Manual

MLGAUSS–version 3.0

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Abstract: MLGAUSS is a computer program for performing geometry optimizations and calculating single-point energies, gradients, and/or Hessians using ten different multi-coefficient correlation methods that include the version 3 of scaling all correlation (SAC/3) method, three balanced multi-coefficient correlation (BMC) methods (BMC-QCISD, BMC-CCSD, BMC-CCSD-C), and the version 3 of six different multi-coefficient correlated (MCCM/3) methods (MC-CO/3, MC-UT/3, MC-QCISD/3, MCG3/3, G3SX(MP3), and G3SX); sixteen multi-coefficient extrapolated DFT methods, also called doubly hybrid DFT (MC3BB, MC3MPW, MC3MPWB, MC3TS, MCCO-MPW, MCCO-MPWB, MCCO-TS, MCUT-MPW, MCUT-MPWB, MCUT-TS, MCQCISD-MPWB, MCUT-TS, MCQCISD-MPW, MCQCISD-MPWB, MCQCISD-TS, MCG3-MPW, MCG3-MPWB, and MCG3-TS); and one infinite basis (IB) method (MP2/IB). The MLGAUSS uses optimizers in GAUSSIAN09 or GAUSSIAN03 for geometry optimization.

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Chapter One

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1. Introduction

MLGAUSS is a computer program for calculating optimized geometries, single-point energies, single-point gradients, and/or single-point Hessians using dual-level and multi-level methods. The present version supports the scaling all correlation (SAC)[1] method, the multi-coefficient correlation methods (MCCMs),[2] the multi-coefficient extrapolated DFT methods,[3] also called doubly hybrid DFT (DHDFT), and the infinite basis set (IB) method.[25] The MCCMs include the MCCM/3 suite,[2] the BMC- QCISD, BMC-CCSD, and BMC-CCSD-C methods,[4] and the G3SX(MP3) and G3SX methods.[5]

The name of MLGAUSS stands for a "multi-level program for GAUSSIAN users". The geometry input file for MLGAUSS is the same as the GAUSSIAN09/03 program, and MLGAUSS also uses the optimizers in GAUSSIAN09/03 for geometry optimization. Potential users of MLGAUSS may also which to consider the MULTILEVEL program. Both programs include MCCMs (MULTILEVEL also has IMO options), with some MCCMs in only one of the programs and others in both. The main difference is that MULTILEVEL uses, in addition to the GAUSSIAN geometry optimizer, its own geometry optimizer and does not require a GAUSSIAN license (although it can be used with GAUSSIAN if such a license is available), but MLGAUSS uses the GAUSSIAN geometry optimizers and does require a GAUSSIAN license.

Figure 1: Classification of all the methods available in MLGAUSS-v3.0
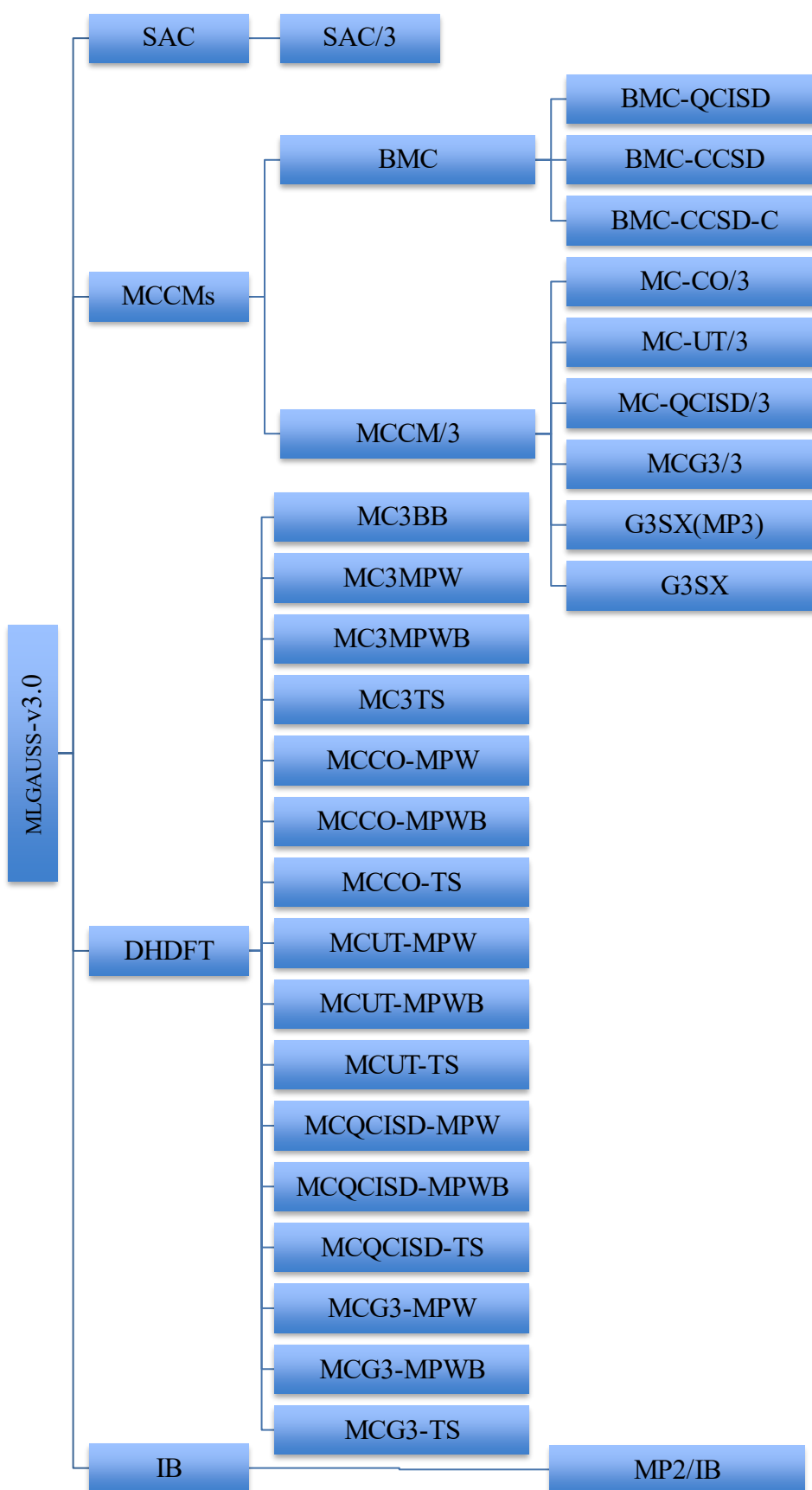
Chapter Two

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2. References for MLGAUSS Program

The recommended reference for the current version of the code is given below in three styles, namely, in *J. Chem. Phys.* style, *J. Amer. Chem. Soc.* style., and *Chem. Phys. Lett.* style.

J. Chem. Phys. style:

Y. Zhao, R. Meana-Pañeda, and D. G. Truhlar, MLGAUSS-version 3.0 (University of Minnesota, Minneapolis,

2004).

J. Amer. Chem. Soc. style:

Zhao, Y.; Meana-Pañeda, R.; Truhlar, D. G. *MLGAUSS-version 3.0*, University of Minnesota: Minneapolis,

2005.

Chem. Phys. Lett. style:

Y. Zhao, R. Meana-Pañeda, D.G. Truhlar, MLGAUSS-version 3.0. University of Minnesota, Minneapolis,

2004.

Of course, the user should also give the GAUSSIAN09 or GAUSSIAN03 reference.

Chapter Three

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3. General Program Description

MLGAUSS is written in the PERL language. MLGAUSS consists of a PERL script *Gau_External*. The overall control of the program is

GAUSSIAN09/03 ↔ *Gau_External* ↔ GAUSSIAN09/03

where GAUSSIAN09/03 is shorthand for "GAUSSIAN09 or GAUSSIAN03". First one needs to provide a GAUSSIAN09/03 input file with the *external* keyword and start the primary GAUSSIAN09/03 calculation. GAUSSIAN09/03 will call *Gau_External* to provide information needed for each single-level calculation. *Gau_External* will write input files for each single-level calculation, and it starts the secondary GAUSSIAN09/03 calculations. When the secondary GAUSSIAN09/03 calculations finish, *Gau_External* extracts results from the formatted checkpoint files of the secondary GAUSSIAN calculations, then it calculates the multi-level energy, gradient and/or Hessian and passes them to the primary GAUSSIAN09/03 calculations.

Chapter 4 presents the theoretical background of all methods in this program. Chapter 5 describes the optimization procedures. Chapter 6 summarizes the input files. Chapters 7 describes installation, and see Chapter 8 for a complete listing of all the files that compose the source code of MLGAUSS, as well as a description of the subprograms within the source code. Chapter 9 presents the test jobs. Chapter 10

describes the computers and operating systems on which the code has been tested.

Chapter 11 gives bibliography, and Chapter 12 is the revision history.

Chapter Four

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4. Theoretical Background

This chapter describes the SAC method, MCCMs, and multi-coefficient extrapolated DFT methods available in this version of the MLGAUSS code.

4.1. Notation

Throughout this manual we will use the pipe "|" to represent the energy difference either between two one-electron basis sets B1 and B2, between two many-body levels L1 and L2, e.g., Møller-Plesset second-order perturbation theory and Hartree-Fock theory, or between the level increments obtained with two different basis sets. The energy difference between two basis sets will be represented as

$$\Delta E(L/B2\,|\,B1) \equiv E(L/B2) - E(L/B1) \tag{2}$$

where L is a particular electronic structure method, and B1 is smaller than B2. The energy change that occurs upon improving the treatment of the correlation energy will be represented by

$$\Delta E(L2\,|\,L1/B) \equiv E(L2/B) - E(L1/B) \tag{3}$$

where L1 is a lower many-electron level of theory than L2, and B is a common basis set. Finally, the change in energy increment due to increasing the many-electron level of the treatment of the correlation energy with one one-electron basis set as compared to the increment obtained with a smaller basis set will be represented as

$$\Delta E(\text{L2} \,|\, \text{L1} \,/\, \text{B2} \,|\, \text{B1}) \equiv E(\text{L2} \,/\, \text{B2}) - E(\text{L1} \,/\, \text{B2}) - [E(\text{L2} \,/\, \text{B1}) - E(\text{L1} \,/\, \text{B1})].$$

(4)

Additionally, some standard abbreviations for electronic structure methods will be used throughout this manual, namely

HF	Hartree-Fock
MP2	Møller-Plesset (MP) perturbation theory at second order
MP4(DQ)	MP perturbation theory at the fourth order with double and quadruple excitations
MP4(SDQ)	MP perturbation theory at the fourth order, with single, double, and quadruple excitations
QCISD	Quadratic configuration interaction with single and double excitations
CCSD	Coupled cluster theory with single and double excitations
QCISD(T)	QCISD plus fourth-order and fifth order quasiperturbative terms involving triple excitations

All of the equations defining the methods will be written in terms of energies. However for all methods, the gradient and Hessian may be determined by applying the analogous equation to each of their components. It should be noted that, in this version of MLGAUSS, the spin-orbit, core-correlation, and scalar relativistic contributions to the energy, if explicitly present in a method, are treated as constants, and as such contribute zero to the gradient and Hessian components.

4.2 Basis Sets

The following abbreviations for standard basis sets are used throughout this manual:

Dd	6-31G(d) [6]
Dd+	6-31+G(d)[6]
DIDZ	6-31+G(d,p)[6]
D2dfp	6-31G(2df,p) [6]
MG3	modified G3large (also called G3largeMP2[7]). This is equivalent to a 6-311++G(3d2f,2df,2p)[8] basis for H–Si, and improved for P–Ar.
MG3S	semidiffuse MG3[9]
MG3S′	MG3S without f functions on Oxygen
6-31G(2d)	6-31G(2d)[6]
6-31B(d)	6-31B(d)[4]
6-311+g(d,p)	6-311+g(d,p)
G3Large	G3Large[10]
G3XLarge	G3XLarge[5]

4.3 Spin-Orbit Energy

In general, the methods employed in MLGAUSS are based on approximating the solution to the non-relativistic Schrödinger equation. However in order to predict experimental effects we must consider the effect of spin-orbit coupling, which is a relativistic effect. Therefore all equations involve a term E_{SO}, which is the spin-orbit energy and which must be supplied by the user. Note that in the Russell-Saunders coupling scheme, E_{SO} vanishes for all closed-shell molecules, atoms in S states, linear molecules in Σ states, and singlet and doublet molecules in A and B states. A table of values of E_{SO} for many common atoms and molecules is given elsewhere.[4] Discussion of the spin-orbit splitting a transition states (it is often negligible there) are given elsewhere.[11,12]

4.4. Scaling All Correlation Method (SAC)

The scaling all correlation (SAC)1 method may be written as:

$$E\,(\text{SAC-L}\,/\,\text{B}) = E\,(\text{HF}\,/\,\text{B}) + c_1 \Delta E\,(\text{L}\,|\,\text{HF}\,/\,\text{B}) + E_{\text{SO}} \qquad (5)$$

where E_{SO} and E_{CC} are the spin-orbit and core-correlation contributions to the energy,

respectively, and c_1 is a constant. The version of SAC that is available in MLGAUSS is the

SAC/3^2 which is SAC-MP2/6-31+(d,2p), and $c_1 = 1.1512$.

Figure 2. Coefficient tree for SAC

HF

c_1

MP2

6-31+G(d,2p)
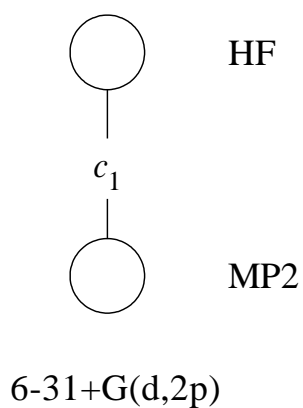
4.5. Multi-Coefficient Correlation Methods (MCCM/3)

4.5.1. MC-CO/3

MC-CO/32 requires two calculations with MP2 theory with two different basis sets. The basis sets used are 6-31G(2d) and MG3S:

$$E(\text{MC-CO/3}) = E(\text{HF/6-31G(2d)})$$
$$+ c_1 \Delta E(\text{HF/MG3S|6-31G(2d)})$$
$$+ c_2 \Delta E(\text{MP2|HF/6-31G(2d)})$$
$$+ c_3 \Delta E(\text{MP2|HF/MG3S|6-31G(2d)}) + E_{\text{SO}} \qquad (6)$$

We note that MC-CO/3 is a special case of a "Colorado" method, as described in a previous paper.[13]

Table 1. Parameters for the MC-CO/3 method

Method	c_1	c_2	c_3
MC-CO/3	0.9436	0.8677	1.8814

Figure 3. Coefficient tree for MC-CO/3
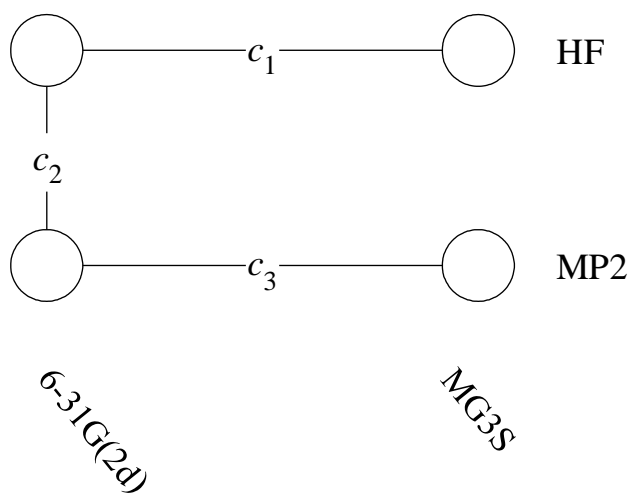
4.5.2. MC-UT/3

MC-UT/3 requires an MP4(SDQ) calculation with the 6-31G(d) basis set and a MP2 calculation with the MG3S basis:

$$
\begin{aligned}
E(\text{MC-UT/3}) = {} & E(\text{HF/6-31G(d)}) \\
& + c_1 \Delta E(\text{HF/MG3S|6-31G(d)}) \\
& + c_2 \Delta E(\text{MP2|HF/6-31G(d)}) \\
& + c_3 \Delta E(\text{MP2|HF/MG3S|6-31G(d)}) \\
& + c_4 \Delta E(\text{MP4(SDQ)|MP2/6-31G(d)}) + E_{\text{SO}}
\end{aligned}
\tag{7}
$$

We note that MC-UT/3 is a special case of "Utah" methods, as described previously.

Table 2. Parameters for the MC-UT/3 method

Method	c_1	c_2	c_3	c_4
MC-UT/3	1.0038	1.142	1.1773	1.3002

Figure 4. Coefficient tree for MC-UT/3
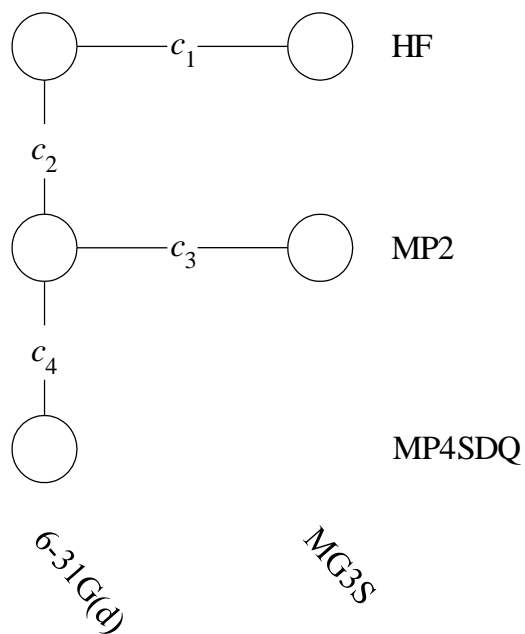
4.5.3. MC-QCISD/3

MC-QCISD/3 requires a QCISD calculation with the 6-31G(d) basis set and a

MP2 calculation with the MG3S basis:

$$
\begin{aligned}
E(\text{MC-QCISD}) = {} & E(\text{HF/6-31G(d)}) + c_1 \Delta E(\text{HF/MG3S|6-31G(d)}) \\
& + c_2 \Delta E(\text{MP2|HF/6-31G(d)}) \\
& + c_3 \Delta E(\text{MP2|HF/MG3S|6-31G(d)}) \\
& + c_4 \Delta E(\text{QCISD|MP2/6-31G(d)}) + E_{\text{SO}} \quad\quad (8)
\end{aligned}
$$

We note that MC-QCISD/3 is a special case of "Utah" methods, as described

previously.[13]

Table 3. Parameters for the MC-QCISD/3 method

Method	c_1	c_2	c_3	c_4
MC-QCISD/3	1.0452	1.1305	1.2302	1.1673

Figure 5. Coefficient tree for MC-QCISD/3
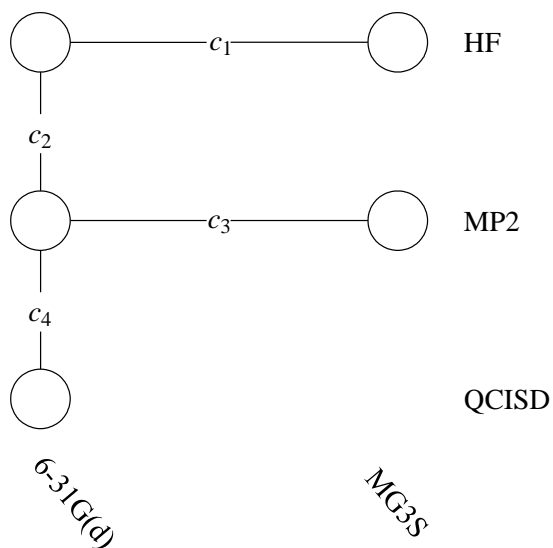
4.5.4. MCG3/3

The MCG3/32 energy can be expressed as:

$$E(\text{MCG3/3}) = c_0 E[\text{HF} / \text{Dd}] + c_1 \Delta E[\text{HF} / \text{MG3S} | \text{Dd}]$$

$$+ c_2 \Delta E[\text{MP2} | \text{HF} / \text{Dd}] + c_3 \Delta E[\text{MP2} | \text{HF} / \text{MG3S} | \text{Dd}]$$

$$+ c_4 \Delta E[\text{MP4(SDQ)} | \text{MP2} / \text{Dd}] + c_5 \Delta E[\text{MP4(SDQ)} | \text{MP2} / \text{D2dfp} | \text{Dd}]$$

$$+ c_6 \Delta E[\text{QCISD(T)} | \text{MP4(SDQ)} / \text{Dd}] + E_{\text{SO}} \tag{9}$$

Table 4. Parameters for the MCG3 method

Method	c_0	c_1	c_2	c_3	c_4	c_5	c_6
MCG3/3	1.0067	1.1249	1.0585	1.2027	1.1369	0.5024	1.2666

Figure 6. Coefficient tree for MCG3/3.
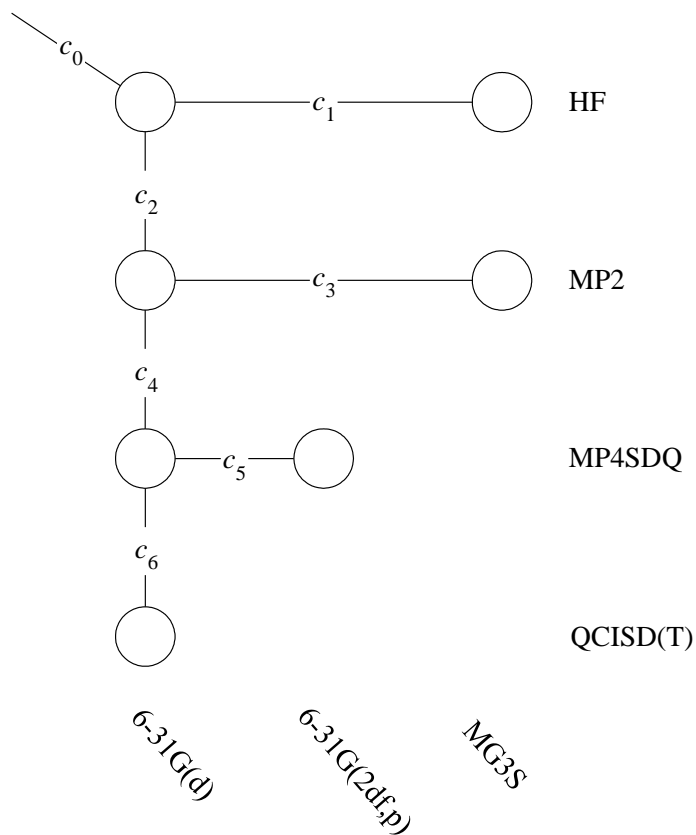
4.6. G3SX and G3SX(MP3)

The G3SX is defined[5] as:

$$E(\text{G3SX(MP3)}) = E[\text{HF} / \text{Dd}] + c_1 \Delta E[\text{MP4}|\text{HF} / \text{Dd}]$$

$$+ c_2 \Delta E[\text{QCISD(T)} | \text{MP4} / \text{Dd}] + c_3 \Delta E[\text{HF} / \text{G3XLarge} | \text{Dd}]$$

$$+ c_4 (\Delta E[\text{MP2(full)}|\text{HF} / \text{G3Large}] - \Delta E[\text{MP2} | \text{HF} / \text{Dd}])$$

$$+ c_5(\Delta E[\text{MP3} | \text{MP2} / \text{Dd+} | \text{Dd}] + \Delta E[\text{MP3} | \text{MP2} / \text{D2dfp} | \text{Dd}]$$

$$+ c_6(\Delta E[\text{MP4} | \text{MP3} / \text{Dd+} | \text{Dd}] + \Delta E[\text{MP4} | \text{MP3} / \text{D2dfp} | \text{Dd}] + E_{\text{SO}} \qquad (10)$$

The G3SX with reduced-order Møller-Plesset perturbation theory method

(G3SX(MP3)) is defined[5] as :

$$E(\text{G3SX(MP3)}) = E[\text{HF} / \text{Dd}] + c_1 \Delta E[\text{MP4}|\text{HF} / \text{Dd}]$$

$$+ c_2 \Delta E[\text{QCISD(T)} | \text{MP4} / \text{Dd}] + c_3 \Delta E[\text{HF} / \text{G3XLarge} | \text{Dd}]$$

$$+ c_4 (\Delta E[\text{MP2(full)}|\text{HF} / \text{G3Large}] - \Delta E[\text{MP2} | \text{HF} / \text{Dd}])$$

$$+ c_5 \Delta E[\text{MP3} | \text{MP2} / \text{D2dfp} | \text{Dd}] + E_{\text{SO}} \qquad (11)$$

Table 5. Parameters for the G3SX and G3SX(MP3) methods

Method	c_1	c_2	c_3	c_4	c_5	c_6
G3SX	1.0487	1.1476	1.0862	1.2040	1.2151	0.6605
G3SX(MP3)	1.0502	1.1854	1.0803	1.2027	1.0081	

4.7. Multi-Coefficient Extrapolated DFT Methods

Multi-coefficient extrapolated density functional theory is a new kind of multi-coefficient correlation method (MCCM) that involves an empirical mix of correlated wave function methods and density functional methods. The new methods constitute a generalization of hybrid density functional theory (DFT); one can think of these new methods as improving the correlation part of hybrid DFT, or one can think of them as adding static correlation and additional dynamic correlation to the best practical single-reference wave function theory methods. The latter interpretation of these methods is based on the fact that DFT exchange includes some effects that would be described in wave function language as static correlation. When these methods are considered as examples of DFT, they may be called doubly hybrid DFT. In both hybrid DFT and doubly hybrid DFT, the exchange-correlation energy depends not only on the spin-labeled densities and their reduced gradients but also on orbitals. In the doubly hybrid methods contained in MLGAUSS, the exchange-correlation energy depends on both Hartree-Fock orbitals and Kohn-Sham orbitals, both of which are functionals of the density. [In unpublished work (Zhao and Truhlar, 2006) are used Kohn-Sham orbitals for all steps of the methods, and we obtained very similar results.]

4.7.1. N^7 methods

The three new N^7 methods are based on the MCG3/3 method[2] as combined with a DFT method. Here and in the creation of the other multi-coefficient extrapolated DFT methods in this manual, we consider three DFT methods, which are either hybrid DFT or hybrid meta DFT. The three DFT*X* methods we use are MPWB*X*, MPW*X*, and TPSSKCIS*X*. MPWB*X* is a hybrid meta DFT methods which use modified Perdew-

Wang (MPW) exchange[14] and the Becke95[15] correlation functional with $X\%$ HF

exchange. MPWX is a hybrid DFT method which uses MPW exchange[14] and Perdew-

Wang-1991[16] (PW91) correlation again with $X\%$ HF exchange. TPSSKCISX is a hybrid

meta DFT method which uses the TPSS exchange[17] and the KCIS correlation functional

of Savin and coworkers.[18-20] Note that X is a parameter that is optimized along with the c_i

parameters. To distinguish the three methods, we use a suffix to specify the

exchange- correlation functional, and the abbreviations of the suffixes we use in

naming these methods are:

> MPWB   MPW exchange + B95 correlation
> MPW   MPW exchange + PW91 correlation
> TS   TPSS exchange + KCIS correlation

We replace the HF/MG3S component of the MCG3/3 method by one or another

of these DFT methods, resulting in three multi-coefficient extrapolated DFT methods of a

type that we will call doubly hybrid MCG3 methods, respectively. The new methods can

be written as:

$$
\begin{aligned}
E\,(\text{MCG3-DFT}) = \; & c_8\,\{E[\text{HF}\,/\,\text{Dd}] + c_1 E[\text{MP2}\,|\,\text{HF/Dd}] \\
& + c_2 E[\text{MP2}\,/\,\text{DIDZ}\,|\,\text{Dd}] + c_3 E[\text{MP2}\,/\,\text{D2dfp}\,|\,\text{DIDZ}] \\
& + c_4 E[\text{MP2}\,/\,\text{MG3S}\,|\,\text{D2dfp}] + c_5 E[\text{MP4(SDQ)}\,|\,\text{MP2}\,/\,\text{Dd}] \\
& + c_6 E[\text{MP4(SDQ)}\,/\,\text{D2dfp}\,|\,\text{Dd}] + c_7\,E[\text{QCISD(T)}\,|\,\text{MP4(SDQ)}\,/\,\text{Dd}]\} \\
& + (1 - c_8)\text{E}(\text{DFT}X/\text{MG3S}) + E_{\text{SO}} \qquad\qquad\qquad\qquad (12)
\end{aligned}
$$

where $c_1, \dots, c_8$ are parameters, DFTX denotes the chosen DFT method with a parameter

X (percentage of Hartree-Fock exchange), and E_{SO} is the spin-orbit energy (which is

often zero).

Table 6. Parameters for the N^7 multi-coefficient extrapolated DFT methods

Method	c_1	c_2	c_3	c_4	c_5	c_6	c_7	c_8	X
MCG3-MPWB	1.085	0.276	0.465	1.329	1.255	0.889	1.057	0.727	34
MCG3-MPW	1.096	0.422	0.622	1.299	1.27	0.742	1.078	0.815	32
MCG3-TS	1.082	0.551	0.734	1.295	1.185	0.626	0.933	0.776	19

Figure 7. Coefficient tree for the new N^7 multi-coefficient extrapolated DFT methods
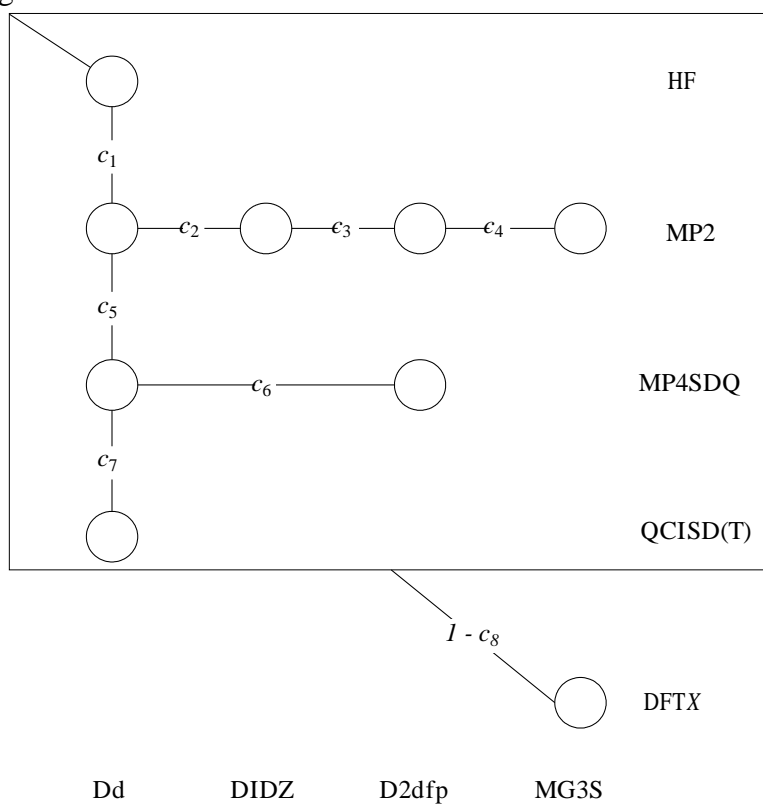
4.7.2. N^6 methods.

MLGAUSS includes three methods that scale as N6 and that are based on the MC-QCISD/3[2] method. We added a MP2/DIDZ calculation, and we replaced the HF/MG3S component of the MC-QCISD/3 method in turn by each of the three DFTX methods used in section 4.7.1, resulting respectively in three multi-coefficient extrapolated DFT methods of a type that we will call doubly hybrid MC-QCISD methods. The new methods can be written as:

$$E\,(\text{MCQCISD-DFT})= c_5\{E[\text{HF}\,/\,\text{Dd}] + c_1 E[\text{MP2}\,|\,\text{HF/Dd}]$$
$$+ c_2\,E[\text{MP2}\,/\,\text{DIDZ}\,|\,\text{Dd}]+ c_3\,E[\text{MP2}\,/\,\text{MG3}\,|\,\text{DIDZ}]$$
$$+ c_4\,E[\text{QCISD}\,|\,\text{MP2}\,/\,\text{Dd}]\,\} + (1 - c_5)\,E(\text{DFT}X\,/\,\text{MG3S}) + E_{\text{SO}} \qquad (13)$$

The c_1-c_5 coefficients and the parameter X were optimized against the databases

described in a previous paper,[3] and they are listed in Table 7.

Figure 8. Coefficient tree for the new N^6 multi-coefficient extrapolated DFT methods

based on MC-QCISD/3
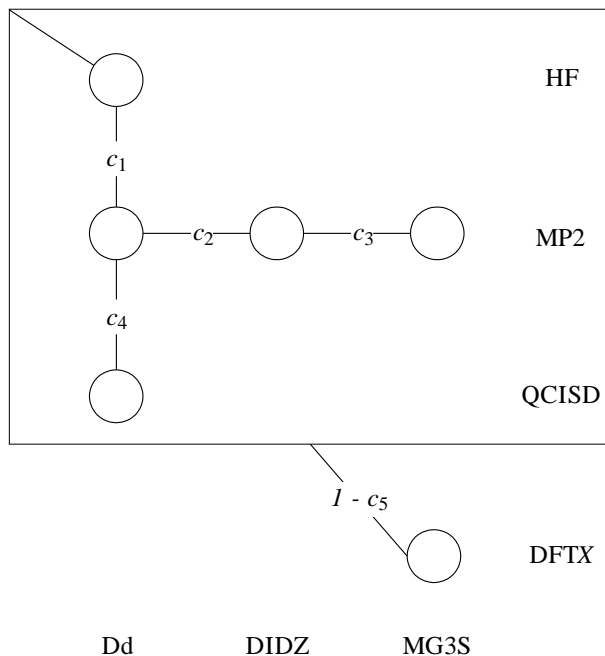
MLGAUSS also includes three methods that scale as N^6 and that are based on

the MC-UT/3[2] method. In each of them, we replace the HF/MG3S component of

the MC-UT/3 method by one of the three DFTX methods, resulting respectively in

three multi-coefficient extrapolated DFT methods of a type that we will call doubly

hybrid

MC-UT methods. Again we also add a MP2/DIDZ calculation. The new methods can be

written as:

$$E\,(\text{MCUT-DFT}) = c_5\,\{E[\text{HF}/\text{Dd}] + c_1\,E[\text{MP2}\,|\,\text{HF}/\text{Dd}]$$
$$+ c_2\,E[\text{MP2}/\text{DIDZ}\,|\,\text{Dd}] + c_3\,E[\text{MP2}/\text{MG3}\,|\,\text{DIDZ}]$$
$$+ c_4\,E[\text{MP4(SDQ)}\,|\,\text{MP2}/\text{Dd}]\,\} + (1-c_5)\,E(\text{DFT}X\,/\text{MG3S}) + E_{\text{SO}} \qquad (14)$$

The optimized c_1 - c_5 and X are listed in Table 7.

Figure 9. Coefficient tree for the new N^6 multi-coefficient extrapolated DFT methods

based on MC-UT/3.
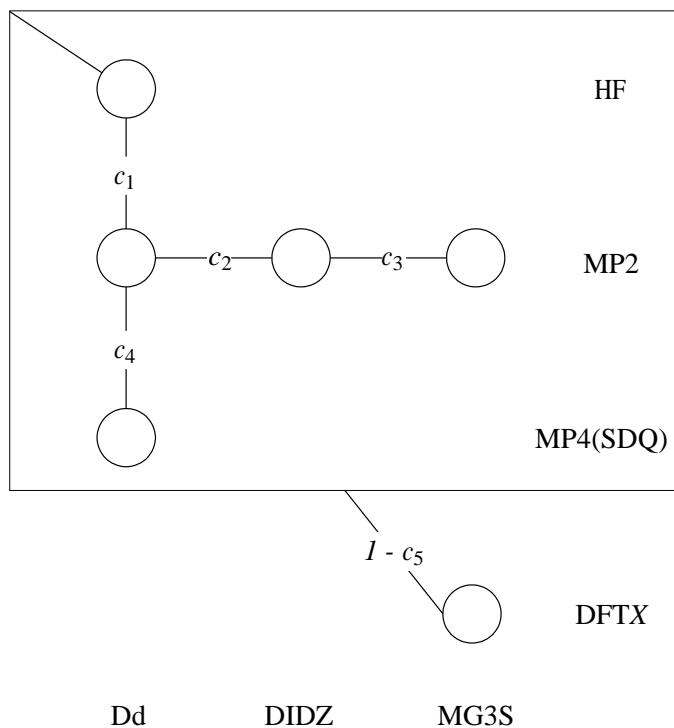
Table 7. Parameters for the N^6 multi-coefficient extrapolated DFT methods

Method	c_1	c_2	c_3	c_4	c_5	X
MCQCISD-MPWB	1.138	1.161	1.26	1.282	0.64	34
MCQCISD-MPW	1.163	1.106	1.324	1.331	0.711	32
MCQCISD-TS	1.127	1.14	1.309	1.144	0.673	19
MCUT-MPWB	1.102	1.171	1.346	1.404	0.526	29
MCUT-MPW	1.134	1.092	1.416	1.545	0.643	17
MCUT-TS	1.104	1.125	1.391	1.241	0.598	13

4.7.3. N^5 methods.

MLGAUSS includes seven multi-coefficient extrapolated methods that scale as N^5.

Three of them are based on the MC-CO/3 method[2] and are called doubly hybrid MC-CO

methods. We replace the HF/MG3S component of the MC-CO/3 method by the

MPWBX, MPWX, and TSX methods respectively. The new methods can be written as:

$$E\,(\text{MCCO-DFT}) = c_3\,\{E[\text{HF}\,/\,\text{Dd}] + c_1\,E[\text{MP2}\,|\,\text{HF/Dd}]$$

$$+ c_2\,E[\text{MP2}\,/\,\text{MG3}\,|\,\text{Dd}]\,\} + \,(1 - c_3)\,E(\text{DFT}X/\text{MG3S}) \,+\, E_{\text{SO}} \tag{15}$$

The optimized c_1-c_3 and X are listed in Table 8.

Figure 10. Coefficient tree for the new N^5 multi-coefficient extrapolated DFT

methods based on MC-CO/3
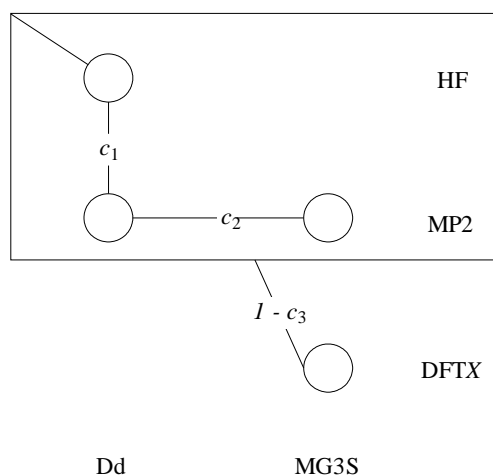
MLGAUSS includes four MC3-type methods, namely, MC3BB, MC3MPW,

MC3MPWB, and MC3TS. All of them scale as N^5. The MC3-type methods can be

described as:

$$E(\text{MC3-type}) = c_2\,[E(\text{HF/DIDZ}) + c_1\Delta E(\,\text{MP2}|\text{HF/DIDZ})]$$

$$+ (1 - c_2)\,E(\text{DFT}X/\text{MG3S}) + E_{\text{SO}} \tag{16}$$

As mentioned in the introduction, the DFTX methods in MC3BB,[21] MC3MPW,[21] MC3MPWB[3] and MC3TS[3] are BBX,[22] MPWX,[23] MPWBX, and TSX, respectively. The optimized values of c_1, c_2, and X for these methods are listed in Table 8.

Figure 11. Coefficient tree for the N^5 MC3-type multi-coefficient hybrid methods.
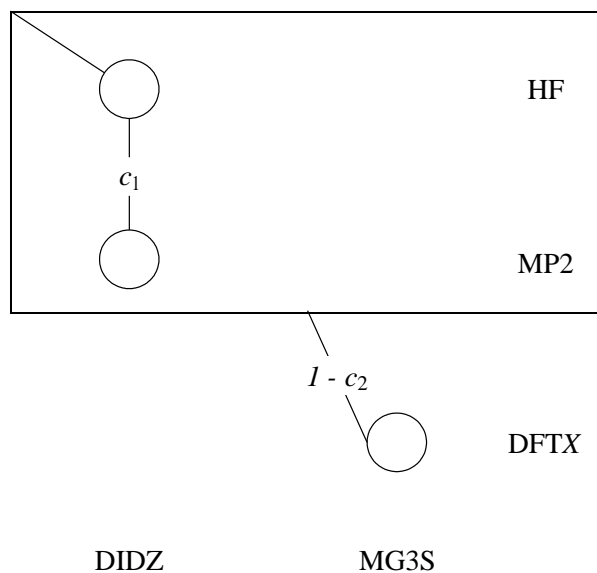
Table 8. Parameters for the N^5 multi-coefficient extrapolated DFT methods

Method	c_1	c_2	c_3	X
MCCO-MPWB	0.828	1.678	0.267	34
MCCO-MPW	0.957	1.546	0.386	32
MCCO-TS	0.952	1.435	0.401	22
MC3BB	1.332	0.205		39
MC3MPW	1.339	0.266		38
MC3MPWB95	1.196	0.257		38
MC3TS	1.256	0.336		31

4.8. BMC Methods

4.8.1 BMC-QCISD

The BMC-QCISD method[4] differs from MC-QCISD/3 in three respects. First, it uses a modified extrapolation scheme which scales the MP4(SDQ) energy increment separately, as shown in Figure 11. Second, it replaces the MG3S basis with the MG3 basis. Finally, it uses a new basis set named 6-31B(d) in place of 6-31G(d). The energy expression for BMC-QCISD is given in Equation 17:

E(BMC-QCISD) = E(HF/6-31B(d)) +

$c_H\Delta$(HF/MG3|6-31B(d)) + $c_1\Delta$(MP2|HF/6-31B(d)) + $c_2\Delta$(MP2|HF/MG3|6-31B(d)) + $c_3\Delta$(MP4(SDQ)|MP2/6-31B(d)) + $c_4\Delta$(QCISD|MP4(SDQ)/6-31B(d))

+ E_{SO} (17)

The new method, named BMC-QCISD, uses the same number of extrapolation coefficients as MC-QCISD. The coefficient c_H comes from Equation 18:

$$c_H = \frac{E_H - E_H[6\text{-}31B(d)]}{E_H[MG3] - E_H[6\text{-}31B(d)]} \tag{18}$$

where E_H is the energy for hydrogen atom.

The coefficients for the BMC-QCISD method are listed in Table 9.

Figure 12. Coefficient tree for the BMC-QCISD method
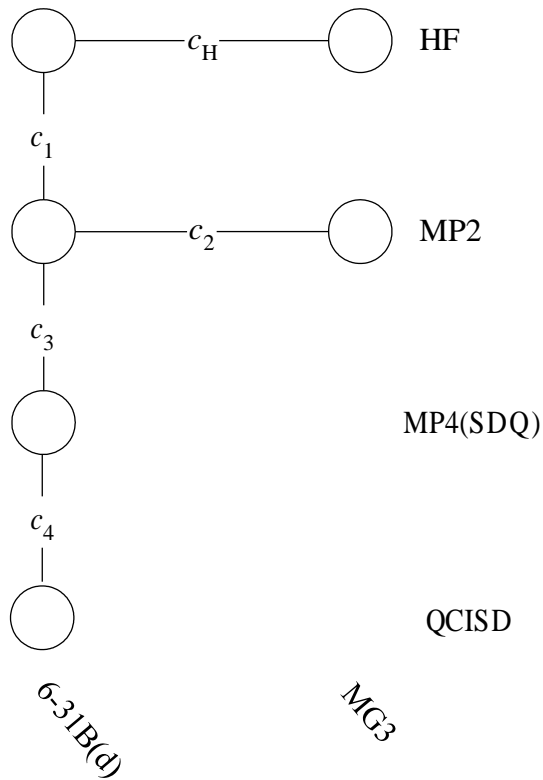
4.8.2 BMC-CCSD and BMC-CCSD-C

The BMC-CCSD method replaces QCISD with CCSD, and it replaces MP4(SDQ) with MP4(DQ), as compared to BMC-QCISD. The BMC-CCSD is illustrated in Figure 12. The five scaling coefficients are given in Table 9. The coefficients are defined by:

E(BMC-CCSD) = E(HF/6-31B(d)) +

$c_H \Delta$(HF/MG3|6-31B(d)) + $c_1 \Delta$(MP2|HF/6-31B(d)) + $c_2 \Delta$(MP2|HF/MG3|6-31B(d)) + $c_3 \Delta$(MP4(DQ)|MP2/6-31B(d)) + $c_4 \Delta$(CCSD|MP4(DQ)/6-31B(d)) +

E_{SO} (19)

Figure 13. Coefficient tree for the BMC-CCSD method
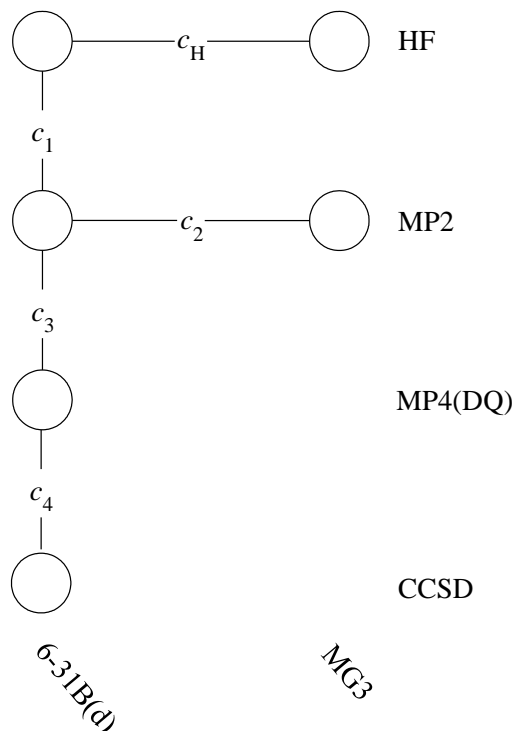
The BMC-QCISD and BMC-CCSD methods use both the 6-31B(d) basis set which uses Cartesian (6D) polarization functions and the MG3 basis set which uses spherical (5D,7F) polarization functions. To allow the BMC-CCSD method to be calculated using only Cartesian polarization functions, we also include the Cartesian variant BMC-CCSD-C where we replace the spherical harmonic d and f functions in MG3 with Cartesian (6D,10F) polarization functions. The scaling coefficients for this method are also in Table 9.

Table 9. Parameters for the BMC-QCISD and BMC-CCSD methods

Method	c_H	c_1	c_2	c_3	c_4
BMC-QCISD	1.06047423	1.10734	1.33058	0.92517	1.53093
BMC-CCSD	1.06047423	1.09791	1.33574	0.90363	1.55622
BMC-CCSD-C	1.06047423	1.09810	1.34076	0.89040	1.56497

4.9 Infinite Basis (IB) method

MP2/IB is an infinite basis set calculation that involves the separate extrapolation of Hartree-Fock and MP2 correlation energies.[24,25] The Hartree-Fock (HF) energies are extrapolated by

$$E^{HF}(n) = E_{\infty}^{HF} + A^{HF} n^{-\alpha} \tag{20}$$

and the MP2 correlation energies are extrapolated by

$$E^{cor}(n) = E_{\infty}^{cor} + A^{cor} n^{-\beta}, \tag{21}$$

where n represents the highest angular momentum in an augmented correlation-consistent basis set; $n = 2$ for the aug-cc-pVDZ basis, and $n = 3$ for the aug-cc-pVTZ basis. The parameters α and β are determined in a previous paper;[25] the value used for α is 4.93, and that for β is 2.13.

Note: 1B is not an MCCM method.

Chapter Five
5

5. Optimization Procedures

This chapter describes the optimization procedures available in this version of the MLGAUSS code.

5.1. Optimization with GAUSSIAN09/03's Optimizer.

MLGAUSS uses the optimizers in the GAUSSIAN09/03 package to do optimization. The overall control for this procedure is:

GAUSSIAN09/03 ↔ *Gau_External* ↔ GAUSSIAN09/03

The primary GAUSSIAN09/03 calculation will call an optimization with EXTERNAL option. This GAUSSIAN09/03 calculation calls an external PERL scripts *Gau_External*, which will provide the primary GAUSSIAN09/03 calculation with the multi-level energy, gradient and Hessian needed for optimization. *Gau_External* will call several secondary GAUSSIAN09/03 calculations and calculate and pass the multi-level energy, gradient, and Hessian to the primary GAUSSIAN09/03 calculation. It should be noted that the default geometry optimization algorithm in GAUSSIAN09 is different than that which was used in earlier versions (The use of the microiterations scheme for geometry optimizations has been made by default in GAUSSIAN09 when the "External" keyword is used). The optimization keywords 'Opt=NoMicro' must be included in the route section of the Gaussian input file in order to use the previous optimization algorithm.

Chapter Six

6

6. Input Description

There are two input files namely, "*runname.g09*" and "*mccm.inp*", where *runname* can be anything except *test*. The "*runname.g09*" input file is the standard GAUSSIAN09/03 input file with the EXTERNAL keyword. GAUSSIAN09/03 will use "*test*" as the names of the files for the intermediate steps when the EXTERNAL keyword is used. The input format for the "*runname.g09*" file is same as the GAUSSIAN09/03 input files, one can refer to the GAUSSIAN09/03 manual[26] for the format and keyword of the "*runname.g09*" input files, or refer to the test runs to see how to prepare the "*runname.g09*" file.

The "*mccm.inp*" file contains only one line which defines the multilevel method used in the calculations. Table 9 gives the keywords for all methods that can be used in the "*mccm.inp*" file. Note that these keywords are not case sensitive.

Table 9. Keywords for the "mccm.inp" input file.

Method	Keyword
BMC-CCSD	BMCCCSD
BMC-CCSD-C	BMCCCSDC
BMC-QCISD	BMCQCISD
G3SX	G3SX
G3SX(MP3)	G3SXMP3
MC3BB	MC3BB
MC3MPW	MC3MPW
MC3MPWB95	MC3MPWB
MC3TS	MC3TS
MC-CO/3	MCCO
MCCO-MPW	MCCOMPW
MCCO-MPWB	MCCOMPWB
MCCO-TS	MCCOTS
MCG3/3	MCG3
MCG3-MPW	MCG3MPW
MCG3-MPWB	MCG3MPWB
MCG3-TS	MCG3TS
MC-QCISD/3	MCQCISD
MCQCISD-MPW	MCQCISDMPW
MCQCISD-MPWB	MCQCISDMPWB
MCQCISD-TS	MCQCISDTS
MC-UT/3	MCUT
MCUT-MPW	MCUTMPW
MCUT-MPWB	MCUTMPWB
MCUT-TS	MCUTTS
MP2/IB	MP2IB
SAC/3	SAC

Chapter Seven

7

7. Installing and Using MLGAUSS

A step-by-step procedure for installing MLGAUSS on a Unix computer and testing it is given here. Compilation of the code can be accomplished with the shell script named *set_path.ml*. The test runs should illustrate the proper way in which to use this program.

7.1. Installation Instructions

Step 1:

The MLGAUSS program should have been obtained in the tar format with the following file name: *mlgauss3.0.tar.gz*. This file should be placed in the directory in which the user wishes to install MLGAUSS, and then the following two commands should be executed:

> *ungzip mlgauss3.0.tar.gz*
>
> *tar –xvf mlgauss3.0.tar*

Once these two commands have been executed the directory structure on the next step should have been created. Please verify that this is true.

Step 2:

Verify that the files have been placed into the directory structure above as follows. In the *mlgauss3.0* directory:

basis/	*script/*	*set_path.ml*	*testo/*
testrun/	*documents/*		

In the basis directory:

631bd.gbs	*g3large.gbs*	*g3xlarge.gbs*	*mg3a.gbs*
mg3s.gbs	*mg3zn.gbs*		

In the *script* directory:

Gau_External	*Gau_External_old*

In the *testo* directory:

testo-g09	*testo-g03.c01*	*testo-g03.d01*

In the *testrun* directory:

test1/	*test2/*	*test3/*	*test4/*
test5/	*test5_g03.c01/*	*test6/*	*test6_g03.c01/*
test7/	*test8/*		

In each *testrun/test*n (where *n* = 1-8) directory:

mccm.inp	*mlgtestn.g09*

In the *documents* directory:

MLGauss_Manual_v3.0.pdf

Step 3:

Change the working directory to the *mlgauss3.0* directory, and run the script *set_path.ml* by typing set_path.ml <Return>. This script will create a file in the home directory named .*mlgauss_path3.0* stating where the MLGAUSS directory structure is located. This file is used by the *Gau_External* scripts to locate MLGAUSS on the user's system.

Step 4:

Make sure the MLGAUSS script directory is listed in the PATH environment variable (you can use the "env" command to check the values of the environment variables, or "echo $PATH" to check the PATH variable). If not, you should use the following command to add the the MLGAUSS directory to the PATH environment variable:

set path=($path /home/user/soft/mlgauss3.0/script)

Step 5:

Change to the *script* directory, and edit the *Gau_External* script present. There are four variables you need to change in the *Gau_External* file.

$gausspath: set the value of this variable to the **installation** directory of GAUSSIAN09/03 directory. The default value for this variable is "/usr/local/g09/g09.c01".

$scratchdir: set this value of this variable to the directory of scratch directory to be used by GAUSSIAN09/03. If you don't have your own scratch directory, you can use the "mkdir" command to make one. For example:

mkdir /scratch2/zhaoy

 The default value for $scratchdir is ''/scratch2/zhaoy".

$gaussver: set the value of this variable to the version of GAUSSIAN (g09 or g03). The default value for this variable is "g09".

$nproc: set the value of this variable to the appropriate number of processors required by the single level calculation in a particular multi-level method. The default value for this variable is "8".

$mem: set the value of this variable to the appropriate memory required by the single-level calculation in a particular multi-level method. The default value for this variable is "1000mb".

$option: set the value of this variable to the appropriate GAUSSIAN09/03 option required by the single-level calculation in a particular multi-level method. The default value for this variable is "scf=(tight, maxcycle=500,xqc)".

After you change the above variables, you must make sure the *Gau_External* script is executable. If not, you should use the *chmod* command.

chmod +x Gau_External

Now you can load the GAUSSIAN09/03 module, and run the test run. For example, you can do the following to interactively run test run called test1:

module load gaussian/g09.c01

g09 <mlgtest1.g09> mlgtest1.out

You can also submit the calculation to a queue by using the appropriate submission script for your system.

You can repeat this step for other test runs.

7.2. Old Version of GAUSSIAN03

The default Gau_External script in the MLGAUSS3.0 program are developed for GAUSSIAN03 Revision D01/D02. It can not work with the older versions of GAUSSIAN03. In the *script* directory, there is script called Gau_External_old, which works with the older version of GAUSSIAN09/03, but it does not work with GAUSSIAN09/03 Revision D01/D02. If the version of your GAUSSIAN03 is older than Revision D01/D02, you need

to use the Gau_External_old script instead of the default Gau_External. The

test5_g03.c01 and *test6_g03.c01* directories contain two test runs (5 and 6) using old

version (C01) of GAUSSIAN03.

Chapter Eight

8

8. Description of Files in MLGAUSS

This chapter gives a description of the files involved in compiling and running MLGAUSS, including the source code needed to compile the program, files required to run MLGAUSS, files created during a run of MLGAUSS.

8.1. Source Coe

MLGAUSS source code is composed of one PERL script file, *Gau_External*. The following subsections give an alphabetical listing and description of each subprogram in *Gau_External*.

8.2. Subprogram List

The listings in this section have the subroutine name in bold. The following lines then give a short description of the subprogram.

printoutput

Print the intermediate *test.out* file.

mccmcalc

Calculate the multi-level composite energy, gradient, and hessian.

gaussian

Call **call_gauss** subroutine to carry out single-level calculations and extract the results from the output.

write_input

Write the input files for each single level calculation.

call_gauss

Call GAUSSIAN 09/03 to carry out single-level calculation.

grabener

Extract the energy from each single-level calculation.

grabgrad

Extract the gradient from each single-level calculation.

grabhess

Extract the Hessian from each single-level calculation.

8.3. Files Required to Run MLGAUSS

Aside from the executable itself, there are three types of files that are necessary to run MLGAUSS: the input files (see chapter 6), the *Gau_External* script file (Section 7.1 and 7.2), and the basis set files. The following two subsections give the details of the basis set files. The input files have been described in detail in the previous chapter. It should be noted that different MLGAUSS jobs must be run in different directories (or at least not in the same directory at the same time) because intermediate directories and files, with the same name, are created in the directory where the MLGAUSS input file is located.

8.3.1. Basis Set Files

Due to the fact that several of the MLGAUSS calculations require electronic structure program calls for non-standard basis sets, one or more of the non-standard GAUSSIAN basis set files may be required. The basis set files and the MLGAUSS methods which require them are listed below:

Basis Set:	File Name:	Methods Required For:
6-31B(d)	631bd.gbs	BMC-QCISD and BMC-CCSD
G3Large	g3large.gbs	G3SX, G3SX(MP3)
G3XLarge	g3xlarge.gbs	G3SX, G3SX(MP3)
MG3	mg3a.gbs	BMC-QCISD and BMC-CCSD
MG3S	mg3s.gbs	MCCM/3, multi-coefficient extrapolated DFT

8.4. Files Created During a MLGAUSS Run

Several files that may be of importance to the user, are created in the process of running MLGAUSS.

8.4.1. The Output File: *.out

The output file is created under the name *runame.out*. The name of the output file can be specified by users otherwise GAUSSIAN09/03 will create *runname.log* file for the output (where *runname* represents the name of the input file). The first portion of the file summarizes the options specified in the input file. The remainder details the results of the external optimization, each step in a MLGAUSS optimization, and all energies, gradients, and Hessians calculated. All values should be clearly identified within the output.

8.4.2. The Single-Level Input and Output Files

Currently there are three files created that fall under this category. Each will be described below. These files should indicate to the user which job is currently being run. A line is also written to standard error for each electronic structure job run by MLGAUSS.

g09.inp

This is the input file for a single-level GAUSSIAN09/03 for all energy, gradient, and Hessian calculation. The method and basis set are those required for the current MLGAUSS calculation. The two options specified in every input file are *FChk=All* (in order to read the GAUSSIAN output) and *NoSymm* (in order to avoid calculation failures due to a changing of the molecular symmetry). The three types of calculations that may be specified in these files are *SP*, *Force*, and *Freq* to obtain the energy, gradient, and Hessian respectively. The option *Force=EnOnly* is always chosen for those methods that do not have analytic gradients, due to the fact that GAUSSIAN09/03 fails otherwise. The user may specify additional options in the *Gau_External* file. The memory requirements are hardwired into the program, to the values of 1000mb for each single-level calculations. If these memory allocations are undesirable for some reason, the user may alter these constant amounts in the *Gau_External* file (see section 8.1), so long as the amount is in a format accepted by GAUSSIAN09/03.

g09.out

This is the output file resulting from each GAUSSIAN09/03 single level run of *g09.inp*. As is true for the input file, this file is overwritten with each run of the electronic structure package. They are not used in the running of MLGAUSS. However, should the user encounter an error reading the checkpoint file, examination of this

output file may prove useful in identifying the problem.

Test.FChk

This is the formatted checkpoint file created by GAUSSIAN09/03. It is integral to the

operation of MLGAUSS in that all energies, gradients, Hessians, and optimized geometries

calculated by GAUSSIAN09/03 are read from this file.

Chapter Nine

9

9.1 The MLGAUSS Test Suite

The test suite has been designed to give the user a sample of the MLGAUSS capabilities and input files and to provide examples of test input and output. It does not give examples of everything that can be done with the program, but each test run demonstrates a key feature of the program. These test runs also allow the user to familiarize himself or herself with MLGAUSS calculations.

In order to use the test suite, change working directory to the *testrun* directory in the *mlgauss3.0* directory. Within the *testrun* directory, there are 7 subdirectories – *test1, ..., test7*. Each of these subdirectories contains MLGAUSS input files and *Gau_External* script.

9.1. Test 1

Test run 1 performs an MC-QCISD/3 optimization of the HF molecule.

9.2. Test 2

Test run 2 is a BMC-CCSD single-point energy calculation of the OH radical.

9.3. Test 3

Test run 3 is an MCQCISD-TS single-point energy calculation of H_2O molecule.

9.4. Test 4

Test run 4 carries out a G3SX(MP3) gradient calculation for H_2.

9.5. Test 5

Test run 5 performs an MC3BB transition state optimization for the H + H$_2$ reaction with the GAUSSIAN09/03 keyword *calcfc*.

9.6. Test 6

Test run 6 performs an MC3TS Hessian calculation for the H$_2$ molecule.

9.7. Test 7

Test run 7 performs an MC3MPW transition state optimization for the OH + H$_2$ reaction.

9.8. Test 8

Test run 8 performs an MP2/IB single-point energy calculation of the H$_2$O molecule.

Chapter Ten

10

10. Computers and Operating Systems Tested

In each case we give the MLGAUSS version number and the computers and operating systems on which MLGAUSS was tested. For each computer, we also specify the operating system.

MLGAUSS2.0

Computer	Operating System
IBM Power4 Regatta	AIX 5.1
Netfinity Cluster	RedHat Linux 9.0
SGI ALTIX	Linux 2.4.21-sgi303r2

MLGAUSS3.0

Computer	Operating System
HP Proliant BL280c G6 Linux cluster	CentOS 6.2
SGI Altix XE 1300 cluster	CentOS 6.2
Constellation of SGI systems	SUSE Linux Enterprise Server 11 SP1
Sun Fire X4600 Linux cluster	SUSE Linux Enterprise Server 10 SP4

Chapter Eleven

11

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Chapter Twelve

12

12. Revision History

12.1. Version 1.0

Authors of this version: Y. Zhao and D. G. Truhlar.

First distributed version

12.2. Version 1.1

Authors of this version: Y. Zhao and D. G. Truhlar.

A bug in the MCCO-MPWB method and a bug in the MCCO/3 method have been fixed.

The MP2-IB method has been implemented. A new test run 8 has been added.

12.2. Version 2.0

Authors of this version: Y. Zhao and D. G. Truhlar.

The MLGAUSS program has been updated to work with GAUSSIAN03.D01

12.3 Version 3.0

Authors of this version: Y. Zhao, R. Meana-Pañeda, and D. G. Truhlar.

The code has been updated to work with GAUSSIAN09 as well as with GAUSSIAN03. The

option of using multiple processors for the single-point calculations has been added. The

optimization keyword "opt=NoMicro" has been included in the testfiles mlgtest1.g09,

mlgtest5.g09, and mlgtest7.g09 in order to use the optimization algorithm used by the

previous versions of MLGAUSS. The coordinates system used by the mlgtest7.g09 test

file has been changed to Cartesian coordinates by adding the keyword "opt=Cartesian" in

order to improve the convergence process.

End of Manual