray, N.C. Handy, and G.L. Laming, Mol. Phys.**78**, 997 (1993).

`mura` Modification of the Murray-Handy-Laming scheme by M.E.Mura and P.J.Knowles, J Chem Phys **104**, 9848 (1996) (we are not using the scaling factors proposed in this paper).

`treutler` Gauss-Chebyshev using the transformation suggested by O.Treutler and R.Alrhichs, J.Chem.Phys **102**, 346 (1995).

11.6.4 Grid Scheme

```
GRID [[old||new]  default new]
```

In Nwchem 4.0 the XC integration code has been re-written using a space decomposiition scheme similar to the one proposed in R.E.Stratmann, G.Scuseria and M.J.Frisch, Chem. Phys. Lett. **257**, 213 (1996) (keyword `new`).

To use the XC integration routines available in older version of NWChem, use the keyword `old`.

11.7 TOLERANCES — Screening tolerances

```
TOLERANCES [[tight] [tol_rho <real tol_rho default 1e-10>] \
            [accCoul <integer accCoul default 10>] \
            [radius <real radius default 25.0>]]
```

The user has the option of controlling screening for the tolerances in the integral evaluations for the DFT module. In most applications, the default values will be adequate for the calculation, but different values can be specified in the input for the DFT module using the keywords described below.

The input parameter `accCoul` is used to define the tolerance in Schwarz screening for the Coulomb integrals. Only integrals with estimated values greater than $10^{(-\mathtt{accCoul})}$ are evaluated.

```
TOLERANCES accCoul <integer accCoul default 10>
```

Screening away needless computation of the XC functional (on the grid) due to negligible density is also possible with the use of,

```
TOLERANCES tol_rho <real tol_rho default 1e-10>
```

XC functional computation is bypassed if the corresponding density elements are less than `tol_rho`.

A screening parameter, `radius`, used in the screening of the Becke or Delley spatial weights is also available as,

```
TOLERANCES radius <real radius default 25.0>
```

where radius is the cutoff value in bohr.

The tolerances as discussed previously are insured at convergence. More sleazy tolerances are invoked early in the iterative process which can speed things up a bit. This can also be problematic at times because it introduces a discontinuity in the convergence process. To avoid use of initial sleazy tolerances the user can invoke the `tight` option:

```
TOLERANCES tight
```

This option sets all tolerances to their default/user specified values at the very first iteration.

11.8 DIRECT and NOIO — Hardware Resource Control

```
DIRECT||INCORE
NOIO
```

The inverted charge-density and exchange-correlation matrices for a DFT calculation are normally written to disk storage. The user can prevent this by specifying the keyword `noio` within the input for the DFT directive. The input to exercise this option is as follows,

```
noio
```

If this keyword is encountered, then the two matrices (inverted charge-density and exchange-correlation) are computed "on-the-fly" whenever needed.

The `INCORE` option is always assumed to be true but can be overridden with the option `DIRECT` in which case all integrals are computed "on-the-fly".

11.9 DFT, ODFT and MULT — Open shell systems

```
DFT||ODFT
MULT <integer mult default 1>
```

Both *closed-shell* and *open-shell* systems can be studied using the DFT module. Specifying the keyword `MULT` within the `DFT` directive allows the user to define the spin multiplicity of the system. The form of the input line is as follows;

```
MULT <integer mult default 1>
```

When the keyword `MULT` is specified, the user can define the integer variable `mult`, where `mult` is equal to the number of alpha electrons minus beta electrons, plus 1.

The keywords `DFT||ODFT` were originally intended to specify closed or open shell and are really unnecessary except in the context of forcing a closed-shell system to be computed as an open shell system (i.e., using a spin-unrestricted wavefunction).

11.10 SIC — Self-Interaction Correction

```
sic [perturbative || oep || oep-loc <default perturbative>]
```

The Perdew and Zunger (see J. P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981)) method to remove the self-interaction contained in many exchange-correlation functionals has been implemented with the Optimized Effective Potential method (see R. T. Sharp and G. K. Horton, Phys. Rev. 90, 317 (1953), J. D. Talman and W. F. Shadwick, Phys. Rev. A 14, 36 (1976)). Three variants of these methods are included in NWChem:

- **sic perturbative** This is the default option for the sic directive. After a self-consistent calculation, the Kohn-Sham orbitals are localized with the Foster-Boys algorithm (see section 10.16) and the self-interaction energy is added to the total energy. All exchange-correlation functionals implemented in the NWChem can be used with this option.
- **sic oep** With this option the optimized effective potential is built in each step of the self-consistent process. Because the electrostatic potential generated for each orbital involves a numerical integration, this method can be expensive.
- **sic oep-loc** This option is similar to the oep option with the addition of localization of the Kohn-Sham orbitals in each step of the self-consistent process.

With oep and oep-loc options a **xfine grid** (see section 11.6) must be used in order to avoid numerical noise, furthermore the hybrid functionals can not be used with these options. More details of the implementation of this method can be found in J. Garza, J. A. Nichols and D. A. Dixon, J. Chem. Phys. 112, 7880 (2000). The components of the sic energy can be printed out using:

```
print "SIC information"
```

11.11 MULLIKEN — Mulliken analysis

```
MULLIKEN
```

Mulliken analysis of the charge distribution is invoked by the keyword:

```
MULLIKEN
```

When this keyword is encountered, Mulliken analysis of both the input density as well as the output density will occur.

11.12 Print Control

```
PRINT||NOPRINT
```

The `PRINT||NOPRINT` options control the level of output in the DFT. Known controllable print options are:

Name	Print Level	Description
"semi-direct info"	default	semi direct algorithm
"coulomb fit"	high	fitting electronic charge density
"io info"	debug	reading from and writing to disk
"information"	low	general information
"quadrature"	high	numerical quadrature
"parameters"	default	input parameters
"convergence"	default	convergence of SCF procedure
"intermediate vectors"	high	intermediate molecular orbitals
"intermediate evals"	high	intermediate orbital energies
"intermediate overlap"	high	overlaps between the alpha and beta sets
"intermediate S2"	high	values of S2
"interm vector symm"	high	symmetries of intermediate orbitals
"dft timings"	high	
"initial vectors"	high	
"common"	debug	dump of common blocks
"screening parameters"	high	integral accuracies
"intermediate energy info"	high	
"intermediate fock matrix"	high	
"final vectors"	high	
"schwarz"	high	integral screening info & stats at completion
"all vector symmetries"	high	symmetries of all molecular orbitals
"final vector symmetries"	default	symmetries of final molecular orbitals
"multipole"	default	moments of alpha, beta, and nuclear charge densities

Table 11.7: DFT Print Control Specifications

Chapter 12

Spin-Orbit DFT (SODFT)

The spin-orbit DFT module (SODFT) in the NWChem code allows for the variational treatment of the one-electron spin-orbit operator within the DFT framework. The implementation requires the definition of an effective core potential (ECP) and a matching spin-orbit potential (SO). The current implementation does NOT use symmetry.

The actual SODFT calculation will be performed when the input module encounters the `TASK` directive (Section 5.10).

```
TASK SODFT
```

Input parameters are the same as for the DFT, see section 11 for specifications. Some of the DFT options are not available in the SODFT. These are `max_ovl` and `sic`.

Besides using the standard ECP and basis sets, see Section 8 for details, one also has to specify a spin-orbit (SO) potential. The input specification for the SO potential can be found in section 8.2. At this time we have not included any spin-orbit potentials in the basis set library.

Note: One should use a combination of ECP and SO potentials that were designed for the same size core, i.e. don't use a small core ECP potential with a large core SO potential (it will produce erroneous results).

The following is an example of a calculation of UO_2:

```
start uo2_sodft
echo

Memory 32 mw

charge 2

geometry noautoz noautosym units angstrom
 U     0.00000     0.00000     0.00000
 O     0.00000     0.00000     1.68000
 O     0.00000     0.00000    -1.68000
end

basis "ao basis" cartesian print
```

```
U    S
       12.12525300         0.02192100
        7.16154500        -0.22516000
        4.77483600         0.56029900
        2.01169300        -1.07120900
U    S
        0.58685200         1.00000000
U    S
        0.27911500         1.00000000
U    S
        0.06337200         1.00000000
U    S
        0.02561100         1.00000000
U    P
       17.25477000         0.00139800
        7.73535600        -0.03334600
        5.15587800         0.11057800
        2.24167000        -0.31726800
U    P
        0.58185800         1.00000000
U    P
        0.26790800         1.00000000
U    P
        0.08344200         1.00000000
U    P
        0.03213000         1.00000000
U    D
        4.84107000         0.00573100
        2.16016200        -0.05723600
        0.57563000         0.23882800
U    D
        0.27813600         1.00000000
U    D
        0.12487900         1.00000000
U    D
        0.05154800         1.00000000
U    F
        2.43644100         0.35501100
        1.14468200         0.40084600
        0.52969300         0.30467900
U    F
        0.24059600         1.00000000
U    F
        0.10186700         1.00000000
O    S
       47.10551800        -0.01440800
        5.91134600         0.12956800
        0.97648300        -0.56311800
O    S
        0.29607000         1.00000000
O    P
```

```
        16.69221900         0.04485600
         3.90070200         0.22261300
         1.07825300         0.50018800
O    P
         0.28418900         1.00000000
O    P
         0.07020000         1.00000000
END

ECP
U nelec 78
  U s
    2         4.06365300       112.92010300
    2         1.88399500        15.64750000
    2         0.88656700        -3.68997100
  U p
    2         3.98618100       118.75801600
    2         2.00016000        15.07722800
    2         0.96084100         0.55672000
  U d
    2         4.14797200        60.85589200
    2         2.23456300        29.28004700
    2         0.91369500         4.99802900
  U f
    2         3.99893800        49.92403500
    2         1.99884000       -24.67404200
    2         0.99564100         1.38948000
O nelec 2
  O s
    2        10.44567000        50.77106900
  O p
    2        18.04517400        -4.90355100
  O d
    2         8.16479800        -3.31212400
END

SO
  U p
  2    3.986181      1.816350
  2    2.000160     11.543940
  2    0.960841      0.794644
  U d
  2    4.147972      0.353683
  2    2.234563      3.499282
  2    0.913695      0.514635
  U f
  2    3.998938      4.744214
  2    1.998840     -5.211731
  2    0.995641      1.867860
END
```

```
dft
  mult 1
  xc hfexch
  odft
  grid fine
  convergence energy 1.000000E-06
  convergence density 1.000000E-05
  convergence gradient 1E-05
  iterations 100
  mulliken
end

task sodft
```

Chapter 13

COSMO

COSMO is the continuum solvation 'Conductor-Like Screening' Model of A. Klamt and G. Schuurmann to describe dielectric screening effects in solvents.

1. A. Klamt and G. Schuurmann, J.Chem.Soc. Perkin Trans. 2, 1993, p799-805.

The NWChem COSMO module implements algorithm for calculation of the energy for Hartree-Fock (RHF and ROHF) and Kohn-Sham (DFT and UDFT) wavefunctions. At the present gradients are calculated by finite difference of the energy and the code does not work with spherical basis functions or ECPs. In the current implementation the code calculates the gas-phase energy of the system followed by the solution-phase energy, and returns the electrostatic contribution to the solvation free energy. The codes does not calculate the non-electrostatic contributions to the free energy.

Invoking the COSMO solvation model is done by specifying the input COSMO input block with the input options as follows:

```
cosmo
    dielec  <real dielec default 78.4>
    radius  <real atom1>
            <real atom2>
       . . .
            <real atomN>
    rsolv   <real rsolv default 0.00>
    iscren  <integer iscren default 0>
    minbem  <integer minbem default 2>
    maxbem  <integer maxbem default 3>
    ificos  <integer ificos default 0>
    lineq   <integer lineq default 1>
END
```

`Dielec` is the value of the dielectric constant of the medium, with a default value of 78.4 (the dielectric constant for water).

`Radius` is an array that specifies the radius of the spheres associated with each atom and that make up the molecule-shaped cavity. Default values are Van der Waals radii. Values are in units of angstroms. The codes uses the following Van der Waals radii by default:

```
 data vdwr(103) /
1   0.80,0.49,0.00,0.00,0.00,1.65,1.55,1.50,1.50,0.00,
2   2.30,1.70,2.05,2.10,1.85,1.80,1.80,0.00,2.80,2.75,
3   0.00,0.00,1.20,0.00,0.00,0.00,2.70,0.00,0.00,0.00,
4   0.00,0.00,0.00,1.90,1.90,0.00,0.00,0.00,0.00,1.55,
5   0.00,1.64,0.00,0.00,0.00,0.00,0.00,0.00,0.00,0.00,
6   0.00,0.00,0.00,0.00,0.00,0.00,0.00,0.00,0.00,0.00,
7   0.00,0.00,0.00,0.00,0.00,0.00,0.00,0.00,0.00,0.00,
8   0.00,0.00,0.00,0.00,0.00,0.00,0.00,0.00,0.00,0.00,
9   0.00,0.00,0.00,0.00,0.00,0.00,0.00,0.00,0.00,0.00,
1   0.00,0.00,0.00,0.00,0.00,0.00,0.00,0.00,0.00,1.65,
2   0.00,0.00,0.00/
```

with 0.0 values replaced by 1.80 . Other radii can be used as well. See for examples:

1. E. V. Stefanovich and T. N. Truong, Chem. Phys. Lett. 244 (1995) p65-74.
2. V. Barone, M. Cossi, and J. Tomasi, J. Chem. Phys. 107 (1997) p3210-3221.

Rsolv is a parameter used to define the solvent accessible surface. See the original reference of Klamt and Schuurmann for a description. The default value is 0.00 (in angstroms).

Iscren is a flag to define the dielectric charge scaling option. "iscren 1" implies the original scaling from Klamt and Schuurmann, mainly "(eps-1)/(eps+1/2)", where 'eps' is the dielectric constant. "iscren 0" implies the modified scaling suggested by Stefanovich and Truong, mainly "(eps-1)/eps". Default is to use the modified scaling. For high dielectric the difference between the scaling is not significant.

The next three parameters define the tesselation of the unit sphere. The approach follows the original proposal by Klamt and Schuurmann. A very fine tesselation is generated from **maxbem** refining passes starting from either an octahedron or an icosahedron. The boundary elements created with the fine tesselation are condensed down to a coarser tesselation based on **minbem**. The induced point charges from the polarization of the medium are assigned to the centers of the coarser tesselation. Default values are "minbem 2" and "maxbem 3". The flag **ificos** serves to select the original tesselation, "ificos 0" for an octahedron (default) and "ificos 1" for an icoshedron. Starting from an icosahedron yields a somewhat finer tesselation that converges somewhat faster. Solvation energies are not really sensitive to this choice for sufficiently fine tesselations.

The **lineq** parameter serves to select the numerical algorithm to solve the linear equations yielding the effective charges that represent the polarization of the medium. "lineq 0" selects an iterative method (default), "lineq 1" selects a dense matrix linear equation solver. For large molecules where the number of effective charges is large, the codes selects the iterative method.

The following example is for a water molecule in 'water', using the HF/6-31G** level of theory:

```
start
echo
 title "h2o"
geometry
o                  .0000000000         .0000000000        -.0486020332
h                  .7545655371         .0000000000         .5243010666
h                 -.7545655371         .0000000000         .5243010666
end
```

```
basis segment cartesian
  o library 6-31g**
  h library 6-31g**
end
cosmo
  dielec 78.0
  radius 1.40
         1.16
         1.16
  rsolv  0.50
  lineq  0
end
task scf energy
```

Chapter 14

DFT for Periodic Systems (GAPSS)

NOTE: A user is working with a prototype version of the GAPSS code. Encountered problems should be reported to J.E. Jaffe, john.jaffe@pnl.gov, or M. Gutowski, maciej.gutowski@pnl.gov.

The NWChem density functional theory module for periodic systems (GAPSS) uses the Gaussian basis set approach to compute electron densities and Kohn-Sham orbitals in the:

- local density approximation (LDA),
- non-local density approximation (NLDA),
- local spin-density approximation (LSD),
- non-local spin-density approximation (NLSD).

GAPSS input is provided using the compound `GAPSS` directive

```
GAPSS
  ...
END
```

The actual DFT calculation will be performed when the input module encounters the `TASK` directive (Section 5.10).

```
TASK GAPSS
```

There are sub-directives which allow for customized application; those currently provided as options for the GAPSS module are:

```
CORRELATION [(vwn||lyp||perdew86||pbe96) default vwn]
EXCHANGE [(slater||becke88||pbe96) default slater]
VXCACC [(low||medium||high||extrahigh||superhigh) default high]
WEIGHT [(lin||becke||delley) default lin]
MONKHORST <integer monkhorst default 3>
ISCREENLAT <integer iscreenlat default 7>
IC1C3CONV <integer ic1c3conv default 7>
```

```
IC2C4CONV <integer ic2c4conv default 6>
INTACC [(standard||high) default standard]
SCFTYPE [(conventional||direct) default conventional]
IPOL <integer ipol default 1>
ITRSCF <integer itrscf default 30>
SCFCONV <integer scfconv default 6>
MIXRATE <integer mixrate default 30>
NCYCMIX <integer ncycmix default 0>
NEWMIXRATE <integer newmixrate default 0>
LEVELSHIFT <real levelshift default 0.0>
NCLSHIFT <integer nclshift default 0>
GAPRESTART [(intsok||noints) default intsok] \
           [(covecs||atomic) default covecs]
```

The following sections describe these keywords and optional sub-directives that can be specified for a `GAPSS` calculation in NWChem.

14.1 Specification of Basis Sets for the GAPSS Module

The GAPSS module requires a basis set for the Kohn-Sham crystal orbitals. This basis set must be in the default basis set named `"ao basis"`, or it must be assigned to this default name using the `SET` directive (see Section 5.7). The valence and polarization shells of standard molecular AO basis sets usually require some modification for solids often by deleting or increasing exponents that are ≤ 0.2 au^{-2} initially. Only s, p, and 6d type functions are allowed at present.

The formal scaling of the computation is reduced by choosing to use auxiliary Gaussian basis sets to fit the charge density (CD). In addition to the basis set for the Kohn-Sham orbitals, the charge density fitting basis set must also be specified in the input directives for the GAPSS module. This basis set is used for the evaluation of the Coulomb potential in the Dunlap scheme[1], slightly modified for periodic systems[2]. The charge density fitting basis set must have the name `"cd basis"`. This can be the actual name of a basis set, or a basis set can be assigned this name using the `SET` directive, as described in Section 5.7. The molecular CD basis sets can often be used unchanged for periodic systems.

For the GAPSS module, the input options for defining the basis sets in a given calculation can be summarized as follows;

- `"ao basis"` – Kohn-Sham crystal orbitals; required for all calculations
- `"cd basis"` – charge density fitting basis set; required for all calculations

14.2 `CORRELATION` and `EXCHANGE` — Exchange-Correlation Potentials

```
CORRELATION [(vwn||lyp||perdew86||pbe96) default vwn]
EXCHANGE [(slater||becke88||pbe96) default slater]
```

[1] B.I. Dunlap, J.W.D. Connolly and J.R. Sabin, J. Chem. Phys. **71**, 4993 (1979)
[2] J.E. Jaffe, A.C. Hess, J. Chem. Phys. **105**, 10983 (1996)

The user has the option of specifying the exchange-correlation treatment in the GAPSS Module. The default exchange-correlation functional is defined as the local density approximation (LDA) for closed shell systems and its counterpart the local spin-density (LSD) approximation for open shell systems. Within this approximation the exchange functional is the Slater $\rho^{1/3}$ functional (from J.C. Slater, *Quantum Theory of Molecules and Solids, Vol. 4: The Self-Consistent Field for Molecules and Solids* (McGraw-Hill, New York, 1974)), and the correlation functional is the Vosko-Wilk-Nusair (VWN) functional (functional V) (S.J. Vosko, L. Wilk and M. Nusair, Can. J. Phys. **58**, 1200 (1980)). The parameters used in this formula are obtained by fitting to the Ceperley and Alder[3] Quantum Monte-Carlo solution of the *homogeneous electron gas*.

These defaults can be invoked explicitly by specifying the following keywords within the GAPSS module input directive,

```
CORRELATION vwn
EXCHANGE slater
```

Several alternative exchange and correlation functionals are available to the user. The following sections describe these options.

14.2.1 Optional Functionals

There are two exchange functionals in addition to the default Slater exchange functional. These are the Becke gradient-corrected functional (see A.D. Becke, J. Chem. Phys. 88, 3098 (1988)), and the Perdew, Burke, Ernzerhof generalized gradient approximation to the exchange-correlation functional (see J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996)).

The Becke gradient-corrected functional is invoked by specifying the input line

```
EXCHANGE becke88
```

The Perdew, Burke, Ernzerhof exchange functional is invoked by specifying the input line

```
EXCHANGE pbe96
```

There are three correlation functionals in addition to the default vwn correlation functional. These are the LYP gradient-corrected functional (C. Lee, W. Yang and R. G. Parr, Phys. Rev. B **37**, 785 (1988)), Perdew86 gradient-corrected functional (J. P. Perdew, Phys. Rev. B **33**, 8822 (1986)), and the Perdew, Burke, Ernzerhof generalized gradient approximation to the exchange-correlation functional (J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996)).

The LYP gradient-corrected functional is invoked by specifying the input line

```
CORRELATION lyp
```

The Perdew86 gradient-corrected functional is invoked by specifying the input line

```
CORRELATION perdew86
```

The Perdew, Burke, Ernzerhof correlation functional is invoked by specifying the input line

```
CORRELATION pbe96
```

[3] D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

14.3 Numerical Integration

```
VXCACC [(low||medium||high||extrahigh||superhigh) default high]
```

A numerical integration is necessary for the evaluation of the exchange-correlation contribution to the total energy and the Fock matrices. The user can specify the level of accuracy with the keywords; low, medium, high, extrahigh, superhigh. The default is high which corresponds to accuracy of ca. 1e-4 for the XC potential and energy. Each level of higher accuracy improves the accuracy of integration by a factor ≈ 10 and increases the cost by a factor of ≈ 3.

```
WEIGHT [(lin||becke||delley) default lin]
```

The three-dimensional integration is reduced to a sum of one-center, atomic-like integrations using either the Lin and Hess scheme (Z. Lin, J.E. Jaffe, A.C. Hess, J. Phys. Chem. A 103, 2117 (1999))

```
WEIGHT lin
```

or the Becke scheme (A.D. Becke, J. Chem. Phys. 88, 2547 (1988))

```
WEIGHT becke
```

or the Delley scheme (B. Delley, J. Chem. Phys. 92, 508 (1990))

```
WEIGHT delley
```

14.4 Summations and Integrations for a Periodic System

```
MONKHORST <integer monkhorst default 3>
ISCREENLAT <integer iscreenlat default 7>
IC1C3CONV <integer ic1c3conv default 7>
IC2C4CONV <integer ic2c4conv default 6>
INTACC [(standard||high) default standard]
```

The wave vectors in the first Brillouin zone are sampled following the Monkhorst-Pack scheme[4] `MONKHORST` = 5 is recommended for systems with 1-2 atoms per primitive unit cell, smaller values may be used for larger cells. Metals at present require `MONKHORST` ≥ 10. The convergence of the C^1-C^3 and C^2-C^4 series is controlled by the IC1C3CONV and IC2C4CONV directives, respectively, see J.E. Jaffe, A.C. Hess, J. Chem. Phys. **105**, 10983 (1996), and the accuracy of H(k) and S(k) with respect to the summation over unit cells is controlled by the ISCREENLAT directive. `ISCREENLAT` = 7 produces errors $\approx 10^{-6}$ E_h, with each higher level reducing this error by ca. 1 order of magnitude at little extra cost. `IC1C3CONV` = `ISCREENLAT` and `IC2C4CONV` = `ISCREENLAT` - 1 are recommended. Finally, the accuracy of two-electron three-center integrals is controlled by the directive INTACC.

[4] H.J. Monkhorst and J.D. Pack, Phys. Rev. B. **13**, 5188 (1976).

14.5 SCF Iterative Procedure

```
SCFTYPE [(conventional||direct) default conventional]
IPOL <integer ipol default 1>
ITRSCF <integer itrscf default 30>
SCFCONV <integer scfconv default 6>
MIXRATE <integer mixrate default 30>
NCYCMIX <integer ncycmix default 0>
NEWMIXRATE <integer newmixrate default 0>
LEVELSHIFT <real levelshift default 0.0>
NCLSHIFT <integer nclshift default 0>
GAPRESTART [(intsok||noints) default intsok] \
           [(covecs||atomic) default covecs]
```

The GAPSS code can work in the conventional mode, with integrals calculated once and written to disk

```
SCFTYPE conventional
```

or in the direct mode, with integrals evaluated at every SCF cycle.

```
SCFTYPE direct
```

The `direct` directive is mandatory in parallel runs.

Both closed-shell systems

```
IPOL 1
```

and open-shell systems

```
IPOL 2
```

may be studied with the GAPSS code.

The default optimization in the GAPSS module is to iterate on the Kohn-Sham equations for a specified number of iterations (default 30). The directive that controls the number of iterations is `ITRSCF`, and has the following general form,

```
ITRSCF <integer iterations default 30>
```

The optimization procedure will stop when the specified number of iterations is reached or convergence is met. Convergence is satisfied when the total energy at iteration N, iteration N-1, and iteration N-2 differ by a value less than some value (the default is 1e-6). This value can be modified using the directive

```
SCFCONV <integer scfconv default 6>
```

The final ΔE is often almost one order of magnitude below the cutoff due to the requirement of two successive ΔE's being below it. A user may control convergence of the self-consistent field procedure by mixing density matrices from the previous and current SCF cycle

```
MIXRATE <integer mixrate default 30>
NCYCMIX <integer ncycmix default 0>
NEWMIXRATE <integer newmixrate default 0>
```

The directive `mixrate` stands for the precentage of the new density, `ncycmix` tells for how many SCF cycles this mixing should be applied, and `newmixrate` tells what is the percentage of the new density matrix after `ncycmix` cycles. If `NCYCMIX` = 0 then the mixing rate is always `MIXRATE` (not `NEWMIXRATE`). `NCYCMIX` = 4 and `NEWMIXRATE` = 55 are recommended for most problems.

A user may also apply "level shifting"[5] to ensure convergence of the SCF procedure in the cases when the HOMO-LUMO separation (band gap) is small

```
LEVELSHIFT <real levelshift default 0.0>
NCLSHIFT <integer nclshift default 0>
```

and `levelshift` defines the amount of shift applied to the diagonal elements of the unoccupied block of the Fock matrix whereas `nclshift` tells for how many cycles the level shifting will be applied.

Finally, the GAPSS calculation may be restarted in the case of a `conventional` run.

```
GAPRESTART [(intsok||noints) default intsok] \
           [(covecs||atomic) default covecs]
```

If the integrals are still available, the `intsok` directive should be applied. Otherwise use `noints`. When restarting, one may use a density formed from crystal orbitals as an initial density (directive `covecs`) or a superposition of atomic densities (directive `atomic`). Runs may be restarted (with `covecs` and `intsok`) when the SCF process was interrupted or when one needs to change the SCF conditions or the `MONKHORST` settings. Runs can be restarted with `covecs` and `noints` when `IC1C3CONV` or `IC2C4CONV` are changed, since this will change the values of some integrals but not their number or orders. Restarting with `atomic` and `intsok` may succeed when the SCF process has failed to converge previously. Restart is not possible at present when `ISCREENLAT`, AO or CD basis sets, or geometry are changed as these result in different sets of integrals being computed and stored.

[5] M.F. Guest and V.R. Saunders, Mol. Phys. **28**, 819 (1974)

Chapter 15

MP2

There are (at least) three algorithms within NWChem that compute the Møller-Plesset (or many-body) perturbation theory second-order correction to the Hartree-Fock energy (MP2). They vary in capability, the size of system that can be treated and use of other approximations

- Semi-direct — this is recommended for most large applications (up to about 2800 basis functions), especially on the IBM SP and other machines with significant disk I/O capability. Partially transformed integrals are stored on disk, multi-passing as necessary. RHF and UHF references may be treated including computation of analytic derivatives. This is selected by specifying `mp2` on the task directive, e.g.

  ```
  task mp2
  ```

- Fully-direct — this is of utility if only limited I/O resources are available (up to about 2800 functions). Only RHF references and energies are available. This is selected by specifying `direct_mp2` on the task directive, e.g.

  ```
  task direct_mp2
  ```

- Resolution of the identity (RI) approximation MP2 (RIMP2) — this uses the RI approximation and is therefore only exact in the limit of a complete fitting basis. However, with some care, high accuracy may be obtained with relatively modest fitting basis sets. An RIMP2 calculation can cost over 40 times less than the corresponding exact MP2 calculation. RHF and UHF references with only energies are available. This is selected by specifying `rimp2` on the task directive, e.g.,

  ```
  task rimp2
  ```

15.1 Input directives

All three MP2 tasks share the same input block.

```
MP2
  [FREEZE [[core] (atomic || <integer nfzc default 0>)] \
          [virtual <integer nfzv default 0>]]
```

```
    [TIGHT]
    [PRINT]
    [NOPRINT]
    [VECTORS <string filename default scf-output-vectors> \
      [swap [(alpha||beta)] <integer pair-list>] ]
    [RIAPPROX <string riapprox default V>]
    [FILE3C <string filename default $file_prefix$.mo3cint">]
  END
```

15.1.1 FREEZE — Freezing orbitals

All MP2 modules support frozen core orbitals, however, only the direct MP2 and RI-MP2 modules support frozen virtual orbitals.

By default, no orbitals are frozen. The `atomic` keyword causes orbitals to be frozen according to the rules in Table 15.1.1. Note that *no* orbitals are frozen on atoms on which the nuclear charge has been modified either by the user or due to the presence of an ECP. The actual input would be

```
freeze atomic
```

For example, in a calculation on $Si(OH)_2$, by default the lowest seven orbitals would be frozen (the oxygen $1s$, and the silicon $1s$, $2s$ and $2p$).

Period	Elements	Core Orbitals	Number of Core
0	H – He	—	0
1	Li – Ne	$1s$	1
2	Na – Ar	$1s2s2p$	5
3	K – Kr	$1s2s2p3s3p$	9
4	Rb – Xe	$1s2s2p3s3p4s3d4p$	18
5	Cs – Rn	$1s2s2p3s3p4s3d4p5s4d5p$	27
6	Fr – Lr	$1s2s2p3s3p4s3d4p5s4d5p6s4f5d6p$	43

Table 15.1: Number of orbitals considered "core" in the "freeze by atoms" algorithm.

Caution: The rule for freezing orbitals "by atoms" are rather unsophisticated: the number of orbitals to be frozen is computed from the Table 15.1.1 by summing the number of core orbitals in each atom present. The corresponding number of lowest-energy orbitals are frozen — if for some reason the actual core orbitals are not the lowest lying, then correct results will not be obtained. From limited experience, it seems that special attention should be paid to systems including third- and higher- period atoms.

The `FREEZE` directive may also be used to specify the number of core orbitals to freeze. For instance, to freeze the first 10 orbitals

```
freeze 10
```

or equivalently, using the optional keyword `core`

```
freeze core 10
```

Again, note that if the 10 orbitals to be frozen do not correspond to the first 10 orbitals, then the `swap` keyword of the `VECTORS` directive must be used to order the input orbitals correctly (Section 15.1.4).

Table 15.2: Printable items in the MP2 modules and their default print levels.

Item	Print Level	Description
RI-MP2		
"2/3 ints"	debug	Partial 3-center integrals
"3c ints"	debug	MO 3-center integrals
"4c ints b"	debug	"B" matrix with approx. 4c integrals
"4c ints"	debug	Approximate 4-center integrals
"amplitudes"	debug	"B" matrix with denominators
"basis"	high	
"fit xf"	debug	Transformation for fitting basis
"geombas"	debug	Detailed basis map info
"geometry"	high	
"information"	low	General information about calc.
"integral i/o"	high	File size information
"mo ints"	debug	
"pair energies"	debug	
"partial pair energies"	debug	Pair energy matrix each time it is updated
"progress reports"	default	Report completion of time-consuming steps
"reference"	high	Details about reference wavefunction
"warnings"	low	Non-fatal warnings

To freeze the highest virtual orbitals, use the `virtual` keyword. For instance, to freeze the top 5 virtuals

```
freeze virtual 5
```

Again, note that this only works for the direct-MP2 and RI-MP2 energy codes.

15.1.2 `TIGHT` — Increased precision

The `TIGHT` directive can be used to increase the precision in the MP2 energy and gradients.

By default the MP2 gradient package should compute energies accurate to better than a micro-Hartree, and gradients accurate to about five decimal places (atomic units). However, if there is significant linear dependence in the basis set the precision might not be this good. Also, for computing very accurate geometries or numerical frequencies, greater precision may be desirable.

This option increases the precision to which both the SCF (from 10^{-6} to 10^{-8}) and CPHF (from 10^{-4} to 10^{-6}) are solved, and also tightens thresholds for computation of the AO and MO integrals (from 10^{-9} to 10^{-11}) within the MP2 code.

15.1.3 `PRINT` and `NOPRINT`

The standard print control options are recognized. The list of recognized names are given in Table 15.2.

15.1.4 VECTORS — MO vectors

All of the (supported) MP2 modules require use of converged canonical SCF (RHF or UHF) orbitals for correct results. The vectors are by default obtained from the preceding SCF calculation, but it is possible to specify a different source using the `VECTORS` directive. For instance, to obtain vectors from the file `/tmp/h2o.movecs`, use the directive

```
vectors /tmp/h2o.movecs
```

As noted above (Section 15.1.1) if the SCF orbitals are not in the correct order, it is necessary to permute the input orbitals using the `swap` keyword of the `VECTORS` directive. For instance, if it is desired to freeze a total six orbitals corresponding to the SCF orbitals 1–5, and 7, it is necessary to swap orbital 7 into the 6th position. This is accomplished by

```
vectors swap 6 7
```

The swap capability is examined in more detail in Section 10.5.

15.1.5 RI-MP2 fitting basis

The RI-MP2 method requires a fitting basis, which must be specified with the name `"ri-mp2 basis"` (see Section 7). For instance,

```
basis "ri-mp2 basis"
  O s; 10000.0 1
  O s;  1000.0 1
  O s;   100.0 1
  ...
end
```

Alternatively, using a standard capability of basis sets (Section 7) another named basis may be associated with the fitting basis. For instance, the following input specifies a basis with the name `"small fitting basis"` and then defines this to be the `"ri-mp2 basis"`.

```
basis "small fitting basis"
  H s; 10    1
  H s;  3    1
  H s;  1    1
  H s;  0.1  1
  H s;  0.01 1
end

set "ri-mp2 basis" "small fitting basis"
```

15.1.6 FILE3C — RI-MP2 3-center integral filename

The default name for the file used to store the transformed 3-center integrals is `"$file_prefix$.mo3cint"` in the scratch directory. This may be overridden using the FILE3C directive. For instance, to specify the file `/scratch/h2o.3c`, use this directive

```
file3c /scratch/h2o.3c
```

15.1.7 RIAPPROX — RI-MP2 Approximation

The type of RI approximation used in the RI-MP2 calculation is controlled by means of the RIAPPROX directive. The two possible values are `V` and `SVS` (case sensitive), which correspond to the approximations with the same names described in O. Vahtras, J Almlöf, and M. W. Feyereisen, *Chem. Phys. Lett.* **213**, 514–518 (1993). The default is `V`.

15.1.8 Advanced options for RI-MP2

These options, which functioned at the time of writing, are not currently supported.

Control of linear dependence

Construction of the RI fit requires the inversion of a matrix of fitting basis integrals which is carried out via diagonalization. If the fitting basis includes near linear dependencies, there will be small eigenvalues which can ultimately lead to non-physical RI-MP2 correlation energies. Eigenvectors of the fitting matrix are discarded if the corresponding eigenvalue is less than **`$mineval$`** which defaults to 10^{-8}. This parameter may be changed by setting the a parameter in the database. For instance, to set it to 10^{-10}

```
set "mp2:fit min eval" 1e-10
```

Reference Spin Mapping for RI-MP2 Calculations

The user has the option of specifying that the RI-MP2 calculations are to be done with variations of the SCF reference wavefunction. This is accomplished with a `SET` directive of the form,

```
set "mp2:reference spin mapping" <integer array default 0>
```

Each element specified for `array` is the SCF spin case to be used for the corresponding spin case of the correlated calculation. The number of elements set determines the overall type of correlated calculation to be performed. The default is to use the unadulterated SCF reference wavefunction.

For example, to perform a spin-unrestricted calculation (two elements) using the alpha spin orbitals (spin case 1) from the reference for both of the correlated reference spin cases, the `SET` directive would be as follows,

```
set "mp2:reference spin mapping" 1 1
```

The SCF calculation to produce the reference wavefunction could be either RHF or UHF in this case.

The `SET` directive for a similar case, but this time using the beta-spin SCF orbitals for both correlated spin cases, is as follows,

```
set "mp2:reference spin mapping" 2 2
```

The SCF reference calculation must be UHF in this case.

The `SET` directive for a spin-restricted calculation (one element) from the beta-spin SCF orbitals using this option is as follows,

```
set "mp2:reference spin mapping" 2
```

The `SET` directive for a spin-unrestricted calculation with the spins flipped from the original SCF reference wavefunction is as follows,

```
set "mp2:reference spin mapping" 2 1
```

Batch Sizes for the RI-MP2 Calculation

The user can control the size of each batch in the transformation and energy evaluation in the MP2 calculation, and consequently the memory requirements and number of passes required. This is done using two `SET` directives of the following form,

```
set "mp2:transformation batch size" <integer size default -1>
set "mp2:energy batch size" <integer isize jsize default -1 -1>
```

The default is for the code to determine the batch size based on the available memory. Should there be problems with the program-determined batch sizes, these variables allow the user to override them. The program will always use the smaller of the user's value of these entries and the internally computed batch size.

The transformation batch size computed in the code is the number of occupied orbitals in the $(occ\,vir|fit)$ three-center integrals to be produced at a time. If this entry is less than the number of occupied orbitals in the system, the transformation will require multiple passes through the two-electron integrals. The memory requirements of this stage are *two* global arrays of dimension $< batchsize > \times vir \times fit$ with the "fit" dimension distributed across all processors (on shell-block boundaries). The compromise here is memory space versus multiple integral evaluations.

The energy evaluation batch sizes are computed in the code from the number of occupied orbitals in the two sets of three-center integrals to be multiplied together to produce a matrix of approximate four-center integrals. Two blocks of integrals of dimension $(< batchisize > \times\ vir)$ and $(< batchjsize > \times\ vir)$ by fit are read in from disk and multiplied together to produce $< batchisize >< batchjsize >\ vir^2$ approximate integrals. The compromise here is performance of the distributed matrix multiplication (which requires large matrices) versus memory space.

Energy Memory Allocation Mode: RI-MP2 Calculation

The user must choose a strategy for the memory allocation in the energy evaluation phase of the RI-MP2 calculation, either by minimizing the amount of I/O, or minimizing the amount of computation. This can be accomplished using a `SET` directive of the form,

```
set "mp2:energy mem minimize" <string mem_opt default I>
```

A value of `I` entered for the string `mem_opt` means that a strategy to minimize I/O will be employed. A value of `C` tells the code to use a strategy that minimizes computation.

When the option to minimize I/O is selected, the block sizes are made as large as possible so that the total number of passes through the integral files is as small as possible. When the option to minimize computation is selected, the blocks are chosen as close to square as possible so that permutational symmetry in the energy evaluation can be used most effectively.

Local Memory Usage in Three-Center Transformation

For most applications, the code will be able to size the blocks without help from the user. Therefore, it is unlikely that users will have any reason to specify values for these entries except when doing very particular performance measurements.

The size of `xf3ci:AO 1 batch size` is the most important of the three, in terms of the effect on performance.

Local memory usage in the first two steps of the transformation is controlled in the RI-MP2 calculation using the following `SET` directives,

```
set "xf3ci:AO 1 batch size" <integer max>
set "xf3ci:AO 2 batch size" <integer max>
set "xf3ci:fit batch size" <integer max>
```

The size of the local arrays determines the sizes of the two matrix multiplications. These entries set limits on the size of blocks to be used in each index. The listing above is in order of importance of the parameters to performance, with `xf3ci:AO 1 batch size` being most important.

Note that these entries are only upper bounds and that the program will size the blocks according to what it determines as the best usage of the available local memory. The absolute maximum for a block size is the number of functions in the AO basis, or the number of fitting basis functions on a node. The absolute minimum value for block size is the size of the largest shell in the appropriate basis. Batch size entries specified for `max` that are larger than these limits are automatically reset to an appropriate value.

15.2 One-electron properties and natural orbitals

If an MP2 energy gradient is computed, all contributions are available to form the MP2 linear-response density. This is the density that when contracted with any spin-free, one-electron operator yields the associated property defined as the derivative of the energy. Thus, the reported MP2 dipole moment is the derivative of the energy w.r.t. an external magnetic field and is *not* the expectation value of the operator over the wavefunction. Only dipole moments are printed by the MP2 gradient code, but natural orbitals are produced and stored in the permanent directory with a file extension of `".mp2nos"`. These may be fed into the property package (see Section 24) to compute more general properties. Note that the MP2 linear response density matrix is not necessarily positive definite so it is not unusual to see a few small negative natural orbital occupation numbers.

Chapter 16

Multiconfiguration SCF

The NWChem multiconfiguration SCF (MCSCF) module can currently perform complete active space SCF (CASSCF) calculations with at most 20 active orbitals and about 500 basis functions. It is planned to extend it to handle 1000+ basis functions.

```
MCSCF
  STATE <string state>
  ACTIVE <integer nactive>
  ACTELEC <integer nactelec>
  MULTIPLICITY <integer multiplicity>
  [SYMMETRY <integer symmetry default 1>]
  [VECTORS [[input] <string input_file default $file_prefix$.movecs>]
         [swap <integer vec1 vec2> ...] \
         [output <string output_file default input_file>] \
         [lock]
  [HESSIAN (exact||onel)]
  [MAXITER <integer maxiter default 20>]
  [THRESH  <real thresh default 1.0e-4>]
  [TOL2E <real tol2e default 1.0e-9>]
  [LEVEL <real shift default 0.1d0>]
END
```

Note that the `ACTIVE`, `ACTELEC`, and `MULTIPLICITY` directives are *required*. The symmetry and multiplicity may alternatively be entered using the `STATE` directive.

16.1 ACTIVE — Number of active orbitals

The number of orbitals in the CASSCF active space must be specified using the `ACTIVE` directive.

E.g.,

```
active 10
```

The input molecular orbitals (see the vectors directive, Sections 16.6 and 10.5) must be arranged in order

1. doubly occupied orbitals,
2. active orbitals, and
3. unoccupied orbitals.

16.2 ACTELEC — Number of active electrons

The number of electrons in the CASSCF active space must be specified using the the **ACTELEC** directive. An error is reported if the number of active electrons and the multiplicity are inconsistent.

The number of closed shells is determined by subtracting the number of active electrons from the total number of electrons (which in turn is derived from the sum of the nuclear charges minus the total system charge).

16.3 MULTIPLICITY

The spin multiplicity must be specified and is enforced by projection of the determinant wavefunction.

E.g., to obtain a triplet state

```
multiplicity 3
```

16.4 SYMMETRY — Spatial symmetry of the wavefunction

This species the irreducible representation of the wavefunction as an integer in the range 1—8 using the same numbering of representations as output by the SCF program. Note that only Abelian point groups are supported.

E.g., to specify a B_1 state when using the C_{2v} group

```
symmetry 3
```

16.5 STATE — Symmetry and multiplicity

The electronic state (spatial symmetry and multiplicity) may alternatively be specified using the conventional notation for an electronic state, such as $^3B_2$ for a triplet state of B_2 symmetry. This would be accomplished with the input

```
state 3b2
```

which is equivalent to

```
symmetry 4
multiplicity 3
```

16.6 `VECTORS` — Input/output of MO vectors

Calculations are best started from RHF/ROHF molecular orbitals (see Section 10), and by default vectors are taken from the previous MCSCF or SCF calculation. To specify another input file use the **`VECTORS`** directive. Vectors are by default output to the input file, and may be redirected using the **`output`** keyword. The **`swap`** keyword of the **`VECTORS`** directive may be used to reorder orbitals to obtain the correct active space. See Section 10.5 for an example.

The **`LOCK`** keyword allows the user to specify that the ordering of orbitals will be locked to that of the initial vectors, insofar as possible. The default is to order by ascending orbital energies within each orbital space. One application where locking might be desirable is a calculation where it is necessary to preserve the ordering of a previous geometry, despite flipping of the orbital energies. For such a case, the **`LOCK`** directive can be used to prevent the SCF calculation from changing the ordering, even if the orbital energies change.

Output orbitals of a converged MCSCF calculation are canonicalized as follows:

- Doubly occupied and unoccupied orbitals diagonalize the corresponding blocks of an effective Fock operator. Note that in the case of degenerate orbital energies this does not fully determine the orbtials.
- Active-space orbitals are chosen as natural orbitals by diagonalization of the active space 1-particle density matrix. Note that in the case of degenerate occupations that this does not fully determine the orbitals.

16.7 `HESSIAN` — Select preconditioner

The MCSCF will use a one-electron approximation to the orbital-orbital Hessian until some degree of convergence is obtained, whereupon it will attempt to use the exact orbital-orbital Hessian which makes the micro iterations more expensive but potentially reduces the total number of macro iterations. Either choice may be forced throughout the calculation by specifying the appropriate keyword on the **`HESSIAN`** directive.

E.g., to specify the one-electron approximation throughout

```
hessian onel
```

16.8 `LEVEL` — Level shift for convergence

The Hessian (Section 16.7) used in the MCSCF optimization is by default level shifted by 0.1 until the orbital gradient norm falls below 0.01, at which point the level shift is reduced to zero. The initial value of 0.1 may be changed using the **`LEVEL`** directive. Increasing the level shift may make convergence more stable in some instances.

E.g., to set the initial level shift to 0.5

```
level 0.5
```

16.9 `PRINT` and `NOPRINT`

Specific output items can be selectively enabled or disabled using the **`print`** control mechanism (5.6) with the available print options listed in table(16.9).

Option	Class	Synopsis
`ci energy`	default	CI energy eigenvalue
`fock energy`	default	Energy derived from Fock matrices
`gradient norm`	default	Gradient norm
`movecs`	default	Converged occupied MO vectors
`trace energy`	high	Trace Energy
`converge info`	high	Convergence data and monitoring
`precondition`	high	Orbital preconditioner iterations
`microci`	high	CI iterations in line search
`canonical`	high	Canonicalization information
`new movecs`	debug	MO vectors at each macro-iteration
`ci guess`	debug	Initial guess CI vector
`density matrix`	debug	One- and Two-particle density matrices

Table 16.1: MCSCF Print Options

Chapter 17

Selected CI

The selected CI module is integrated into NWChem but as yet no input module has been written. The input thus consists of setting the appropriate variables in the database.

It is assumed that an initial SCF/MCSCF calculation has completed, and that MO vectors are available. These will be used to perform a four-index transformation, if this has not already been performed.

17.1 Background

This is a general spin-adapted, configuration-driven CI program which can perform arbitrary CI calculations, the only restriction being that all spin functions are present for each orbital occupation. CI wavefunctions may be specified using a simple configuration generation program, but the prime usage is intended to be in combination with perturbation correction and selection of new configurations. The second-order correction (Epstein-Nesbet) to the CI energy may be computed, and at the same time configurations that interact greater than a certain threshold with the current CI wavefunction may be chosen for inclusion in subsequent calculations. By repeating this process (typically twice is adequate) with the same threshold until no new configurations are added, the CI expansion may be made consistent with the selection threshold, enabling tentative extrapolation to the full-CI limit.

A typical sequence of calculations is as follows:

1. Pick as an initial CI reference the previously executed SCF/MCSCF.
2. Define an initial selection threshold.
3. Determine the roots of interest in the current reference space.
4. Compute the perturbation correction and select additional configurations that interact greater than the current threshold.
5. Repeat steps 3 and 4.
6. Lower the threshold (a factor of 10 is common) and repeat steps 3, 4, and 5. The *first* pass through step 4 will yield the approximately self-consistent CI and CI+PT energies from the *previous* selection threshold.

To illustrate this, below is some abbreviated output from a calculation on water in an augmented cc-PVDZ basis set with one frozen core orbital. The SCF was converged to high precision in C_{2v} symmetry with the following input

```
start h2o
geometry; symmetry c2v
  O 0 0 0; H 0 1.43042809 -1.10715266
end
basis
  H library aug-cc-pvdz; O library aug-cc-pvdz
end
task scf
scf; thresh 1d-8; end
```

The following input restarts from the SCF to perform a sequence of selected CI calculations with the specified tolerances, starting with the SCF reference.

```
restart h2o
set fourindex:occ_frozen 1
set "selci:selection thresholds" \
    0.001 0.001 0.0001 0.0001 0.00001 0.00001 0.000001
task selci
```

Table 17.1 summarizes the output from each of the major computational steps that were performed.

Step	Description	CI dimension	Energy
1	Four-index, one frozen-core		
2	Config. generator, SCF default	1	
3+4	CI diagonalization	1	$E_{CI} = -76.041983$
5	PT selection T=0.001	1	$E_{CI+PT} = -76.304797$
6+7	CI diagonalization	75	$E_{CI} = -76.110894$
8	PT selection T=0.001	75	$E_{CI+PT} = -76.277912$
9+10	CI diagonalization	75	$E_{CI}(T = 0.001) = -76.110894$
11	PT selection T=0.0001	75	$E_{CI+PT}(T = 0.001) = -76.277912$
12+13	CI diagonalization	823	$E_{CI} = -76.228419$
14	PT selection T=0.0001	823	$E_{CI+PT} = -76.273751$
15+16	CI diagonalization	841	$E_{CI}(T = 0.0001) = -76.2300544$
17	PT selection T=0.00001	841	$E_{CI+PT}(T = 0.0001) = -76.274073$
18+19	CI diagonalization	2180	$E_{CI} = -76.259285$
20	PT selection T=0.00001	2180	$E_{CI+PT} = -76.276418$
21+22	CI diagonalization	2235	$E_{CI}(T = 0.00001) = -76.259818$
23	PT selection T=0.000001	2235	$E_{CI+PT}(T = 0.00001) = -76.276478$
24	CI diagonalization	11489	

Table 17.1: Summary of steps performed in a selected CI calculation on water.

17.2 Files

Currently, no direct control is provided over filenames. All files are prefixed with the standard file-prefix, and any files generated by all nodes are also postfixed with the processor number. Thus, for example the molecular integrals file, used only by process zero, might be called `h2o.moints` whereas the off-diagonal Hamiltonian matrix element file used by process number eight would be called `h2o.hamil.8`.

- `ciconf` — the CI configuration file, which holds information about the current CI expansion, indexing vectors, etc. This is the most important file and is required for all restarts. Note that the CI configuration generator is only run if this file does not exist. Referenced only by process zero.
- `moints` — the molecular integrals, generated by the four-index transformation. As noted above these must currently be manually deleted, or the database entry `selci:moints:force` set, to force regeneration. Referenced only by process zero.
- `civecs` — the CI vectors. Referenced only by process zero.
- `wmatrx` — temporary file used to hold coupling coefficients. Deleted at calculation end. Referenced only by process zero.
- `rtname, roname` — restart information for the PT selection. Should be automatically deleted if no restart is necessary. Referenced only by process zero.
- `hamdg` — diagonal elements of the Hamiltonian. Deleted at calculation end. Referenced only by process zero.
- `hamil` — off-diagonal Hamiltonian matrix elements. All processes generate a file containing a subset of these elements. These files can become very large. Deleted at calculation end.

17.3 Configuration Generation

If no configuration is explicitly specified then the previous SCF/MCSCF wavefunction is used, adjusting for any orbitals frozen in the four-index transformation. The four-index transformation must have completed successfully before this can execute. Orbital configurations for use as reference functions may also be explicitly specified.

Once the default/user-input reference configurations have been determined additional reference functions may be generated by applying multiple sets of creation-annihilation operators, permitting for instance, the ready specification of complete or restricted active spaces.

Finally, a uniform level of excitation from the current set of configurations into all orbitals may be applied, enabling, for instance, the simple creation of single or single+double excitation spaces from an MCSCF reference.

17.3.1 Specifying the reference occupation

A single orbital configuration or occupation is specified by

```
ns  (socc(i),i=1,ns)  (docc(i),i=1,nd)
```

where `ns` specifies the number of singly occupied orbitals, `socc()` is the list of singly occupied orbitals, and `docc()` is the list of doubly occupied orbitals (the number of doubly occupied orbitals, `nd`, is inferred from `ns` and the total number of electrons). All occupations may be strung together and inserted into the database as a single integer array with name `"selci:conf"`. For example, the input

```
set "selci:conf" \
  0               1  2  3  4 \
  0               1  2  3 27 \
  0               1  3  4 19 \
  2   11 19       1  3  4 \
  2    8 27       1  2  3 \
  0               1  2  4 25 \
  4   3  4 25 27  1  2 \
  4   2  3 19 20  1 4 \
  4   2  4 20 23  1 3
```

specifies the following nine orbital configurations

```
1(2)  2(2)  3(2)  4(2)
1(2)  2(2)  3(2) 27(2)
1(2)  3(2)  4(2) 19(2)
1(2)  3(2)  4(2) 11(1) 19(1)
1(2)  2(2)  3(2)  8(1) 27(1)
1(2)  2(2)  4(2) 25(2)
1(2)  2(2)  3(1)  4(1) 25(1) 27(1)
1(2)  2(1)  3(1)  4(2) 19(1) 20(1)
1(2)  2(1)  3(2)  4(1) 20(1) 23(1)
```

The optional formatting of the input is just to make this arcane notation easier to read. Relatively few configurations can be currently specified in this fashion because of the input line limit of 1024 characters.

17.3.2 Applying creation-annihilation operators

Up to 10 sets of creation-annihilation operator pairs may be specified, each set containing up to 255 pairs. This suffices to specify complete active spaces with up to ten electrons.

The number of sets is specified as follows,

```
set selci:ngen 4
```

which indicates that there will be four sets. Each set is then specified as a separate integer array

```
set "selci:refgen  1" 5 4    6 4   5 3   6 3
set "selci:refgen  2" 5 4    6 4   5 3   6 3
set "selci:refgen  3" 5 4    6 4   5 3   6 3
set "selci:refgen  4" 5 4    6 4   5 3   6 3
```

In the absence of friendly, input note that the names `"selci:refgen n"` must be formatted with n in `I2` format. Each set specifies a list of creation-annihilation operator pairs (in that order). So for instance, in the above example each set is the same and causes the excitations

```
4->5  4->6  3->5  3->6
```

If orbitals 3 and 4 were initially doubly occupied, and orbitals 5 and 6 initially unoccupied, then the application of this set of operators four times in succession is sufficient to generate the four electron in four orbital complete active space.

The precise sequence in which operators are applied is

1. loop through sets of operators
2. loop through reference configurations
3. loop through operators in the set
4. apply the operator to the configuration, if the result is new add it to the new list
5. end the loop over operators
6. end the loop over reference configurations
7. augment the configuration list with the new list
8. end the loop over sets of operators

17.3.3 Uniform excitation level

By default no excitation is applied to the reference configurations. If, for instance, you wanted to generate a single excitation CI space from the current configuration list, specify

```
set selci:exci 1
```

Any excitation level may be applied, but since the list of configurations is explicitly generated, as is the CI Hamiltonian matrix, you will run out of disk space if you attempt to use more than a few tens of thousands of configurations.

17.4 Number of roots

By default, only one root is generated in the CI diagonalization or perturbation selection. The following requests that 2 roots be generated

```
set selci:nroot 2
```

There is no imposed upper limit. If many roots are required, then, to minimize root skipping problems, it helps to perform an initial approximate diagonalization with several more roots than required, and then resetting this parameter once satisfied that the desired states are obtained.

17.5 Accuracy of diagonalization

By default, the CI wavefunctions are converged to a residual norm of 10^{-6} which provides similar accuracy in the perturbation corrections to the energy, and much higher accuracy in the CI eigenvalues. This may be adjusted with

```
set "selci:diag tol" 1d-3
```

the example setting much lower precision, appropriate for the approximate diagonalization discussed in the preceding section.

17.6 Selection thresholds

When running in the selected-CI mode the program will loop through a list of selection thresholds (T), performing the CI diagonalization, computing the perturbation correction, and augmenting the CI expansion with configurations that make an energy lowering to any root greater than T. The list of selection thresholds is specified as follows

```
set "selci:selection thresholds" \
    0.001 0.001 0.0001 0.0001 0.00001 0.00001 0.000001
```

There is no default for this parameter.

17.7 Mode

By default the program runs in `"ci+davids"` mode and just determines the CI eigenvectors/values in the current configuration space. To perform a selected-CI with perturbation correction use the following

```
set selci:mode select
```

and remember to define the selection thresholds.

17.8 Memory requirements

No global arrays are used inside the selected-CI, though the four-index transformation can be automatically invoked and it does use GAs. The selected CI replicates inside each process

- all unique two-electron integrals in the MO basis that are non-zero by symmetry, and
- all CI information, including the CI vectors.

These large data structures are allocated on the local stack. A fatal error will result if insufficient memory is available.

17.9 Forcing regeneration of the MO integrals

When scanning a potential energy surface or optimizing a geometry the MO integrals need to be regenerated each time. Specify

```
set selci:moints:force logical .true.
```

to accomplish this.

17.10 Disabling update of the configuration list

When computing CI+PT energy the reference configuration list is normally updated to reflect all configurations that interact more than the specified threshold. This is usually desirable. But when scanning a potential energy surface or optimizing a geometry the reference list must be kept fixed to keep the potential energy surface continuous and well defined. To do this specify

```
set selci:update logical .false.
```

17.11 Orbital locking in ci geometry optimization

The selected CI wavefunction is not invariant to orbital rotations or to swapping two or more orbitals. Orbitals could be swapped or rotated when the geometry is changed in a geometry optimization step. The keyword `lock` has to be set in the SCF/MCSCF (vectors) input block to keep the orbitals in the same order throughout the geometry optimization.

Chapter 18

Coupled Cluster Calculations

The NWChem coupled cluster energy module is primarily the work of Alistair Rendell and Rika Kobayashi, with contributions from David Bernholdt, and is derived from the Titan parallel coupled cluster program.

The coupled cluster code can perform calculations with full iterative treatment of single and double excitations and non-iterative inclusion of triple excitation effects. It is presently limited to closed-shell (RHF) references.

Note that symmetry is not used within most of the CCSD(T) code. This can have a profound impact on performance since the speed-up from symmetry is roughly the square of the number of irreducible representations. In the absence of symmetry, the performance of this code is competitive with other programs.

The operation of the coupled cluster code is controlled by the input block

```
CCSD
  [MAXITER <integer maxiter default 20>]
  [THRESH  <real thresh default 10^-6>]
  [TOL2E <real tol2e default min(10^-12 , 0.01*$thresh$)>]
  [DIISBAS  <integer diisbas default 5>]
  [FREEZE [[core] (atomic || <integer nfzc default 0>)] \
          [virtual <integer nfzv default 0>]]
  [IPRT  <integer IPRT default 0>]
  [PRINT ...]
  [NOPRINT ...]
END
```

Note that the keyword `CCSD` is used for the input block regardless of the actual level of theory desired (specified with the `TASK` directive). The following directives are recognized within the `CCSD` group.

18.1 `MAXITER` — Maximum number of iterations

The maximum number of iterations is set to 20 by default. This should be quite enough for most calculations, although particularly troublesome cases may require more.

```
MAXITER  <integer maxiter default 20>
```

18.2 THRESH — Convergence threshold

Controls the convergence threshold for the iterative part of the calculation. Both the RMS error in the amplitudes *and* the change in energy must be less than `thresh`.

```
THRESH  <real thresh default 10^-6>
```

18.3 TOL2E — integral screening threshold

```
TOL2E <real tol2e default min(10^-12 , 0.01*$thresh$)>
```

The variable `tol2e` is used in determining the integral screening threshold for the evaluation of the energy and related quantities.

CAUTION! At the present time, the `tol2e` parameter only affects the three- and four-virtual contributions, and the triples, all of which are done "on the fly". The transformations used for the other parts of the code currently have a hard-wired threshold of 10^{-12}. The default for `tol2e` is set to match this, and since user input can only make the threshold smaller, setting this parameter can only make calculations take longer.

18.4 DIISBAS — DIIS subspace dimension

Specifies the maximum size of the subspace used in DIIS convergence acceleration. Note that DIIS requires the amplitudes and errors be stored for each iteration in the subspace. Obviously this can significantly increase memory requirements, and could force the user to reduce `DIISBAS` for large calculations.

Measures to alleviate this problem, including more compact storage of the quantities involved, and the possibility of disk storage are being considered, but have not yet been implemented.

```
DIISBAS  <integer diisbas default 5>
```

18.5 FREEZE — Freezing orbitals

```
[FREEZE [[core] (atomic || <integer nfzc default 0>)] \
        [virtual <integer nfzv default 0>]]
```

This directive is idential to that used in the MP2 module, Section 15.1.1.

18.6 IPRT — Debug printing

This directive controls the level of output from the code, mostly to facilitate debugging and the like. The larger the value, the more output printed. From looking at the source code, the interesting values seem to be `IPRT` $>$ 5, 10, and 50.

```
IPRT  <integer IPRT default 0>
```

18.7 PRINT and NOPRINT

The coupled cluster module supports the standard NWChem print control keywords, although very little in the code is actually hooked into this mechanism yet.

Item	Print Level	Description
"reference"	high	Wavefunction information
"guess pair energies"	debug	MP2 pair energies
"byproduct energies"	default	Intermediate energies
"term debugging switches"	debug	Switches for individual terms

18.8 Methods (Tasks) Recognized

Currently available methods are

- `CCSD` – Full iterative inclusion of single and double excitations
- `CCSD+T(CCSD)` – The fourth order triples contribution computed with converged singles and doubles amplitudes
- `CCSD(T)` – The linearized triples approximation due to Raghavachari.

The calculation is invoked using the the `TASK` directive, so to perform a CCSD+T(CCSD) calculation, for example, the input file should include the directive

```
TASK CCSD+T(CCSD)
```

Lower-level results which come as by-products (such as MP3/MP4) of the requested calculation are generally also printed in the output file and stored on the run-time database, but the method specified in the `TASK` directive is considered the primary result.

18.9 Debugging and Development Aids

The information in this section is intended for use by experts (both with the methodology and with the code), primarily for debugging and development work. Messing with stuff in listed in this section will probably make your calculation quantitatively **wrong**! Consider yourself warned!

18.9.1 Switching On and Off Terms

The `/DEBUG/` common block contains a number of arrays which control the calculation of particular terms in the program. These are 15-element integer arrays (although from the code only a few elements actually effect anything) which can be set from the input deck. See the code for details of how the arrays are interpreted.

Printing of this data at run-time is controlled by the `"term debugging switches"` print option. The values are checked against the defaults at run-time and a warning is printed to draw attention to the fact that the calculation does not correspond precisely to the requested method.

```
DOA  <integer array default 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2>
DOB  <integer array default 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2>
DOG  <integer array default 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1>
DOH  <integer array default 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1>
DOJK <integer array default 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2>
DOS  <integer array default 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1>
DOD  <integer array default 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1>
```

Chapter 19

Geometry Optimization with DRIVER

The DRIVER module is one of two drivers (see Section 20 for documentation on STEPPER) to perform a geometry optimization function on the molecule defined by input using the `GEOMETRY` directive (see Section 6). Geometry optimization is either an energy minimization or a transition state optimization. The algorithm programmed in DRIVER is a quasi-newton optimization with line searches and approximate energy Hessian updates.

DRIVER is selected by default out of the two available modules to perform geometry optimization. In order to force use of DRIVER (e.g., because a previous optimization used STEPPER) provide a DRIVER input block (below) — even an empty block will force use of DRIVER.

Optional input for this module is specified within the compound directive,

```
DRIVER
  (LOOSE || DEFAULT || TIGHT)
  GMAX <real value>
  GRMS <real value>
  XMAX <real value>
  XRMS <real value>

  EPREC <real eprec default 1e-7>

  TRUST <real trust default 0.3>
  SADSTP <real sadstp default 0.1>

  CLEAR
  REDOAUTOZ

  INHESS <integer inhess default 0>

  (MODDIR || VARDIR) <integer dir default 0>
  (FIRSTNEG || NOFIRSTNEG)

  MAXITER <integer maxiter default 20>
```

```
    BSCALE <real BSCALE default 1.0>
    ASCALE <real ASCALE default 0.25>
    TSCALE <real TSCALE default 0.1>
    HSCALE <real HSCALE default 1.0>

    PRINT ...

    XYZ [<string xyz default $file_prefix$>]
    NOXYZ

  END
```

19.1 Convergence criteria

```
  (LOOSE || DEFAULT || TIGHT)
  GMAX <real value>
  GRMS <real value>
  XMAX <real value>
  XRMS <real value>
```

In version 3.3 Gaussian-style convergence criteria have been adopted. The defaults may be used, or the directives `LOOSE`, `DEFAULT`, or `TIGHT` specified to use standard sets of values, or the individual criteria adjusted. All criteria are in atomic units. `GMAX` and `GRMS` control the maximum and root mean square gradient in the coordinates being used (Z-matrix, redundant internals, or Cartesian). `XMAX` and `XRMS` control the maximum and root mean square of the Cartesian step.

	LOOSE	DEFAULT	TIGHT
GMAX	0.0045d0	0.00045	0.000015
GRMS	0.0030d0	0.00030	0.00001
XMAX	0.0054d0	0.00180	0.00006
XRMS	0.0036d0	0.00120	0.00004

The old criterion may be recovered with the input

```
gmax 0.0008; grms 1; xrms 1; xmax 1
```

19.2 Available precision

```
  EPREC <real eprec default 1e-7>
```

In performing a line search the optimizer must know the precision of the energy (this has nothing to do with convergence criteria). The default value of 1e-7 should be adjusted if less, or more, precision is available. Note that the default EPREC for DFT calculations is 5e-6 instead of 1e-7.

19.3 Controlling the step length

```
TRUST <real trust default 0.3>
SADSTP <real sadstp default 0.1>
```

A fixed trust radius (`trust`) is used to control the step during minimizations, and is also used for modes being minimized during saddle-point searches. It defaults to 0.3 for minimizations and 0.1 for saddle-point searches. The parameter `sadstp` is the trust radius used for the mode being maximized during a saddle-point search and defaults to 0.1.

19.4 Maximum number of steps

```
MAXITER <integer maxiter default 20>
```

By default at most 20 geometry optimization steps will be taken, but this may be modified with this directive.

19.5 Discard restart information

```
CLEAR
```

By default Driver reuses Hessian information from a previous optimization, and, to facilitate a restart also stores which mode is being followed for a saddle-point search. This option deletes all restart data.

19.6 Regenerate internal coordinates

```
REDOAUTOZ
```

Deletes Hessian data and regenerates internal coordinates at the current geometry. Useful if there has been a large change in the geometry that has rendered the current set of coordinates invalid or non-optimal.

19.7 Initial Hessian

```
INHESS <integer inhess default 0>
```

- 0 = Default ... use restart data if available, otherwise use diagonal guess.
- 1 = Use diagonal initial guess.
- 2 = Use restart data if available, otherwise transform Cartesian Hessian from previous frequency calculation.

In addition, the diagonal elements of the initial Hessian for internal coordinates may be scaled using separate factors for bonds, angles and torsions with the following

```
BSCALE <real bscale default 1.0>
ASCALE <real ascale default 0.25>
TSCALE <real tscale default 0.1>
```

These values typically give a two-fold speedup over unit values, based on about 100 test cases up to 15 atoms using 3-21g and 6-31g* SCF. However, if doing many optimizations on physically similar systems it may be worth fine tuning these parameters.

Finally, the entire Hessian from any source may be scaled by a factor using the directive

```
HSCALE <real hscale default 1.0>
```

It might be of utility, for instance, when computing an initial Hessian using SCF to start a large MP2 optimization. The SCF vibrational modes are expected to be stiffer than the MP2, so scaling the initial Hessian by a number less than one might be beneficial.

19.8 Mode or variable to follow to saddle point

```
(MODDIR || VARDIR) <integer dir default 0>
(FIRSTNEG || NOFIRSTNEG)
```

When searching for a transition state the program, by default, will take an initial step uphill and then do mode following using a fuzzy maximum overlap (the lowest eigen-mode with an overlap with the previous search direction of 0.7 times the maximum overlap is selected). Once a negative eigen-value is found, that mode is followed regardless of overlap.

The initial uphill step is appropriate if the gradient points roughly in the direction of the saddle point, such as might be the case if a constrained optimization was performed at the starting geometry. Alternatively, the initial search direction may be chosen to be along a specific internal variable (using the directive `VARDIR`) or along a specific eigen-mode (using `MODDIR`). Following a variable might be valuable if the initial gradient is either very small or very large. Note that the eigen-modes in the optimizer have next-to-nothing to do with the output from a frequency calculation. You can examine the eigen-modes used by the optimizer with

```
    driver; print hvecs; end
```

The selection of the first negative mode is usually a good choice if the search is started in the vicinity of the transition state and the initial search direction is satisfactory. However, sometimes the first negative mode might not be the one of interest (e.g., transverse to the reaction direction). If `NOFIRSTNEG` is specified, the code will not take the first negative direction and will continue doing mode-following until that mode goes negative.

19.9 Optimization history as XYZ files

```
XYZ [<string xyz default $fileprefix>]
NOXYZ
```

The `XYZ` directive causes the geometry at each step (but not intermediate points of a line search) to be output into separate files in the permanent directory in XYZ format. The optional string will prefix the filename. The `NOXYZ` directive turns this off.

For example, the input

```
driver; xyz test; end
```

will cause files test-000.xyz, test-001.xyz, ... to be created in the permanent directory.

The script `rasmolmovie` in the NWChem `contrib` directory can be used to turn these into an animated GIF movie.

19.10 Print options

The UNIX command `"egrep '^@' < output"` will extract a pretty table summarizing the optimization.

If you specify the NWChem input

```
scf; print none; end
driver; print low; end
task scf optimize
```

you'll obtain a pleasantly terse output.

For more control, these options for the standard print directive are recognized

- `debug` - prints a large amount of data. Don't use in parallel.
- `high` - print the search direction in internals
- `default` - prints geometry for each major step (not during the line search), gradient in internals (before and after application of constraints)
- `low` - prints convergence and energy information. At convergence prints final geometry, change in internals from initial geometry

and these specific print options

- finish (low) - print geometry data at end of calculation
- bonds (default) - print bonds at end of calculation
- angles (default) - print angles at end of calculation
- hvecs (never) - print eigen-values/vectors of the Hessian
- searchdir (high) - print the search direction in internals
- 'internal gradient' (default) - print the gradient in internals
- sadmode (default) - print the mode being followed to the saddle point

Chapter 20

Geometry Optimization with STEPPER

The STEPPER module performs a search for critical points on the potential energy surface of the molecule defined by input using the `GEOMETRY` directive (see Section 6). Since STEPPER is **not** the primary geometry optimization module in NWChem the compound directive is required; the DRIVER module is the default (see Section 19). Input for this module is specified within the compound directive,

```
STEPPER
  ...
END
```

The presence of the STEPPER compound directive automatically turns off the default geometry optimization tool driver. Input specified for the STEPPER module must appear in the input file *after* the `GEOMETRY` directive, since it must know the number of atoms that are to be used in the geometry optimization. In the current version of NWChem, STEPPER can be used only with geometries that are defined in Cartesian coordinates. STEPPER removes translational and rotational components before determining the step direction (5 components for linear systems and 6 for others) using a standard Eckart algorithm. The default initial guess nuclear Hessian is the identity matrix.

The default in STEPPER is to minimize the energy as a function of the geometry with a maximum of 20 geometry optimization iterations. When this is the desired calculation, no input is required other than the STEPPER compound directive. However, the user also has the option of defining different tasks for the STEPPER module, and can vary the number of iterations and the convergence criteria from the default values. The input for these options is described in the following sections.

20.1 `MIN` and `TS` — Minimum or transition state search

The default is for STEPPER to minimize the energy with respect to the geometry of the system. This default behavior may be forced with the directive

```
MIN
```

STEPPER can also be used to find the transition state by following the lowest eigenvector of the nuclear Hessian. This is usually invoked by using the `saddle` keyword on the `TASK` directive (Section 5.10), but it may also be selected by specifying the directive

```
TS
```

in the STEPPER input.

20.2 TRACK — Mode selection

STEPPER has the ability to "track" a specific mode during an optimization for a transition state search, the user can also have the module track the eigenvector corresponding to a specific mode. This is done by specifying the directive

```
TRACK [nmode <integer nmode default 1>]
```

The keyword `TRACK` tells STEPPER to track the eigenvector corresponding to the integer value of `<nmode>` during a transition state walk. (Note: this input is invalid for a minimization walk since following a specific eigenvector will not necessarily give the desired local minimum.) The step is constructed to go up in energy along the `nmode` eigenvector and down in all other degrees of freedom.

20.3 MAXITER — Maximum number of steps

In most applications, 20 stepper iterations will be sufficient to obtain the energy minimization. However, the user has the option of specifying the maximum number of iterations allowed, using the input line,

```
MAXITER <integer maxiter default 20>
```

The value specified for the integer `<maxiter>` defines the maximum number of geometry optimization steps. The geometry optimization will restart automatically.

20.4 TRUST — Trust radius

The size of steps that can be taken in STEPPER is controlled by the trust radius which has a default value of 0.1. Steps are constrained to be no larger than the trust radius. The user has the option of overriding this default using the keyword `TRUST`, with the following input line,

```
TRUST <real radius default 0.1>
```

The larger the value specified for the variable `radius`, the larger the steps that can be taken by STEPPER. Experience has shown that for larger systems (i.e., those with 20 or more atoms), a value of 0.5, or greater, usually should be entered for `<radius>`.

20.5 CONVGGM, CONVGG and CONVGE — Convergence criteria

Three convergence criteria can be specified explicitly for the STEPPER calculations. The keyword `CONVGGM` allows the user to specify the convergence tolerance for the largest component of the gradient. This is the primary convergence criterion, as per the default settings, although all three criteria are in effect. this default setting is consistent with the other optimizer module DRIVER. The input line for CONVGGM has the following form,

```
CONVGGM <real convggm default 8.0d-04>
```

The keyword CONVGG allows the user to specify the convergence tolerance for the gradient norm for all degrees of freedom. The input line is of the following form,

```
CONVGG <real convgg default 1.0d-02>
```

The entry for the real variable `<convgg>` should be approximately equal to the square root of the energy convergence tolerance.

The energy convergence tolerance is the convergence criterion for the energy difference in the geometry optimization in STEPPER. It can be specified by input using a line of the following form,

```
CONVGE <real convge default 1.0d-04>
```

20.6 Backstepping in Stepper

If a step taken during the optimization is too large (e.g., the step causes the energy to go up for a minimization or down for a transition state search), the STEPPER optimizer will automatically "backstep" and correct the step based on information prior to the faulty step. If you have an optimization that "backsteps" frequently then the initial trust radius should most likely be decreased.

20.7 Initial Nuclear Hessian Options

Stepper uses a modified Fletcher-Powell algorithm to find the transition state or energy minimum on the potential energy hypersurface. There are two files left in the user's permanent directory that are used to provide an initial hessian to the critical point search algorithm. If these files do not exist then the default is to use a unit matrix as the initial hessian. Once Stepper executes it generates a binary dump file by the name of `name.stpr41` which will be used on all subsequent stepper runs and modified with the current updated hessian. The default file prefix is the "name" that is used (c.f., 5.1). It also stores the information for the last valid step in case the algorithm must take a "backstep" (c.f., 20.6). This file is the working data store for all stepper-based optimizations. This file is never deleted by default and is the *first* source of an initial hessian. The second source of an inital hessian is an ascii file that contains the lower triangular values of the initial hessian. This is stored in file `name.hess`, where "name" is again the default file prefix. This is the *second* source of an initial hessian and is the method used to incorporate an initial hessian from any other source (e.g., another *ab initio* code, a molecular mechanics code, etc.,). To get a decent starting hessian at a given point you can use the task specification `task scf hessian`, with a smaller basis set, which will by default generate the `name.hess` file. Then you may define your basis set of choice and proceed with the optimization you desire.[1]

[1] If you have done a geometry optimization and hessian generation in the same input deck using a small basis set, you must make sure you delete the `name.stpr41` file since stepper will by default use that hessian and not the one in the `name.hess` file

Chapter 21

Hybrid Calculations with ONIOM

ONIOM is the hybrid method of Morokuma and co-workers that enables different levels of theory to be applied to different parts of a molecule/system and combined to produce a consistent energy expression. The objective is to perform a high-level calculation on just a small part of the system and to include the effects of the remainder at lower levels of theory, with the end result being of similar accuracy to a high-level calculation on the full system.

1. M. Svensson, S. Humbel, R.D.J. Froese, T. Mastubara, S. Sieber and K. Morokuma, J. Phys. Chem, 100, 1996, p19357.
2. S. Dapprich, I. Komaromi, K.S. Byun, K. Morokuma and M.J. Frisch, J. Mol. Struct (Theochem), 461-462, 1999, p1-21.
3. R.D.J. Froese and K. Morokuma in "Encylopedia of Computational Chemistry," volume 2, p1244-1257, (ed. P. von Rague Schleyer, John Wiley and Sons, Chichester, Sussex, 1998).

The NWChem ONIOM module implements two- and three-layer ONIOM models for use in energy, gradient, geometry optimization, and vibrational frequency calculations with any of the pure quantum mechanical methods within NWChem. At the present time, it is not possible to perform ONIOM calculations with either solvation models or classical force fields. Nor is it yet possible to compute properties except as derivatives of the total energy.

Using the terminology of Morokuma et al., the full molecular geometry including all atoms is referred to as the "real" geometry and it is treated using a "low"-level of theory. A subset of these atoms (referred to as the "model" geometry) are treated using both the "low"-level and a "high"-level of theory. A three-layer model also introduces an "intermediate" model geometry and a "medium" level of theory.

The two-layer model requires a high and low level of theory and a real and model molecular geometry. The energy at the high-level of theory for the real geometry is estimated as

```
E(High,Real) = E(Low,Real) + [E(High,Model) - E(Low,Model)].
```

The three-layer model requires high, medium and low levels of theory, and real, intermediate and model geometries and the corresponding energy estimate is

```
E(High,Real) = E(Low,Real) + [E(High,Model) - E(Medium,Model)]
               +  [E(Medium,Inter) - E(Low,Inter)].
```

When does ONIOM work well? The approximation for a two-layer model will be good if

- the model system includes the interactions that dominate the energy difference being computed and the high-level of theory describes these to the required precision, and
- the interactions between the model and the rest of the real system (substitution effects) are described to sufficient accuracy at the lower level of theory.

ONIOM is used to compute energy differences and the absolute energies are not all that meaningful even though they are well defined. Due to cancellation of errors, ONIOM actually works better than you might expect, but a poorly designed calculation can yield very bad results. Please read and heed the caution at the end of the article by Dapprich et al.

The input options are as follows

```
ONIOM
  HIGH   <string theory> [basis <string basis default "ao basis">] \
                         [ecp <string ecp>] [input <string input>]
 [MEDIUM <string theory> [basis <string basis default "ao basis">] \
                         [ecp <string ecp>] [input <string input>]]
  LOW    <string theory> [basis <string basis default "ao basis">] \
                         [ecp <string ecp>] [input <string input>]
  MODEL <integer natoms> [charge <double charge>] \
                         [<integer i1 j1> <real g1> [<string tag1>] ...]
 [INTER <integer natoms> [charge <double charge>] \
                         [<integer i1 j1> <real g1> [<string tag1>] ...]]
 [VECTORS [low-real <string mofile>] [low-model <string mofile>] \
          [high-model <string mofile>] [medium-model <string mofile]\
          [medium-inter <string mofile>] [low-inter <string mofile>]]
 [PRINT ...]
 [NOPRINT ...]
END
```

which are described in detail below.

For better validation of user input, the `HIGH`, `LOW` *and* `MODEL` *directives must always be specified. If the one of the* `MEDIUM` *or* `INTER` *directives are specified, then so must the other.*

21.1 Real, model and intermediate geometries

The geometry and total charge of the full or real system should be specified as normal using the geometry directive (see Section 6). If N_{model} of the atoms are to be included in the model system, then these should be specified first in the geometry. Similarly, in a three-layer calculation, if there are N_{inter} atoms to be included in the intermediate system, then these should also be arranged together at the beginning of the geometry. The implict assumption is that the model system is a subset of the intermediate system which is a subset of the real system. The number of atoms to be included in the model and intemediate systems are specified using the `MODEL` and `INTER` directives. Optionally, the total charge of the model and intermediate systems may be adjusted. The default is that all three systems have the same total charge.

Example 1. A two-layer calculation on $K^+(H_2O)$ taking the potassium ion as the model system. Note that no bonds are broken so no link atoms are introduced. The real geometry would be specified with potassium (the model) first.

```
geometry autosym
  K  0    0.00    1.37
  O  0    0.00   -1.07
  H  0   -0.76   -1.68
  H  0    0.76   -1.68
end
```

and the following directive in the ONIOM input block indicates that one atom (implicitly the first in the geometry) is in the model system

```
model 1
```

21.1.1 Link atoms

Link atoms for bonds spanning two regions are automatically generated from the bond information. The additional parameters on the `MODEL` and `INTER` directives describe the broken bonds including scale factors for placement of the link atom and, optionally, the type of link atom. The type of link atom defaults to hydrogen, but any type may be specified (actually here you are specifying a geometry tag which is used to associate a geometrical center with an atom type and basis sets, etc.. See section 6.3). For each broken bond specify the numbers of the two atoms (i and j), the scale factor (g) and optionally the tag of the link atom. Link atoms are placed along the vector connecting the the first to the second atom of the bond according to the equation

$$\underline{R}_{link} = (1-g)\underline{R}_1 + g * \underline{R}_2$$

where g is the scale factor. If the scale factor is one, then the link atom is placed where the second atom was. More usually, the scale factor is less than one, in which case the link atom is placed between the original two atoms. The scale factor should be chosen so that the link atom (usually hydrogen) is placed near its equilibrium bond length from the model atom. E.g., when breaking a single carbon-carbon bond (typical length 1.528 Angstrøms) using a hydrogen link atom we will want a carbon-hydrogen bond length of about 1.084 Angstrøms, so the scale factor should be chosen as $1.084/1.528 \approx 0.709$.

Example 2. A calculation on acetaldehyde ($H_3C - CHO$) using aldehyde ($H - CHO$) as the model system. The covalent bond between the two carbon atoms is broken and a link atom must be introduced to replace the methyl group. The link atom is automatically generated — all you need to do is specify the atoms in the model system that are also in the real system (here CHO) and the broken bonds. Here is the geometry of acetaldehyde with the CHO of aldehyde first

```
geometry
  C    -0.383    0.288    0.021
  H    -1.425    0.381    0.376
  O     0.259    1.263   -0.321

  H     0.115   -1.570    1.007
  H    -0.465   -1.768   -0.642
  H     1.176   -1.171   -0.352
  C     0.152   -1.150    0.005
end
```

There are three atoms (the first three) of the real geometry included in the model geometry, and we are breaking the bond between atoms 1 and 7, replacing atom 7 with a hydrogen link atom. This is all accomplished by the directive

```
model 3   1 7 0.709 H
```

Since the default link atom is hydrogen there is actually no need to specify the "H".

See also Section 21.6.3 for a more complex example.

21.1.2 Numbering of the link atoms

The link atoms are appended to the atoms of the model or intermediate systems in the order that the broken bonds are specified in the input. This is of importance only if manually constructing an initial guess.

21.2 High, medium and low theories

The two-layer model requires both the high-level and low-level theories be specified. The three-layer model also requires the medium-level theory. Each of these includes a theory (such as SCF, MP2, DFT, CCSD, CCSD(T), etc.), an optional basis set, an optional ECP, and an optional string containing general NWChem input.

21.2.1 Basis specification

The basis name on the theory directive (high, medium, or low) is that specified on a basis set directive (see Section 7) and *not* the name of a standard basis in the library. If not specified, the basis set for the high-level theory defaults to the standard `"ao basis"`. That for the medium level defaults to the high-level basis, and the low-level basis defaults to the medium-level basis. Other wavefunction parameters are obtained from the standard wavefunction input blocks. See 21.6.2 for an example.

21.2.2 Effective core potentials

If an effective core potential is specified in the usual fashion (see Section 8) outside of the ONIOM input then this will be used in all calculations. If an alternative ECP name (the name specified on the ECP directive in the same manner as done for basis sets) is specified on one of the theory directives, then this ECP will be used in preference for that level of theory. See Section 21.6.2 for sample input.

21.2.3 General input strings

For many purposes, the ability to specify the theory, basis and effective core potential is adequate. All of the options for each theory are determined from their independent input blocks. However, if the same theory (e.g., DFT) is to be used with different options for the ONIOM theoretical models, then the general input strings must be used. These strings are processed as NWChem input each time the theoretical model is invoked. The strings may contain any NWChem input, except for options pertaining to ONIOM and the task directive. The intent that the strings be used just to control the options pertaining to the theory being used.

A word of caution. Be sure to check that the options are producing the desired results. Since the NWChem database is persistent and the ONIOM calculations happen in an undefined order, the input strings should fully define the calculation you wish to have happen.

For instance, if the high model is DFT/B3LYP/6-311g** and the low model is DFT/LDA/3-21g, the ONIOM input might look like this

```
oniom
  model 3
  low  dft basis 3-21g    input "dft\; xc\; end"
  high dft basis 6-311g** input "dft\; xc b3lyp\; end"
end
```

The empty `XC` directive restores the default LDA exchange-correlation option (see Section 11.3). Note that semi-colons and other quotation marks inside the input string must be preceded by a backslash to avoid special interpretation.

See Section 21.6.4 for another example.

21.3 Use of symmetry

Symmetry should work just fine as long as the model and intermediate regions respect the symmetry — i.e., symmetry equivalent atoms need to be treated equivalently. If symmetry equivalent atoms must be treated in separate regions then the symmetry must be lowered (or completely switched off).

21.4 Molecular orbital files

The `VECTORS` directive in the ONIOM block is different to that elsewhere in NWChem. For each of the necessary combinations of theory and geometry you can specify a different file for the molecular orbitals. By default each combination will store the MO vectors in the permanent directory using a file name created by appending to the name of the calculation the following string

- low-real — `".lrmos"`
- low-inter — `".limos"`
- low-model — `".lmmos"`
- medium-inter — `".mimos"`
- medium-model — `".mmmos"`
- high-model — `".hmmos"`

Each calculation will utilize the appropriate vectors which is more efficient during geometry optimizations and frequency calculations, and is also useful for the initial calculation. In the absence of existing MO vectors files, the default atomic guess is used (see Section 10.5).

If special measures must be taken to converge the initial SCF, DFT or MCSCF calculation for one or more of the systems, then initial vectors may be saved in a file with the default name, or another name may be specified using the `VECTORS` directive. Note that subsequent vectors (e.g., from a geometry optimization) will be written back to this file, so take a copy if you wish to preserve it. To generate the initial guess for the model or intermediate systems it is necessary to generate the geometries which is most readily done, if there are link atoms, by just running NWChem on the input for the ONIOM calculation on your workstation. It will print these geometries before starting any calculations which you can then terminate.

E.g., in a calculation on Fe(III) surrounded by some ligands, it is hard to converge the full (real) system from the atomic guess so as to obtain a d^5 configuration for the iron atom since the d orbitals are often nominally lower in energy than some of the ligand orbitals. The most effective mechanism is to converge the isolated Fe(III) and then to use the fragment guess (see Section 10.5.1) as a starting guess for the real system. The resulting converged molecular orbitals can be saved either with the default name (as described above in this section), in which case no additional input is necessary. If an alternative name is desired, then the **VECTORS** directive may be used as follows

```
vectors low-real /u/rjh/jobs/fe_ether_water.mos
```

21.5 Restarting

Restart of ONIOM calculations does not currently work as smoothly as we would like. For geometry optimizations that terminated gracefully by running out of iterations, the restart will work as normal. Otherwise, specify in the input of the restart job the last geometry of the optimization. The Hessian information will be reused and the calculation should proceed losing at most the cost of one ONIOM gradient evaluation. For energy or frequency calculations, restart may not currently be possible.

21.6 Examples

21.6.1 Hydrocarbon bond energy

A simple two-layer model changing just the wavefunction with one link atom.

This reproduces the two-layer ONIOM (MP2:HF) result from Dapprich et al. for the reaction $R-CH_3 = R-CH_2+H$ with $R = CH_3$ using CH_4 as the model . The geometries of $R-CH_3$ and $R-CH_2$ are optimized at the DFT-B3LYP/6-311++G** level of theory, and then ONIOM is used to compute the binding energy using UMP2 for the model system and HF for the real system. The results, including MP2 calculations on the full system for comparison, are as given in Table 21.1

Theory	Me-CH2	Me-Me	H	De(Hartree)	De(kcal/mol)
B3LYP	-79.185062	-79.856575	-0.502256	0.169257	106.2
HF	-78.620141	-79.251701	-0.499817	0.131741	82.7
MP2	-78.904716	-79.571654	-0.499817	0.167120	104.9
MP2:HF	-78.755223	-79.422559	-0.499817	0.167518	105.1

Table 21.1: Energies for ONIOM example 1, hydrocarbon bond energy using MP2:HF two-layer model.

The following input first performs a calculation on $CH_3 - CH_2$, and then on $CH_3 - CH_3$. Note that in the second calculation we cannot use the full symmetry since we are breaking the C-C bond in forming the model system (the non-equivalence of the methyl groups is perhaps more apparent if we write $R - CH_3$).

```
start

basis spherical
  H library 6-311++G**; C library 6-311++G**
end
```

```
title "ONIOM Me-CH2"

geometry autosym
  H    -0.23429328     1.32498565     0.92634814
  H    -0.23429328     1.32498565    -0.92634814
  C    -0.13064265     0.77330370     0.00000000
  H    -1.01618703    -1.19260361     0.00000000
  H     0.49856072    -1.08196901    -0.88665533
  H     0.49856072    -1.08196901     0.88665533
  C    -0.02434414    -0.71063687     0.00000000
end

scf; uhf; doublet; thresh 1e-6; end
mp2; freeze atomic; end

oniom
  high mp2
  low  scf
  model 3   3 7 0.724
end

task oniom

title "ONIOM Me-Me"

geometry   # Note cannot use full D3D symmetry here
  H   -0.72023641     0.72023641    -1.16373235
  H    0.98386124     0.26362482    -1.16373235
  H   -0.26362482    -0.98386124    -1.16373235
  C    0.00000000     0.00000000    -0.76537515
  H    0.72023641    -0.72023641     1.16373235
  H   -0.98386124    -0.26362482     1.16373235
  H    0.26362482     0.98386124     1.16373235
  C    0.00000000     0.00000000     0.76537515
end

scf; rhf; singlet; end

oniom
  high mp2
  low  scf
  model 4   4 8 0.724
end

task oniom
```

21.6.2 Optimization and frequencies

A two-layer model including modification of theory, basis, ECP and total charge and no link atoms.

This input reproduces the ONIOM optimization and vibrational frequency calculation of $Rh(CO)_2Cp$ of Dapprich et al. The model system is $Rh(CO)_2^+$. The low theory is the Gaussian LANL2MB model (Hay-Wadt n+1 ECP with minimal basis on Rh, STO-3G on others) with SCF. The high theory is the Gaussian LANL2DZ model (another Hay-Wadt ECP with a DZ basis set on Rh, Dunning split valence on the other atoms) with DFT/B3LYP. Note that different names should be used for the basis set and ECP since the same mechanism is used to store them in the database.

```
start

ecp LANL2DZ_ECP
  rh library LANL2DZ_ECP
end

basis LANL2DZ spherical
  rh library LANL2DZ_ECP
  o library SV_(Dunning-Hay); c library SV_(Dunning-Hay); h library SV_(Dunning-Hay)
end

ecp Hay-Wadt_MB_(n+1)_ECP
  rh library Hay-Wadt_MB_(n+1)_ECP
end

# This is the minimal basis used by Gaussian.  It is not the same
# as the one in the EMSL basis set library for this ECP.
basis Hay-Wadt_MB_(n+1) spherical
  Rh s; .264600D+01 -.135541D+01; .175100D+01  .161122D+01; .571300D+00  .589381D+00
  Rh s; .264600D+01  .456934D+00; .175100D+01 -.595199D+00; .571300D+00 -.342127D+00
        .143800D+00  .410138D+00; .428000D-01  .780486D+00
  Rh p; .544000D+01 -.987699D-01; .132900D+01  .743359D+00; .484500D+00  .366846D+00
  Rh p; .659500D+00 -.370046D-01; .869000D-01  .452364D+00; .257000D-01  .653822D+00
  Rh d; .366900D+01  .670480D-01; .142300D+01  .455084D+00; .509100D+00  .479584D+00
        .161000D+00  .233826D+00
  o  library sto-3g; c  library sto-3g; h  library sto-3g
end

charge 0
geometry autosym
  rh       0.00445705    -0.15119674     0.00000000
  c       -0.01380554    -1.45254070     1.35171818
  c       -0.01380554    -1.45254070    -1.35171818
  o       -0.01805883    -2.26420212     2.20818932
  o       -0.01805883    -2.26420212    -2.20818932
  c        1.23209566     1.89314720     0.00000000
  c        0.37739392     1.84262319    -1.15286640
  c       -1.01479160     1.93086461    -0.70666350
  c       -1.01479160     1.93086461     0.70666350
  c        0.37739392     1.84262319     1.15286640
  h        2.31251453     1.89903673     0.00000000
  h        0.70378132     1.86131979    -2.18414218
  h       -1.88154273     1.96919306    -1.35203550
  h       -1.88154273     1.96919306     1.35203550
```

```
  h        0.70378132     1.86131979     2.18414218
end

dft; grid fine; convergence gradient 1e-6 density 1e-6; xc b3lyp; end
scf; thresh 1e-6; end

oniom
  low scf basis Hay-Wadt_MB_(n+1) ecp  Hay-Wadt_MB_(n+1)_ECP
  high dft basis LANL2DZ ecp LANL2DZ_ECP
  model 5 charge 1
  print low
end

task oniom optimize
task oniom freq
```

21.6.3 A three-layer example

A three layer example combining CCSD(T), and MP2 with two different quality basis sets, and using multiple link atoms.

The full system is tetra-dimethyl-amino-ethylene (TAME) or (N(Me)2)2-C=C-(N(Me)2)2. The intermediate system is (NH2)2-C=C-(NH2)2 and H2C=CH2 is the model system. CCSD(T)+aug-cc-pvtz is used for the model region, MP2+aug-cc-pvtz for the intermediate region, and MP2+aug-cc-pvdz for everything.

In the real geometry the first two atoms (C, C) are the model system (link atoms will be added automatically). The first six atoms (C, C, N, N, N, N) describe the intermediate system (again with link atoms to be added automatically). The atoms have been numbered using comments to make the bonding input easier to generate.

To make the model system, four C-N bonds are broken between the ethylene fragment and the dimethyl-amino groups and replaced with C-H bonds. To make the intermediate system, eight C-N bonds are broken between the nitrogens and the methyl groups and replaced with N-H bonds. The scaling factor could be chosen differently for each of the bonds.

```
start

geometry
  C  0.40337795 -0.17516305 -0.51505208  # 1
  C -0.40328664  0.17555927  0.51466084  # 2
  N  1.87154979 -0.17516305 -0.51505208  # 3
  N -0.18694782 -0.60488524 -1.79258692  # 4
  N  0.18692927  0.60488318  1.79247594  # 5
  N -1.87148219  0.17564718  0.51496494  # 6
  C  2.46636552  1.18039452 -0.51505208  # 7
  C  2.48067731 -1.10425355  0.46161675  # 8
  C -2.46642715 -1.17982091  0.51473105  # 9
  C -2.48054940  1.10495864 -0.46156202  # 10
  C  0.30027136  0.14582197 -2.97072148  # 11
  C -0.14245927 -2.07576980 -1.96730852  # 12
  C -0.29948109 -0.14689874  2.97021079  # 13
  C  0.14140463  2.07558249  1.96815181  # 14
```

```
  H  0.78955302  2.52533887  1.19760764
  H -0.86543435  2.50958894  1.88075113
  ... and 22 other hydrogen atoms on the methyl groups
end

basis aug-cc-pvtz spherical
  C library aug-cc-pvtz; H library aug-cc-pvtz
end

basis aug-cc-pvdz spherical
  C library aug-cc-pvtz; H library aug-cc-pvtz
end

oniom
  high ccsd(t) basis aug-cc-pvtz
  medium mp2 basis aug-cc-pvtz
  low mp2 basis aug-cc-pvdz
  model 2   1 3  0.87   1 4  0.87   2 5  0.87   2 6  0.87

  inter 6   3 7  0.69   3 8  0.69   4 11 0.69   4 12 0.69 \
            5 13 0.69   5 14 0.69   6 9  0.69   6 10 0.69
end

task oniom
```

21.6.4 DFT with and without charge fitting

Demonstrates use of general input strings.

A two-layer model for anthracene (a linear chain of three fused benzene rings) using benzene as the model system. The high-level theory is DFT/B3LYP/TZVP with exact Coulomb. The low level is DFT/LDA/DZVP2 with charge fitting.

Note the following.

1. The semi-colons and quotation marks inside the input string must be quoted with backslash.
2. The low level of theory sets the fitting basis set and the high level of theory unsets it.

```
start
geometry
  symmetry d2h
  C    0.71237329    -1.21458940     0.0
  C   -0.71237329    -1.21458940     0.0
  C    0.71237329     1.21458940     0.0
  C   -0.71237329     1.21458940     0.0
  C   -1.39414269     0.00000000     0.0
  C    1.39414269     0.00000000     0.0
  H   -2.47680865     0.00000000     0.0
  H    2.47680865     0.00000000     0.0
  C    1.40340535    -2.48997027     0.0
```

```
  C   -1.40340535    -2.48997027     0.0
  C    1.40340535     2.48997027     0.0
  C   -1.40340535     2.48997027     0.0
  C    0.72211503     3.64518615     0.0
  C   -0.72211503     3.64518615     0.0
  C    0.72211503    -3.64518615     0.0
  C   -0.72211503    -3.64518615     0.0
  H    2.48612947     2.48094825     0.0
  H    1.24157357     4.59507342     0.0
  H   -1.24157357     4.59507342     0.0
  H   -2.48612947     2.48094825     0.0
  H    2.48612947    -2.48094825     0.0
  H    1.24157357    -4.59507342     0.0
  H   -1.24157357    -4.59507342     0.0
  H   -2.48612947    -2.48094825     0.0
end

basis small
  h library DZVP_(DFT_Orbital)
  c library DZVP_(DFT_Orbital)
end

basis fitting
  h library DGauss_A1_DFT_Coulomb_Fitting
  c library DGauss_A1_DFT_Coulomb_Fitting
end

basis big
  h library TZVP_(DFT_Orbital)
  c library TZVP_(DFT_Orbital)
end

oniom
  model 8   1 9 0.75   2 10 0.75   3 11 0.75   4 12 0.75
  high dft basis big   input "unset \"cd basis\"\; dft\; xc b3lyp\; end"
  low  dft basis small input "set \"cd basis\" fitting\; dft\; xc\; end"
end

task oniom
```

Chapter 22

Vibrational frequencies

The nuclear hessian which is used to compute the vibrational frequencies can be computed by finite difference for any ab initio wave-function that has analytic gradients. The appropriate nuclear hessian generation algorithm is chosen based on the user input when `TASK <theory> frequencies` is the task directive.

The vibrational package was integrated from the Utah Messkit and can use any nuclear hessian generated from the driver routines, finite difference routines or any analytic hessian modules. There is no required input for the "VIB" package. VIB computes the Infra Red frequencies and intensities[1] for the computed nuclear hessian and the "projected" nuclear hessian. The VIB module projects out the translations and rotations of the nuclear hessian using the standard Eckart projection algorithm. It also computes the zero point energy for the molecular system based on the frequencies obtained from the projected hessian.

The default mass of each atom is used unless an alternative mass is provided via the geometry input, (c.f., 6) or redefined using the vibrational module input. The default mass is the mass of the most abundant isotope of each element.[2] If the abundance was roughly equal, the mass of the isotope with the longest half life was used.

22.1 Vibrational Module Input

All input for the Vibrational Module is optional since the default definitions will compute the frequencies and IR intensities[3]. The generic module input can begin with `vib`, `freq`, `frequency` and has the form:

```
{freq || vib || frequency}
  reuse [<string> hessian_filename]
  mass <integer> lexical_index <real> new_mass
  mass <string> tag_identifier <real> new_mass
  animate [<real> step_size_for_animation]
end
```

[1] Intensities are only computed if the dipole derivatives are available; these are computed by default for most methods that use the finite difference driver routines

[2] c.f., "The Elements" by John Emsley, Oxford University Press, (C) 1989, ISBN 0-19-855237-8.

[3] The geometry specification at the point where the hessian is computed must be the default "geometry" on the current run-time-data-base for the projection to work properly.

22.1.1 Hessian File Reuse

By default the `task <theory> frequencies` directive will recompute the hessian. To reuse the previously computed hessian you need only specify `reuse` in the module input block. If you have stored the hessian in an alternate place you may redirect the reuse directive to that file by specifying the path to that file.

```
reuse /path_to_hessian_file
```

This will reuse your saved Hessian data but one caveat is that the geometry specification at the point where the hessian is computed must be the default "geometry" on the current run-time-data-base for the projection to work properly.

22.1.2 Redefining Masses of Elements

You may also modify the mass of a specific center or a group of centers via the input.

To modify the mass of a specific center you can simply use:

```
mass 3 4.00260324
```

which will set the mass of center 3 to 4.00260324 AMUs. The lexical index of centers is determined by the geometry object.

To modify all Hydrogen atoms in a molecule you may use the tag based mechanism:

```
mass hydrogen 2.014101779
```

The mass redefinitions always start with the default masses and change the masses in the order given in the input. Care must be taken to change the masses properly. For example, if you want all hydrogens to have the mass of Deuterium and the third hydrogen (which is the 6th atomic center) to have the mass of Tritium you must set the Deuterium masses first with the tag based mechanism and then set the 6th center's mass to that of Tritium using the lexical center index mechanism.

The mass redefinitions are not fully persistent on the run-time-data-base. Each input block that redefines masses will invalidate the mass definitions of the previous input block. For example,

```
freq
  reuse
  mass hydrogen 2.014101779
end
task scf frequencies
freq
  reuse
  mass oxygen 17.9991603
end
task scf frequencies
```

will use the new mass for all hydrogens in the first frequency analysis. The mass of the oxygen atoms will be redefined in the second frequency analysis but the hydrogen atoms will use the default mass. To get a modified oxygen and hydrogen analysis you would have to use:

```
freq
  reuse
  mass hydrogen 2.014101779
end
task scf frequencies
freq
  reuse
  mass hydrogen 2.014101779
  mass oxygen 17.9991603
end
task scf frequencies
```

22.1.3 Animation

The "VIB" module also can generate mode animation input files in the standard xyz file format for graphics packages like RasMol or XMol There are scripts to automate this for RasMol in .../nwchem/contrib/rasmolmovie. Each mode will have 20 xyz files generated that cycle from the equilibrium geometry to 5 steps in the positive direction of the mode vector, back to 5 steps in the negative direction of the mode vector, and finally back to the equilibrium geometry. By default these files are **not** generated. To activate this mechanism simply use the following input directive

```
  animate
```

anywhere in the frequency/vib input block.

Controlling the Step Size Along the Mode Vector

By default, the step size used is 0.15 a.u. which will give reliable animations for most systems. This can be changed via the input directive

```
  animate real <step_size>
```

where `<step_size>` is the real number that is the magnitude of each step along the eigenvector of each nuclear hessian mode in atomic units.

22.1.4 An Example Input Deck

This example input deck will optimize the geometry for the given basis set, compute the frequencies for H_2O, D_2O, HDO, and TDO.

```
start  h2o
title Water
geometry units au autosym
  O      0.00000000    0.00000000    0.00000000
  H      0.00000000    1.93042809   -1.10715266
  H      0.00000000   -1.93042809   -1.10715266
end
basis noprint
  H library sto-3g
  O library sto-3g
end
scf; thresh 1e-6; end
driver; tight; end
task scf optimize

scf; thresh 1e-8; print none; end
task scf freq

freq
 reuse; mass H 2.014101779
end
task scf freq

freq
 reuse; mass 2 2.014101779
end
task scf freq

freq
 reuse; mass 2 2.014101779 ; mass 3 3.01604927
end
task scf freq
```

Chapter 23

DPLOT

```
DPLOT
  ...
END
```

This directive is used to obtain the plots of various types of electron densities (or orbitals) of the molecule. The electron density is calculated on a specified set of grid points using the molecular orbitals from SCF or DFT calculation. The output file is either in MSI Insight II contour format (default) or in the Gaussian Cube format. DPLOT is not executed until the "task dplot" directive is given. Different sub-directives are described below.

23.1 GAUSSIAN — Gaussian Cube format

```
GAUSSIAN
```

A ouptfile is generate in Gaussian Cube format. You can visualize this file using gOpenMol after converting the Gaussian Cube file with gcube2plt.

23.2 TITLE — Title for *Insight*

```
TITLE
<string Title default Unknown Title>
```

This sub-directive specifies a title line for the generated input to the *Insight* program. Only one line is allowed.

23.3 LIMITXYZ — Plot limits

```
LIMITXYZ [units <string Units default angstroms>]
<real X_From> <real X_To> <integer No_Of_Spacings_X>
```

```
<real Y_From> <real Y_To> <integer No_Of_Spacings_Y>
<real Z_From> <real Z_To> <integer No_Of_Spacings_Z>
```

This sub-directive specifies the limits of the cell to be plotted. The grid is generated using `No_Of_Spacings` + `1` points along each direction. The known names for `Units` are `angstroms`, `au` and `bohr`.

23.4 SPIN — Density to be plotted

```
SPIN <string Spin default total>
```

This sub-directive specifies, what kind of density is to be computed. The known names for `Spin` are `total`, `alpha`, `beta` and `spindens`, the last being computed as the difference between α and β electron densities.

23.5 OUTPUT — Filename for *Insight*

```
OUTPUT <string File_Name default dplot>
```

This sub-directive specifies the name of the generated input to the *Insight* program. The name `OUTPUT` is reserved for the standard NWChem output.

23.6 VECTORS — MO vector file name

```
VECTORS <string File_Name default movecs> [<string File_Name2>]
```

This sub-directive specifies the name of the molecular orbital file. If the second file is optionally given the density is computed as the difference between the corresponding electron densities. The vector files have to match.

23.7 WHERE — Density evaluation

```
WHERE <string Where default grid>
```

This sub-directive specifies where the density is to be computed. The known names for `Where` are `grid` (the calculation of the density is performed on the set of a grid points specified by the sub-directive `LimitXYZ` and the file specified by the sub-directive `Output` is generated), `nuclei` (the density is computed at the position of the nuclei and written to the NWChem output) and `g+n` (both).

23.8 ORBITAL — Orbital sub-space

```
ORBITALS [<string Option default density>]
<integer No_Of_Orbitals>
<integer Orb_No_1 Orb_No_2 ...>
```

This sub-directive specifies the subset of the orbital space for the calculation of the electron density. The density is computed using the occupation numbers from the orbital file modified according to the `Spin` directive. If the contours of the orbitals are to be plotted `Option` should be set to `view`. Note, that in this case `No_Of_Orbitals` should be set to `1` and sub-directive `Where` is automatically set to `grid`. Also specification of two orbital files conflicts with the `view` option. α orbitals are always plotted unless `Spin` is set to `beta`.

23.9 Examples

Charge Density

Example of charge density plot (with Gaussian Cube output):

```
start n2
geometry
  n  0 0   0.53879155
  n  0 0  -0.53879155
end
basis;  n library cc-pvdz;end
scf
vectors  output n2.movecs
end
dplot
  TITLE;HOMO
  vectors n2.movecs
   LimitXYZ
 -3.0 3.0 10
-3.0 3.0 10
-3.0  3.0  10
  spin total
  gaussian
  output lumo.cube
end
task scf
task dplot
```

Molecular Orbital

Example of orbital plot (with Insight II contour output):

```
start n2
geometry
  n  0 0   0.53879155
  n  0 0  -0.53879155
end
basis;  n library cc-pvdz;end
scf
vectors  output n2.movecs
```

```
end
dplot
  TITLE;HOMO
  vectors n2.movecs
   LimitXYZ
 -3.0 3.0 10
-3.0 3.0 10
-3.0  3.0  10
  spin total
  orbitals view; 1; 7
  output homo.grd
end
task scf
task dplot
```

Chapter 24

Properties

```
PROPERTY
  [property name]
  [CENTER ((com || coc || origin || arb <real x y z>) default coc)]
  [VECTORS ...]
END
```

Calculation of properties is accomplished with `TASK PROPERTY` after the completion of an energy (or MP2 gradient) calculation. The following properties can be computed for all wavefunctions that produce orbitals, including Hartree-Fock (closed-shell RHF, open-shell ROHF, and open-shell UHF), DFT (closed-shell and open-shell spin unrestricted), MCSCF (complete active space), and MP2 (closed-shell RHF and open-shell UHF).

- natural bond analysis
- dipole moment
- quadrupole moment
- octupole moment
- Mulliken population analysis and bond order analysis
- electrostatic potential (diamagnetic shielding) at nuclei
- electric field at nuclei
- electric field gradient at nuclei
- electron and spin density at nuclei
- NMR chemical shifts (GIAO method) only for closed-shell RHF

The default molecular orbital file `$file_prefix$.movecs` is used unless a vectors directive (Section 10.5) is provided. It is therefore only necessary to include a vectors directive if the MO vectors to be analyzed are not coming from the default file, e.g., if they have been previously redirected, or if MP2 natural orbitals (file extension `".mp2nos"`) are being anaylzed. The MP2 natural orbitals MUST be used if the user wants MP2 properties.

24.1 Subdirectives

Note that presenting any property input causes all previous property input to be "forgotten", unlike other NWChem modules.

Each property can be requested by means of a subdirective among the subdirectives provided :

- nbofile
- dipole
- quadrupole
- octupole
- mulliken
- esp
- efield
- efieldgrad
- electrondensity
- giao
- all

The "all" keyword generates all currently available properties.

The request to NBOFILE does not execute the Natural Bond Analysis code, but simply creates an input file to be used as input to the stand-alone NBO code. To execute the NBO analysis directly, see Section 33.1. All other properties are calculated upon request.

An additional subdirective is provided to specify the origin of the molecular orbitals used in the calculation of the molecular properties. This is the 'vectors' subdirective, also used in the SCF and DFT tasks. For a full description of this subdirective the user is refered to the description found in the SCF description. By default, the input file used for the calculation of the properties has the .movecs name extension.

The user also has the option to choose the center of expansion for the dipole, quadrupole, and octupole calculations.

```
[CENTER ((com || coc || origin || arb <real x y z>) default coc)]
```

com is the center of mass, coc is the center of charge, origin is (0.0, 0.0, 0.0) and arb is any arbitrary point which must be accompanied by the coordinated to be used. Currently the x, y, and z coordinates must be given in the same units as UNITS in GEOMETRY (See Section 6.1).

24.1.1 Nbofile

Following the successful completion of an electronic structure calculation, a Natural Bond Orbital (NBO) analysis may be carried out in the following way. On restart specify the TASK as PROPERTY and supply the sub-directive NBOFILE to the PROPERTY directive. NWChem will query the rtdb and construct an

ASCII file, `<file_prefix>.gen`, that may be used as input to the stand alone version of the NBO program, gennbo. `<file_prefix>` is equal to string following the RESTART directive. The input deck may be edited to provide additional options to the NBO calculation, (see the NBO user's manual for details.) The other option in to directly run the NBO analysis (See Section 33.1 for more information).

Chapter 25

Electrostatic potentials

The NWChem Electrostatic Potential (ESP) module derives partial atomic charges that fit the quantum mechanical electrostatic potential on selected grid points.

The ESP module is specified by the NWChem task directive

```
task esp
```

The input for the module is taken from the ESP input block

```
esp
end
```

25.1 Grid specification

The grid points for which the quantum mechanical electrostatic potential is evaluated and used in the fitting procedure of the partial atomic charges all lie outside the van der Waals radius of the atoms and within a cutoff distance from the atomic centers. The following input parameters determine the selection of grid points.

- If a grid file is found, the grid will be read from that file. If no grid file is found, or the keyword

  ```
  recalculate
  ```

  is given, the grid and the electrostatic potential is recalculated.

- The extent of the grid is determined by

  ```
  range <real rcut>
  ```

  where `rcut` is the maximum distance in nm between a grid point and any of the atomic centers. When omitted, a default value for `rcut` of 0.3 nm is used.

- The grid spacing is specified by

  ```
  spacing <real spac>
  ```

where `spac` is the grid spacing in nm for the regularly spaced grid points. If not specified, a default spacing of 0.05 nm is used.

- The van der Waals radius of an element can be specified by

```
radius <integer iatnum> <real atrad>
```

where `iatnum` is the atomic number for which a van der Waals radius of `atrad` in nm will be used in the grid point determination. Default values will be used for atoms not specified.

- The probe radius in nm determining the envelope around the molecule is specified by

```
probe <real probe default 0.07>
```

- The distance between atomic center and probe center can be multiplied by a constant factor specified by

```
factor <real factor default 1.0>
```

All grid points are discarded that lie within a distance `factor*(radius(i)+probe)` from any atom i.

- Schwarz screening is applied using

```
screen [<real scrtol default 1.0D-5>]
```

25.2 Constraints

Additional constraints to the partial atomic charges can be imposed during the fitting procedure.

- The net charge of a subset of atoms can be constrained using

```
constrain <real charge> {<integer iatom>}
```

where `charge` is the net charge of the set of atoms `{iatom}`. A negative atom number `iatom` can be used to specify that the partial charge of that atom is substracted in the sum for the set.

- The net charge of a sequence of atoms can be constrained using

```
constrain <real charge> <integer iatom> through <integer jatom>
```

where `charge` is the net charge of the set of atoms `{[iatom:jatom]}`.

- A group of atoms can be constrained to have the same charge with

```
constrain equal {<integer iatom>}
```

- The individual charge of a group of atoms can be constrained to be equal to those of a second group of atoms with

```
constrain group <integer iatom> <integer jatom> to <integer katom> <integer latom>
```

resulting in the same charge for atoms `iatom` and `katom`, for atoms `iatom+1` and `katom+1`, ... for atoms `jatom` and `latom`.

- A special constraint

```
constrain xhn <integer iatom> {<integer jatom>}
```

can be used to constrain the set `{iatom,{jatom}}` to zero charge, and constrain all atoms in `{jatom}` to have the same charge. This can be used, for example, to restrain a methyl group to zero charge, and have all hydrogen carrying identical charges.

25.3 Restraints

Restraints can be applied to each partial charge using the RESP charge fitting procedure.

- The directive for charge restraining is

```
restrain [hfree] (harmonic [<real scale>] | \
 hyperbolic [<real scale> [<real tight>]]  \
  [maxiter <integer maxit>]  [tolerance <real toler>])
```

where `hfree` can be specified to exclude hydrogen atoms from the restaining procecure. Variable `scale` is the strength of the restraint potential, with a default of $0.005au$ for the harmonic restraint and a default value of $0.001au$ for the hyperbolic restraint. For the hyperbolic restraints the tightness `tight` can be specified to change the default value of $0.1e$. The iteration count that needs to be carried out for the hyperbolic restraint is determined by the maximum number of allowed iterations `maxiter`, with a default value of 25, and the tolerance in the convergence of the partial charges `toler`, with a default of $0.001e$.

Chapter 26

Prepare

The **prepare** module is used to set up the necessary files for a molecular dynamics simulation with **NWChem**. User supplied coordinates can be used to generate topology and restart files. The topology file contains all static information about a molecular system, such as lists of atoms, bonded interactions and force field parameters. The restart file contains all dynamic information about a molecular system, such as coordinates, velocities and properties.

Without any input, the prepare module checks the existence of a topology and restart file for the molecular systems. If these files exist, the module returns to the main task level without action. The module will generate these files when they do not exist. Without any input to the module, the generated system will be for a non-solvated isolated solute system.

To update existing files, including solvation, the module requires input directives read from an input deck,

```
prepare
 ...
end
```

The prepare module performs three sub-tasks:

* **sequence generation**
  This sub-task analyzes the supplied coordinates from a PDB-formatted file or from the input geometry, and generates a sequence file, containing the description of the system in terms of basic building blocks found as fragment or segment files in the database directories for the force field used. If these files do not exist, they are generated based on the supplied coordinates. This process constists of generating a fragment file with the list of atoms with their force field dependent atom types, partial atomic charges calculated from a Hartree Fock calculation for the fragment, followed by a restrained electrostatic potential fit, and a connectivity list. From the information on this fragment file the lists of all bonded interactions are generated, and the complete lists are written to a segment file.

* **topology generation**
  Based on the generated or user-supplied sequence file and the force field specific segment database files, this sub-task compiles the lists of atoms, bonded interactions, excluded pairs, and substitutes the force field parameters. Special commands may be given to specify interaction parameters that will be changing in a free energy evaluation.

* **restart generation**
  Using the user supplied coordinates and the topology file for the chemical system, this sub-task generates a restart file for the system with coordinates, velocities and other dynamic information. This step may include solvation of the chemical system and specifying periodic boundary conditions.

Files involved in the preparation phase exist in the following hierarchy:

* **standards**
  The standard database files contain the original force field information. These files are to reside in a directory that is specified in the file $HOME/.nwchemrc. There will be such a directory for each supported force field. These directories contain fragment files (with extension frg), segment files (with extension sgm) and a parameter file (with the name of the force field and with extension par).
* **extensions**
  These database files contain generally accepted extensions to the original force field and are to reside in a separate directory that is specified in the file $HOME/.nwchemrc. There will be such a directory for each supported force field. These directories contain fragment files (with extension frg), segment files (with extension sgm) and a parameter file (with the name of the force field and with extension par).
* **user preferences**
  These database files contain user preferred extensions to the original force field and are to reside in a separate directory that is specified in the file $HOME/.nwchemrc. Separate directories of this type should be defined for each supported force field. These directories may contain fragment files (with extension frg), segment files (with extension sgm) and a parameter file (with the name of the force field and with extension par).
* **temporary files**
  Temporary database files contain user preferred extensions to the original force field and are to reside in a separate directory that is specified in the file $HOME/.nwchemrc. There be such a directory for each supported force field. These directories may contain fragment files (with extension frg), segment files (with extension sgm) and a parameter file (with the name of the force field and with extension par). If not specified, temporary files will be taken from the current directory.

Data is taken from the database files searched in the above order. If data is specified more than once, the last found values are used. For example, if some standard segment is redefined in a temporary file, the latter one will be used. This allows the user to redefine standards or extensions without having to modify those database files, which may reside in a generally available, non-modifyable directory.

The most common problems with the **prepare** module are

The format of the pdb file does not conform to the pdb standard. In particular, atom names need to correspond with definitions in the fragment and segment database files, and should adhere to IUPAC recommendations as adopted by the pdb standard. If this problem occurs, the pdb file will need to be corrected.

Non-standard segments may contain atoms that could not be atom typed with the existing typing rules in the force field parameter files. When this happens, additional typing rules can be included in the parameter file, or the fragment file may be manually typed.

Parameters for atom types or bonded interactions do not exist in the force field. When this happens, additional parameters may be defined in the parameter files, or the segment file may be edited to include explicit parameters.

26.1 Default database directories

The file $HOME/.nwchemrc may contain the following entries that determine which files are used by the prepare module.

```
ffield <string ffname>
```

This entry specifies the default force field. Database files supplied with **NWChem** currently support values for `ffname` of **amber**, referring to AMBER95, and **charmm**, referring to the academic CHARMM22 force field.

```
<string ffname>_(s | x | u | t) <string ffdir>
```

Entries of this type specify the directory `ffdir` in which force field database files can be found. The prepare module will only use files in directories specified here. One exception is that files in the current work directory will be used if no directory with temporary files is specified.

```
<string solvnam> <string solvfil>
```

This entry may be used to identify a pure solvent restart file `solvfil` by a name `solvnam`

An example file $HOME/.nwchemrc is:

```
ffield amber
amber_s /msrc/proj/nwchem/share/amber/amber_s/
amber_x /msrc/proj/nwchem/share/amber/amber_x/
amber_u /usr/people/d3j191/data/amber/amber_u/
spce /msrc/proj/nwchem/share/solvents/spce.rst
charmm_s /msrc/proj/nwchem/share/charmm/charmm_s/
charmm_x /msrc/proj/nwchem/share/charmm/charmm_x/
```

26.2 System name and coordinate source

```
system <string sys_calc>
```

The system name can be explicitly specified for the **prepare** module. If not specified, the system name will be taken from a specification in a previous **md** input block, or derived from the run time database name.

```
source ( pdb | rtdb )
```

The source of the coordinates can be explicitly specified to be from a PDB formatted file `calc`.pdb, or from a geometry object in the run time database. If not specified, a pdb file will be used when it exists in the current directory or the rtdb geometry otherwise.

```
model <integer modpdb default 0>
```

If a PDB formatted source file contains different MODELs, the `model` keyword can be used to specify which MODEL will be used to generate the topology and restart file. If not specified, the first MODEL found on the PDB file will be read.

```
altloc <character locpdb default ' '>
```

The `altloc` keyword may be used to specify the use of alternate location coordinates on a PDB file.

```
chain <character chnpdb default ' '>
```

The `chain` keyword may be used to specify the chain identifier for coordinates on a PDB file.

```
sscyx
```

Keyword `sscyx` may be used to rename cysteine residues that form sulphur bridges to CYX.

```
hbuild
```

Keyword `hbuild` may be used to add hydrogen atoms to the unknown segments of the structure found on the pdb file.

26.3 Sequence file generation

If no existing sequence file is present in the current directory, or if the `new_seq` keyword was specified in the **prepare** input deck, a new sequence file is generated from information from the pdb file, and the following input directives.

```
maxscf <integer maxscf default 20>
```

Variable maxscf specifies the maximum number of atoms in a segment for which partial atomic charges will be determined from an SCF calculation followed by RESP charge fitting. For larger segments a crude partial charge guestimation will be done.

```
qscale <real qscale default 1.0>
```

Variable qscale specifies the factor with which SCF/RESP determined charges will be multiplied.

```
modify sequence { <integer sgmnum>:<string sgmnam> }
```

This command specifies that segment **sgmnam** should be used for segment with number *sgmnum*. This command can be used to specify a particular protonation state. For example, the following command specifies that residue 114 is a hystidine protonated at the N_ϵ site and residue 202 is a hystidine protonated at the N_δ site:

```
modify sequence 114:HIE 202:HID
```