

# SMXGAUSS

## User's Manual

version 3.4.2

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## Executive Summary

SMXGAUSS is a program that carries out liquid-phase calculations by solvation models 5.42, 5.43, 6 and 6 with temperature dependence (SM5.42, SM5.43, SM6 and SM6T), which are quantum mechanical free energy calculations based on the self-consistent reaction field (SCRF) method augmented by atomic surface tensions. SMXGAUSS can be used to carry out a single-point calculation in the liquid phase, a geometry optimization in the liquid phase to a minimum or to a transition state, or a Hessian calculation in the liquid phase.

SMXGAUSS can run in two basic modes. In mode 1, all calculations are performed using the intrinsic supplied code for Hartree-Fock (HF), density functional theory (DFT), hybrid DFT, generalized Born, analytic surface area calculations, geometry optimizations, and Hessian calculations. In this mode no other electronic structure software is required. The program running in this mode has been designed, however, to take as input a GAUSSIAN output file to obtain the charge, multiplicity, and geometry. Thus, for example, one can optionally begin by optimizing a geometry in the gas-phase using GAUSSIAN, then use the output file from this calculation and an SMXGAUSS input file to carry out a liquid-phase free energy calculation, either at the gas-phase geometry or with re-optimization in the liquid phase. Because SMXGAUSS input files have the same format as GAUSSIAN input files, the program is especially user friendly to GAUSSIAN users, and it provides a way for them to add SM $x$  liquid-phase free energy calculations to their research. SMXGAUSS running in mode 1 can also read an SMXGAUSS summary file, which is created from a previous SMXGAUSS calculation. This file contains the charge, multiplicity, and the Cartesian coordinates and can be used to restart calculations (this is explained in more detail below).

In mode 2, one requires a GAUSSIAN03 executable (GAUSSIAN source code is not required). In mode 2, the intrinsic Hartree-Fock (HF), density functional theory (DFT), hybrid DFT, generalized Born, and analytic surface area capabilities of SMXGAUSS are used in conjunction with the "External" option of GAUSSIAN03. This allows GAUSSIAN03 to be the driver and to carry out geometry optimizations with the powerful GAUSSIAN optimizers but using the SMXGAUSS liquid-phase free energy routines, which are more accurate than those in GAUSSIAN (cf. Thompson et al., *J. Phys. Chem. A* **2004**, *108*, 6532 and Kelly et al., *J. Chem. Theory Comput.* **2005**, *1*, 1133). In mode 2, SMXGAUSS input files also have the same format as GAUSSIAN input files and the charge, multiplicity, and geometry can be specified in the SMXGAUSS input file (by the same methods as they are in GAUSSIAN, e.g., the geometry can be specified with Cartesian coordinates, Z-matrix coordinates, a combination of Cartesian and Z-matrix coordinates, etc.) or they can be read from a GAUSSIAN output file or from an SMXGAUSS summary file created from a previous SMXGAUSS calculation.

SMXGAUSS–version 3.4.1 has the following capabilities:

- Single-point liquid-phase free energy calculations based on gas-phase geometries are available by the following methods:

|                         |                       |
|-------------------------|-----------------------|
| SM5.42/HF/MIDI!         | SM5.42/BPW91/MIDI!    |
| SM5.42/HF/MIDI!6D       | SM5.42/BPW91/MIDI!6D  |
| SM5.42/HF/6-31G(d)      | SM5.42/BPW91/6-31G(d) |
| SM5.42/HF/6-31+G(d)     | SM5.42/BPW91/DZVP     |
| SM5.42/HF/cc-pVDZ       | SM5.42/B3LYP/MIDI!    |
| SM5.43/HF/6-31G(d)      | SM5.43/B3LYP/6-31G(d) |
| SM5.43/MPWX/MIDI!       | SM5.43/MPWX/MIDI!6D   |
| SM5.43/MPWX/6-31G(d)    | SM5.43/MPWX/6-31+G(d) |
| SM5.43/MWPX/6-31+G(d,p) |                       |
| SM6/BLYP/MIDI!6D        | SM6/BLYP/6-31G*       |
| SM6/BLYP/6-31+G*        | SM6/BLYP/6-31+G**     |
| SM6/B3LYP/MIDI!6D       | SM6/B3LYP/6-31G*      |
| SM6/B3LYP/6-31+G*       | SM6/B3LYP/6-31+G**    |
| SM6/BPW91/MIDI!6D       | SM6/BPW91/6-31G*      |
| SM6/BPW91/6-31+G*       | SM6/BPW91/6-31+G**    |
| SM6/B3PW91/MIDI!6D      | SM6/B3PW91/6-31G*     |
| SM6/B3PW91/6-31+G*      | SM6/B3PW91/6-31+G**   |
| SM6/MPWX/MIDI!6D        | SM6/MPWX/6-31G*       |
| SM6/MPWX/6-31+G*        | SM6/MPWX/6-31+G**     |
| SM6T/BLYP/MIDI!6D       | SM6T/BLYP/6-31G*      |
| SM6T/BLYP/6-31+G*       | SM6T/BLYP/6-31+G**    |
| SM6T/B3LYP/MIDI!6D      | SM6T/B3LYP/6-31G*     |
| SM6T/B3LYP/6-31+G*      | SM6T/B3LYP/6-31+G**   |
| SM6T/BPW91/MIDI!6D      | SM6T/BPW91/6-31G*     |
| SM6T/BPW91/6-31+G*      | SM6T/BPW91/6-31+G**   |
| SM6T/B3PW91/MIDI!6D     | SM6T/B3PW91/6-31G*    |
| SM6T/B3PW91/6-31+G*     | SM6T/B3PW91/6-31+G**  |
| SM6T/MPWX/MIDI!6D       | SM6T/MPWX/6-31G*      |
| SM6T/MPWX/6-31+G*       | SM6T/MPWX/6-31+G**    |

where  $X$  in MPWX is the fraction of Hartree-Fock exchange in the modified version of Perdew and Wang's exchange functional (allowed values of  $X$  can be between 0 and 99.9).

- Liquid-phase geometry optimizations, liquid-phase Hessian calculations, and single-point liquid-phase free energy calculations at arbitrary geometries may be carried out by the following methods:

|                       |                         |
|-----------------------|-------------------------|
| SM5.42/HF/MIDI!6D     | SM5.42/BPW91/MIDI!6D    |
| SM5.42/HF/6-31G(d)    | SM5.42/BPW91/6-31G(d)   |
| SM5.42/HF/6-31+G(d)   | SM5.42/BPW91/DZVP       |
| SM5.43/HF/6-31G(d)    | SM5.43/B3LYP/6-31G(d)   |
| SM5.43/MPWX/MIDI!6D   | SM5.43/MPWX/6-31G(d)    |
| SM5.43/MPWX/6-31+G(d) | SM5.43/MPWX/6-31+G(d,p) |
| SM6/BLYP/MIDI!6D      | SM6/BLYP/6-31G*         |
| SM6/BLYP/6-31+G*      | SM6/BLYP/6-31+G**       |
| SM6/B3LYP/MIDI!6D     | SM6/B3LYP/6-31G*        |
| SM6/B3LYP/6-31+G*     | SM6/B3LYP/6-31+G**      |
| SM6/BPW91/MIDI!6D     | SM6/BPW91/6-31G*        |
| SM6/BPW91/6-31+G*     | SM6/BPW91/6-31+G**      |
| SM6/B3PW91/MIDI!6D    | SM6/B3PW91/6-31G*       |
| SM6/B3PW91/6-31+G*    | SM6/B3PW91/6-31+G**     |
| SM6/MPWX/MIDI!6D      | SM6/MPWX/6-31G*         |
| SM6/MPWX/6-31+G*      | SM6/MPWX/6-31+G**       |

## Background References

Below are the references for the solvation models available in SMXGAUSS.

### **SM5.42**

Zhu, T.; Li, J.; Hawkins, G. D.; Cramer, C. J.; Truhlar, D. G. "Density Functional Solvation Model Based on CM2 Atomic Charges," *J. Chem. Phys.* **1998**, *109*, 9117.

Li, J.; Hawkins, G. D.; Cramer, C. J.; Truhlar, D. G. "Universal Reaction Field Model Based on Ab Initio Hartree-Fock Theory," *Chem. Phys. Lett.* **1998**, *288*, 293.

Li, J.; Zhu, T.; Hawkins, G. D.; Winget, P.; Liotard, D. A.; Cramer, C. J.; Truhlar, D. G. "Extension of the Platform of Applicability of the SM5.42R Universal Solvation Model," *Theor. Chem. Acc.* **1999**, *103*, 9.

Winget, P.; Thompson, J. D.; Cramer, C. J.; Truhlar, D. G. "Parameterization of a Universal Solvation Model for Molecules Containing Silicon," *J. Phys. Chem. B* **2002**, *106*, 5160.

### **Analytic Free Energy Gradients**

Zhu, T.; Li, J.; Liotard, D. A.; Cramer, C. J.; Truhlar, D. G. "Analytical Gradients of a Self-Consistent Reaction-Field Solvation Model Based on CM2 Atomic Charges," *J. Chem. Phys.* **1999**, *110*, 5503.

### **Application of SM5.42**

Chuang, Y.-Y.; Radhakrishnan, M. L.; Fast, P. L.; Cramer, C. J.; Truhlar, D. G. "Direct Dynamics for Free Radical Kinetics in Solution: Solvent Effect on the Rate Constant for the Reaction of Methanol with Atomic Hydrogen," *J. Phys. Chem. A* **1999** *103*, 4893.

### **SM5.43**

Thompson, J. D.; Cramer, C. J.; Truhlar, D. G. "New Universal Solvation Model and Comparison of the Accuracy of the SM5.42R, SM5.43R, C-PCM, D-PCM, and IEF-PCM Continuum Solvation Models for Aqueous and Organic Solvation Free Energies and for Vapor Pressures," *J. Phys. Chem A* **2004**, *108*, 6532.

Thompson, J. D.; Cramer, C. J.; Truhlar, D. G. "Density-Functional and Hybrid-DFT SM5.43R Continuum Solvation Models for Aqueous and Organic Solvents," *Theor. Chem. Acc.* **2005**, *113*, 107.

### **SM6**

Kelly, C. P.; Cramer, C. J.; Truhlar, D. G. "SM6: A Density Functional Theory Continuum Solvation Model for Predicting Aqueous Solvation Free Energies of Neutrals, Ions, and Solute-Water Clusters" *J. Chem. Theory and Comput.* **2005**, *1*, 1133.

### **SM6T**

Chamberlin, A. C.; Cramer, C. J.; Truhlar, D. G. "Predicting Aqueous Free Energies of Solvation as Functions of Temperature" *J. Phys. Chem. B.* in press.

### ***Basis Set References***

The following list gives the references for all basis sets supported by SMXGAUSS:

- MIDI! for H

Tatewaki, H.; Huzinaga, S. *J. Comput. Chem.* **1980**, *1*, 205.

- MIDI! for Li

Tatewaki, H.; Huzinaga, S. *J. Comput. Chem.* **1980**, *1*, 205.

Thompson, J. D.; Winget, P.; Truhlar, D. G. *PhysChemComm.* **2001**, *4*, 4116.

- MIDI! for C-F

Tatewaki, H.; Huzinaga, S. *J. Comput. Chem.* **1980**, *1*, 205.

Easton, R. E.; Giesen, D. J.; Welch, A.; Cramer, C. J.; Truhlar, D. G. *Theor Chim Acta.* **1996**, *93*, 281.

- MIDI! for Si

Huzinaga, S.; Andzelm, J.; Klobukowski, M.; Radzio-Audzelm, E.; Sakai, Y.; Tatewaki, H. *Gaussian basis sets for molecular calculations*; Huzinaga, S., Ed.; Elsevier: Amsterdam, 1984.

Li, J.; Cramer, C. J.; Truhlar, D. G. *Theor. Chem. Acc.* **1998**, *99*, 192.

- MIDI! for P-Cl

Huzinaga, S.; Andzelm, J.; Klobukowski, M.; Radzio-Audzelm, E.; Sakai, Y.; Tatewaki, H. *Gaussian basis sets for molecular calculations*; Huzinaga, S., Ed.; Elsevier: Amsterdam, 1984.

Easton, R. E.; Giesen, D. J.; Welch, A.; Cramer, C. J.; Truhlar, D. G. *Theor Chim Acta.* **1996**, *93*, 281.

- MIDI! for Br and I

Dobbs, K. D.; Hehre, W. J. *J. Comput. Chem.* **1986**, *7*, 359.

Li, J.; Cramer, C. J.; Truhlar, D. G. *Theor. Chem. Acc.* **1998**, *99*, 192.

- 6-31G for H

Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724

- 6-31G for Li  
Dill, J. D.; Pople, J. A. *J. Chem. Phys.* **1975**, *62*, 2921.
- 6-31G for C, N, O, and F  
Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.
- 6-31G for Si, P, S, and Cl  
Francl, M. M.; Petro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.
- *d*-polarization for 6-31G for Li  
Dill, J. D.; Pople, J. A. *J. Chem. Phys.* **1975**, *62*, 2921.
- *d*-polarization for 6-31G for C, N, O, and F  
Hairharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.
- *d*-polarization for 6-31G for Si, P, S, and Cl  
Francl, M. M.; Petro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.
- *sp*-diffuse for 6-31G for Li, C, N, O, F, Si, P, S, and Cl  
Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.
- 6-31G(d) and 6-31+G(d) for Br  
GAUSSIAN94, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakszewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, 1995.
- 6-31G(d) for I  
MIDI!6D is used.

- *sp*-diffuse for 6-31G for I

MIDI!6D augmented with a set of *sp* functions with an orbital exponent of 0.03 is used.

- cc-pVDZ for H, Li, C, N, O, and F

Dunning, T. H. Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

- cc-pVDZ for Si, P, S, and Cl

Woon, D. E.; Dunning, T. H. Jr. *J. Chem. Phys.* **1993**, *98*, 1358.

- cc-pVDZ for Br and I

MIDI! is used.

- DZVP

Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560.

### ***Free Energy, Vapor Pressure, Solubility, Kinetics, and Electrostatics***

The basic output of an SMXGAUSS calculation is a free energy of solvation. Free energies of solvation may be used to calculate Henry's law constants, partition coefficients, chemical potentials, solubilities, and other thermodynamic properties. A general reference is

Cramer, C. J.; Truhlar, D. G. in *Free Energy Calculations in Rational Drug Design*; Reddy, M. R. and Erion M. D., Eds.; Kluwer Academic/Plenum: New York, 2001; pp. 63-95.

A general reference for the use of solvation free energies to calculate partition coefficients is

Giesen, D. J.; Hawkins, G. D.; Liotard, D. A.; Cramer, C. J.; Truhlar, D. G. *Theor. Chem. Acc.* **1997**, *98*, 85.

A general reference for the use of solvation free energies to calculate vapor pressures is

Winget, P.; Hawkins, G. D.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2000**, *104*, 4726.

A general reference for the use of solvation free energies to calculate solubilities is

Thompson, J. D.; Cramer, C. J.; Truhlar, D. G. *J. Chem. Phys.* **2003**, *119*, 1661.

General references for the use of solvation free energies to calculate rate constants are

Chuang, Y.-Y.; Cramer, C. J.; Truhlar, D. G. *Int. J. Quantum Chem.* **1998**, *70*, 887.  
Chuang, Y.-Y.; Radhakrishnan, M. L.; Fast, P. L.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. A* **1999**, *103*, 4893.

In addition to solvation free energies, another quantity available in the output is class IV partial atomic charges, which may be used for calculating electrostatic interactions.

General references are

Storer, J. W.; Giesen, D. J.; Cramer, C. J.; Truhlar, D. G. *J. Comput.-Aid. Mol. Des.* **1995**, *9*, 87.

Barrows, S. E.; Cramer, C. J.; Truhlar, D. G.; Elovitz, M. S.; Weber, E. J. *Environ. Sci. Technol.* **1996**, *30*, 3028.

Winget, P.; Thompson, J. D.; Xidos, J. D.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. A* **2002**, *106*, 10707.

Kelly, C. P.; Cramer, C. J.; Truhlar, D. G. *Theor. Chem. Acc.* **2005**, *113*, 133.

## Required Citations

Publications based on results obtained with this package should give the following reference plus one or more of the background references (given in the previous section) for whatever method is used:

Chamberlin, A. C.; Kelly, C. P.; Thompson, J. D.; Lynch, B. J.; Xidos, J. D.; Li, J.; Hawkins, G. D.; Zhu, T.; Volobuev, Y.; Dupuis, M.; Rinaldi, D.; Liotard, D. A.; Cramer, C. J.; Truhlar, D. G. SMXGAUSS-version 3.3, University of Minnesota, Minneapolis, MN 55455, 2004.

In addition, of course, if the GAUSSIAN program is also used, to supply GAUSSIAN output files for SMXGAUSS calculations and/or to utilize the "External" option provided by the GAUSSIAN03 executable, one should give any references required by GAUSSIAN.

## SMXGAUSS Input and Keywords

The format and syntax of an SMXGAUSS input file is similar to the format and syntax of a GAUSSIAN input file (see the *Gaussian Input* section of the GAUSSIAN manual). In particular, the route section is specified first (currently, Link 0 commands, such as %chk, %rwf, %subst, etc. are not allowed). The route section is initiated with the "#" symbol, can be on multiple lines, and is terminated with a blank line. After the route section, the title section is specified, which can also be on more than one line and is terminated with a blank line.

When the program is run in mode 1 a GAUSSIAN03 executable is not required to run SMXGAUSS. When the program is run in mode 2 (i.e., you do have a GAUSSIAN03 executable and wish to use it for geometry optimization with the "External" option), the charge, multiplicity, and geometry can be specified in the molecular specifications section in the input file; this section follows the title section. In addition, the charge, multiplicity, and geometry can be taken from a GAUSSIAN output file or from an SMXGAUSS summary file created from a previous SMXGAUSS calculation.

The route section is comprised of keywords and options to keywords. These keywords are used to specify the electronic structure method, basis set, solvation model, solvent, type of calculation to carry out (i.e., a single-point calculation in the liquid phase, a geometry optimization in the liquid phase to a minimum or transition state, or a Hessian calculation in the liquid phase), and several other optional keywords and options. This input can be on multiple lines (but the specification of an individual keyword must be all on one line). See the sample runs below for examples of multiple-line input. Options to keywords are specified in a similar fashion as they are in GAUSSIAN, e.g., keyword = option, keyword = (option), or keyword = (option1, option2, ...).

There are two types of keywords in SMXGAUSS; (i) basic keywords, which specify the electronic structure method, basis set, solvation model, solvent, and several other simple options and (ii) advanced keywords, which are used to override several defaults automatically set by SMXGAUSS. Most users will only need to be familiar with the basic keywords. Note that the defaults set by SMXGAUSS have been tested on a large test set of calculations in water and organic solvents (about 2200 calculations), so these defaults should work in most cases.

Although keywords are given in the recommended combination of capital letters and lower case letters, SMXGAUSS is actually case-insensitive for all input.

## ***Basic Keywords***

Below are descriptions of the basic keywords available in SMXGAUSS.

### Specification of the Solvation Model

There are three solvation models available in SMXGAUSS:

|        |  |
|--------|--|
| SM5.42 | Requests a calculation using the SM5.42 solvation model. |
| SM5.43 | Requests a calculation using the SM5.43 solvation model. |
| SM6    | Requests a calculation using the SM6 solvation model.    |

### Specification of the Electronic Structure Method and Basis Set

The following electronic structure methods are available in SMXGAUSS (where their names also indicate their keywords):

HF  
 BLYP  
 B3LYP  
 BPW91  
 B3PW91  
 mPWPW91  
 mPW1PW91  
 MPW1K

MPWX, where X is the fraction of Hartee-Fock exchange\*1000 in the modified version of Perdew and Wang's exchange functional. The value X must only be three significant figures. Example: to specify a fraction of Hartree-Fock exchange of 0.428, the correct keyword would be MPW428.

The following basis sets are available in SMXGAUSS (where their names also indicate their keywords):

MIDI! (can also be specified as MIDIX, MIDIX5D, or MIDI!5D)  
 MIDI!6D (can also be specified as MIDIX6D)  
 6-31G(d) (can also be specified as 6-31G\*)  
 6-31+G(d) (can also be specified as 6-31+G\*)  
 cc-pVDZ  
 DZVP

Note: Not all of the methods listed above are compliant with SM5.42, SM5.43, and SM6. See the section entitled “*Allowed Combinations of Solvation Model, Electronic Structure Method, and Basis Set*” for more details.

### Allowed Combinations of Solvation Model, Electronic Structure Method, and Basis Set

The SM $x$  ( $x = 5.42, 5.43,$  and  $6$ ) solvation models are parameterized models, where the parameters are determined for particular combinations of an electronic structure method and basis set. Allowed combinations are given in the tables below. Any other combinations will result in an error message.

#### For SM5.42 single-point calculations

| electronic structure method | basis set |
|-----------------------------|-----------|
| HF                          | MIDI!     |
| HF                          | MIDI!6D   |
| HF                          | 6-31G(d)  |
| HF                          | 6-31+G(d) |
| HF                          | cc-pVDZ   |
| BPW91                       | MIDI!     |
| BPW91                       | MIDI!6D   |
| BPW91                       | 6-31G(d)  |
| BPW91                       | DZVP      |
| B3LYP                       | MIDI!     |

#### For SM5.42 liquid-phase geometry optimizations and Hessian calculations

| electronic structure method | basis set |
|-----------------------------|-----------|
| HF                          | MIDI!6D   |
| HF                          | 6-31G(d)  |
| HF                          | 6-31+G(d) |
| BPW91                       | MIDI!6D   |
| BPW91                       | 6-31G(d)  |
| BPW91                       | DZVP      |

## For SM5.43 single-point calculations

| electronic structure method | basis set   |
|-----------------------------|-------------|
| HF                          | 6-31G(d)    |
| B3LYP                       | 6-31G(d)    |
| mPWPW91                     | MIDI!       |
| mPWPW91                     | MIDI!6D     |
| mPWPW91                     | 6-31G(d)    |
| mPWPW91                     | 6-31+G(d)   |
| mPWPW91                     | 6-31+G(d,p) |
| mPW1PW91                    | MIDI!       |
| mPW1PW91                    | MIDI!6D     |
| mPW1PW91                    | 6-31G(d)    |
| mPW1PW91                    | 6-31+G(d)   |
| mPW1PW91                    | 6-31+G(d,p) |
| MPW1K                       | MIDI!       |
| MPW1K                       | MIDI!6D     |
| MPW1K                       | 6-31G(d)    |
| MPW1K                       | 6-31+G(d)   |
| MPW1K                       | 6-31+G(d,p) |
| MPW1KK                      | MIDI!       |
| MPW1KK                      | MIDI!6D     |
| MPW1KK                      | 6-31G(d)    |
| MPW1KK                      | 6-31+G(d)   |
| MPW1KK                      | 6-31+G(d,p) |
| MPWX                        | MIDI!       |
| MPWX                        | MIDI!6D     |
| MPWX                        | 6-31G(d)    |
| MPWX                        | 6-31+G(d)   |
| MPWX                        | 6-31+G(d,p) |

For SM5.43 liquid-phase geometry optimizations and Hessian calculations

| electronic structure method | basis set   |
|-----------------------------|-------------|
| HF                          | 6-31G(d)    |
| B3LYP                       | 6-31G(d)    |
| mPWPW91                     | MIDI!6D     |
| mPWPW91                     | 6-31G(d)    |
| mPWPW91                     | 6-31+G(d)   |
| mPWPW91                     | 6-31+G(d,p) |
| mPW1PW91                    | MIDI!6D     |
| mPW1PW91                    | 6-31G(d)    |
| mPW1PW91                    | 6-31+G(d)   |
| mPW1PW91                    | 6-31+G(d,p) |
| MPW1K                       | MIDI!6D     |
| MPW1K                       | 6-31G(d)    |
| MPW1K                       | 6-31+G(d)   |
| MPW1K                       | 6-31+G(d,p) |
| MPW1KK                      | MIDI!6D     |
| MPW1KK                      | 6-31G(d)    |
| MPW1KK                      | 6-31+G(d)   |
| MPW1KK                      | 6-31+G(d,p) |
| MPWX                        | MIDI!6D     |
| MPWX                        | 6-31G(d)    |
| MPWX                        | 6-31+G(d)   |
| MPWX                        | 6-31+G(d,p) |

## For SM6 and SM6T single-point calculations

| electronic structure method | basis set   |
|-----------------------------|-------------|
| BLYP                        | MIDI!6D     |
| BLYP                        | 6-31G(d)    |
| BLYP                        | 6-31+G(d)   |
| BLYP                        | 6-31+G(d,p) |
| B3LYP                       | MIDI!6D     |
| B3LYP                       | 6-31G(d)    |
| B3LYP                       | 6-31+G(d)   |
| B3LYP                       | 6-31+G(d,p) |
| BPW91                       | MIDI!6D     |
| BPW91                       | 6-31G(d)    |
| BPW91                       | 6-31+G(d)   |
| BPW91                       | 6-31+G(d,p) |
| B3PW91                      | MIDI!6D     |
| B3PW91                      | 6-31G(d)    |
| B3PW91                      | 6-31+G(d)   |
| B3PW91                      | 6-31+G(d,p) |
| mPWPW91                     | MIDI!6D     |
| mPWPW91                     | 6-31G(d)    |
| mPWPW91                     | 6-31+G(d)   |
| mPWPW91                     | 6-31+G(d,p) |
| mPW1PW91                    | MIDI!6D     |
| mPW1PW91                    | 6-31G(d)    |
| mPW1PW91                    | 6-31+G(d)   |
| mPW1PW91                    | 6-31+G(d,p) |
| MPW1K                       | MIDI!6D     |
| MPW1K                       | 6-31G(d)    |
| MPW1K                       | 6-31+G(d)   |
| MPW1K                       | 6-31+G(d,p) |
| MPW1KK                      | MIDI!6D     |
| MPW1KK                      | 6-31G(d)    |
| MPW1KK                      | 6-31+G(d)   |
| MPW1KK                      | 6-31+G(d,p) |
| MPWX                        | MIDI!6D     |
| MPWX                        | 6-31G(d)    |
| MPWX                        | 6-31+G(d)   |
| MPWX                        | 6-31+G(d,p) |

For SM6 liquid-phase geometry optimizations and  
Hessian calculations

| electronic structure method | basis set   |
|-----------------------------|-------------|
| BLYP                        | MIDI!6D     |
| BLYP                        | 6-31G(d)    |
| BLYP                        | 6-31+G(d)   |
| BLYP                        | 6-31+G(d,p) |
| B3LYP                       | MIDI!6D     |
| B3LYP                       | 6-31G(d)    |
| B3LYP                       | 6-31+G(d)   |
| B3LYP                       | 6-31+G(d,p) |
| BPW91                       | MIDI!6D     |
| BPW91                       | 6-31G(d)    |
| BPW91                       | 6-31+G(d)   |
| BPW91                       | 6-31+G(d,p) |
| B3PW91                      | MIDI!6D     |
| B3PW91                      | 6-31G(d)    |
| B3PW91                      | 6-31+G(d)   |
| B3PW91                      | 6-31+G(d,p) |
| mPWPW91                     | MIDI!6D     |
| mPWPW91                     | 6-31G(d)    |
| mPWPW91                     | 6-31+G(d)   |
| mPWPW91                     | 6-31+G(d,p) |
| mPW1PW91                    | MIDI!6D     |
| mPW1PW91                    | 6-31G(d)    |
| mPW1PW91                    | 6-31+G(d)   |
| mPW1PW91                    | 6-31+G(d,p) |
| MPW1K                       | MIDI!6D     |
| MPW1K                       | 6-31G(d)    |
| MPW1K                       | 6-31+G(d)   |
| MPW1K                       | 6-31+G(d,p) |
| MPW1KK                      | MIDI!6D     |
| MPW1KK                      | 6-31G(d)    |
| MPW1KK                      | 6-31+G(d)   |
| MPW1KK                      | 6-31+G(d,p) |
| MPWX                        | MIDI!6D     |
| MPWX                        | 6-31G(d)    |
| MPWX                        | 6-31+G(d)   |
| MPWX                        | 6-31+G(d,p) |

## Specification of the Solvent

The SM5x ( $x = 42$  and  $43$ ) solvation models are universal; they are defined for water and any organic solvent that has known values for a set of seven solvent descriptors. (currently, SM6 calculations can only be performed in aqueous solution; a universal model for SM6 will be available in future implementations of SMXGAUSS). The seven solvent descriptors are the bulk dielectric constant,  $\epsilon$ ; the refractive index (at the wavelength of the Na D line),  $n$ ; Abraham's hydrogen bond acidity parameter,  $\alpha$  (which Abraham denotes as  $\sum \alpha_2$ ); Abraham's hydrogen bond basicity parameter,  $\beta$  (which Abraham denotes as  $\sum \beta_2$ ); the reduced surface tension,  $\gamma$ ; which equals  $\gamma_m / \gamma^\circ$  where  $\gamma_m$  is the macroscopic surface tension at a liquid-air interface at 298 K and  $\gamma^\circ$  is  $1 \text{ cal mol}^{-1} \text{ \AA}^{-2}$ ; the fraction of nonhydrogenic solvent atoms that are aromatic carbon atoms (carbon aromaticity),  $\phi$ ; and the fraction of nonhydrogenic solvent atoms that are F, Cl, or Br (electronegative halogenicity),  $\psi$ .

When the solvent is water, it is specified with the keyword "Solvent = Water". Organic solvents can be specified with one of two keywords:

Solvent = Solvent\_Name, where Solvent\_Name is the name of the solvent given in a file named solvent.txt. This file is provided in the SMXGAUSS distribution and contains the seven required solvent descriptors for 175 organic solvents. The user can add additional solvents to this file. The solvent.txt file is tab-delimited, and the descriptors for a particular solvent in this file appear in this order:  $n$ ,  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\epsilon$ ,  $\phi$ , and  $\psi$ . A list of available solvents is given in the section entitled *Available Solvents in the solvent.txt File* below.

If the solvent of interest is not provided in the solvent.txt file, then the Solvent\_Descriptors keyword must be used. The seven descriptors are specified as options to the Solvent\_Descriptors keyword. The options are:

Dielectric =  $d$ , where  $d$  is the solvent's bulk dielectric constant, also called the relative permittivity

N =  $n$  where  $n$  is the solvent's index of refraction

Alpha =  $a$ , where  $a$  is Abraham's acidity parameter

Beta =  $b$ , where  $b$  is Abraham's basicity parameter

Gamma =  $g$ , where  $g$  is the macroscopic surface tension coefficient

Phi =  $p$ , where  $p$  is the solvent's carbon aromaticity parameter

Psi =  $s$ , where  $s$  is the solvent's electronegative halogenicity parameter

**Example:** Request toluene solvent with the Solvent\_Descriptors keyword.

The seven solvent descriptors for toluene are  $n = 1.496$ ,  $\epsilon = 2.37$ ,  $\alpha = 0.0$ ,  $\beta = 0.14$ ,  $\gamma = 41.4$ ,  $\phi = 0.86$ , and  $\psi = 0.0$ . The Solvent\_Descriptors keyword would be:

```
Solvent_Descriptors=(n=1.496,Alpha=0.0,Beta=0.14,Gamma=41.4,Phi=0.86,Psi=0.0,  
Dielectric=2.37)
```

### Specification of the Solvent Temperature

Computation of solute thermodynamic properties at a given temperature using SM6T can be requested using the SolK keyword.

In test7a, test7b, test7c, and test7d the SolK keyword is tested for water in water at temperatures 273, 298, 348 and 373 K respectively.

The SolK keyword is currently only applicable to the aqueous solutions in the temperature range 273 to 373 K, a request for anything outside this range, or the use of non-aqueous solvents will produce an error. Additionally the model SM6T is currently restricted to H, C, and O containing compounds, use of compounds containing atoms other than H, C, or O will not produce an error, however the results should be used with caution. Additionally this method does not yet have gradients; it can only be used to compute single-point energies.

## Specification of the Type of Calculation

There are three types of calculations that can be performed with SMXGAUSS: a liquid-phase single-point calculation on the geometry provided in the input file, a GAUSSIAN output file, or an SMXGAUSS summary file, a liquid-phase geometry optimization to a minimum or to a transition state, or a liquid-phase Hessian calculation. For single-point calculations no further input other than the specification of the electronic structure method, basis set, solvent, and, when applicable, the Coordinates keyword (described below) is required in the route section. To carry out geometry optimizations in the liquid phase, the Opt keyword is used, and to carry out frequency or Hessian calculations, the Freq keyword is used. The usage of these two keywords is as follows:

**Opt**        Requests a geometry optimization. When this keyword is specified, a gas-phase geometry optimization is first performed, using the input geometry as an initial guess. Once the gas-phase geometry optimization is complete, a liquid-phase geometry optimization is then carried out, using the gas-phase optimized geometry as an initial guess.

This keyword has the following options (but note that using this keyword alone will request a geometry optimization to a minimum with reasonable defaults):

**TS**        Requests a liquid-phase geometry optimization to a transition state.

**MaxCycles =  $n$** , where  $n$  is an integer number that specifies the maximum number of geometry optimization steps allowed (default is 100).

**Converge =  $c$** , where  $c$  specifies the convergence threshold on the maximum gradient component in hartree/bohr (default is 0.005). This option is only available if you do not have GAUSSIAN03 installed. If you have GAUSSIAN03, then the convergence criteria used in GAUSSIAN03 is used.

**CalcFCGas**        Requests a calculation of the gas-phase Hessian at the initial set of gas-phase coordinates (see the section entitled *Using a Hessian Matrix for Geometry Optimizations*).

**CalcFCSol**        Requests a calculation of the liquid-phase Hessian at the initial set of liquid-phase coordinates (see the section entitled *Using a Hessian Matrix for Geometry Optimizations*).

**Freq**        Requests a liquid-phase Hessian calculation followed by a vibrational frequency analysis. This keyword can be used to characterize stationary points as minima or transition states (see the section entitled *Identifying Minima and Transition States with a Hessian Calculation*).

Note that the Opt and Freq cannot be used in the same calculation.

## Specification of the Charge, Multiplicity, and Geometry

The charge, multiplicity, and coordinates for an SMXGAUSS calculation can be taken from a GAUSSIAN output file or from an SMXGAUSS summary file created from a previous SMXGAUSS calculation. This file is specified with the Coordinates keyword in the route section of the SMXGAUSS input file:

Coordinates = *file*, where *file* is a GAUSSIANX ( $X = 94, 98,$  or  $03$ ) output file or an SMXGAUSS summary file created from a previous SMXGAUSS calculation.

For users who do not have a GAUSSIAN03 executable, specification of the Coordinates keyword is required. For users who have a GAUSSIAN03 executable, the geometry can be specified either with the Coordinates keyword or in the molecular specifications section of the input file. In the latter case, the coordinates can be specified in the usual GAUSSIAN formats, i.e., by using Cartesian coordinates, a Z-matrix, a combination of Cartesian coordinates and Z-matrix coordinates, etc.

The SMXGAUSS summary file is useful for restarting geometry optimizations, using accurate Hessians to facilitate geometry optimizations, and for characterizing optimized geometries as minima or transition states. For examples of these types of calculations, see the sections entitled *Restarting Geometry Optimizations*, *Using a Hessian Matrix for Geometry Optimizations*, and *Identifying Minima and Transition States with a Hessian Calculation* below.

### ***Advanced Keywords***

Every attempt has been made to assign reasonable default values to all numerical parameters. Therefore the hope is that this section is not needed. Nevertheless, below are available keywords in SMXGAUSS that can be used to change some of the options used to override some of the normal defaults that are used in the SCF portion of SM $x$  ( $x = 5.42, 5.43,$  and 6) calculations.

SCF        Changes some of the default options used to converge the SCF. This keyword has the following options:

MaxCycles =  $n$ , where  $n$  is an integer number specifying the maximum number of SCF cycles allowed (default is 300).

Acuracy =  $x$ , where  $x$  is the convergence criterion for the SCF (default is 0.0000001). This criterion applies to the density matrix.

Conventional    Requests a conventional SCF calculation, i.e., store two-electron integrals on disk (this is the default).

Semi-Direct     Specifies that some of the two-electron integrals are stored on disk and that some of them are calculated as needed, depending on the available memory. This option is currently only available for HF.

Direct        Specifies that all two-electron integrals are calculated as needed and none are stored on disk. This option is currently only available for HF.

## Installing SMXGAUSS

A working version of PERL is required to install and run SMXGAUSS. To run in mode 2, a GAUSSIAN03 executable is required. SMXGAUSS is distributed as a tarred and gzipped file named `smxgaussv3.4.1.tar.gz`.

To install SMXGAUSS:

- 1.) Unzip the file `smxgaussv3.4.1.tar.gz`, which creates a tar file named `smxgaussv3.4.1.tar`:

```
gunzip smxgaussv3.4.1.tar.gz
```

- 2.) Untar the file `smxgaussv3.4.1.tar`, which creates a directory named `SMxGauss-v3.4.1`:

```
tar -xvf smxgaussv3.4.1.tar
```

- 3.) Change into the directory `SMxGauss-v3.4.1`

```
cd SMxGauss-v3.4.1
```

**To finish installing SMXGAUSS for mode 1 (the “External” option in GAUSSIAN03 will NOT be used; no GAUSSIAN executables are needed):**

- 4.) Execute the c-shell script named `install.csh`

```
/bin/csh install.x.csh
```

where *x* is one of the install files distributed with SMXGAUSS. Currently, install files exist for a number of combinations of machine/operating system and compiler (for example, the install file `install.sun-g77.csh` is intended for installation on a Sun machine with the gnu `g77` compiler). If you are unsure which install file to use, refer to the section entitled “*Platforms*” near the end of this manual for a list of platforms that SMXGAUSS has been tested on. Once the proper install script has been chosen and executed with the above command, this script will ask you if you have GAUSSIAN03 installed and where the `g03` executable is located. Answer no, press enter, and then wait for the source code to compile. This may take some time, depending on the system.

**To finish installing SMXGAUSS for mode 2 (the “External” option in GAUSSIAN03 will be used):**

- 4.) Unload GAUSSIAN03 (as well as any previous versions of GAUSSIAN)

```
module unload g03
```

- 5.) Add the absolute path of the location of the SMXGAUSS distribution to your `$PATH` variable. For example, if you untar and unzip the SMXGAUSS distribution in `/home/thompson`, then use the command:

```
set path = (. $path /home/thompson/SMxGauss-v3.4.1)
```

6.) Load GAUSSIAN03

*module load g03*

7.) Verify that the absolute path of the location of the SMXGAUSS distribution to your \$PATH variable is listed *before* the absolute path of the location of GAUSSIAN03 by typing

*echo \$path*

If the absolute path of the location of the SMXGAUSS distribution is NOT listed before the absolute path of the location of GAUSSIAN03, steps 4 – 7 must be repeated.

8.) Use the command

*which g03*

to determine the location of the GAUSSIAN03 executable on your system. Copy or write down this absolute path, as it will be used in step 9.

9.) Execute the c-shell script named *install.x.csh*

*/bin/csh install.x.csh*

where *x* is one of the install files distributed with SMXGAUSS. Currently, install files exist for a number of combinations of machine/operating system and compiler (for example, the install file *install.sun-g77.csh* is intended for installation on a Sun machine with the gnu *g77* compiler). If you are unsure which install file to use, refer to the section entitled “*Platforms*” near the end of this manual for a list of platforms that SMXGAUSS has been tested on. Once the proper install script has chosen and executed with the above command, this script will ask you if you have GAUSSIAN03. Answer yes, and press enter. The script will then ask you for the absolute path to the *g03* executable. Give the absolute path from step 8, press enter. Finally, the script will ask you whether you have version D01 or later of Gaussian 03. This information should be available in the Gaussian users manual or from your system administrator. Then wait for the source code to compile. This may take some time, depending on the system.

Important note for running in mode 2: Because running SMXGAUSS in mode 2 requires executing step 5 each time a new session is started, it is recommended that step 5 be added to the user’s “.cshrc” file, or any initialization file read in during the login process. Keep in mind that step 5 must always be executed when GAUSSIAN03 is unloaded in order for SMXGAUSS to run in mode 2.

## Setting up the Location of the SMXGAUSS Scratch Directory

SMXGAUSS creates and uses several scratch files during a given calculation, which are deleted after the calculation has finished. Because the length of the path to the scratch directory cannot exceed 80 characters, it is highly recommended that the user set the location of the scratch directory before running SMXGAUSS. By default, SMXGAUSS creates a directory named *input.\$\$*, where *input* is the name of the input file for the calculation and *\$\$* is a random number, in the same directory in which the calculation is run. If the path containing this default directory name is more than 80 characters in length, the SMXGAUSS calculation will not run properly. The location of *input.\$\$* can be changed from this default by defining the environment variable *SCRPATH*.

**Example:** Set the scratch directory to be located in */scratch/smxgauss*.

Use the command:

```
setenv SCRPATH /scratch/smxgauss
```

Be sure that the directory to which *SCRPATH* is set exists.

## Running SMXGAUSS

To run an SMXGAUSS calculation, use the command:

```
Executable_Path/smxgX.pl input output
```

where *Executable\_Path* is the location of the SMXGAUSS program, and *X* is either 1 (if SMXGAUSS was installed under mode 1) or 2, (if SMXGAUSS was installed under mode 2), *input* is the name of the SMXGAUSS input file and *output* is the name of the SMXGAUSS output file. The *output* file contains intermediate and final results of the SCRF calculation and of the geometry optimization steps and a summary of the solvation calculation, including the predicted standard-state free energy of solvation (see the sample output below).

In addition to the output file, SMXGAUSS also creates a summary file, named *input.pun*. This file contains useful information for restarting liquid-phase single-point calculations, liquid-phase geometry optimizations (see the section entitled *Restarting Geometry Optimizations* and *Using a Hessian Matrix for Geometry Optimizations* below), and for characterizing liquid-phase optimized structures via vibrational frequency analysis (see the section entitled *Identifying Minima and Transition States with Hessian a Calculation* below). Because *input.pun* is a text file, it is transferable to other machines.

## Restarting Geometry Optimizations

In general, a liquid-phase geometry optimization with SMXGAUSS is an automated, two-step procedure. In the first step, the geometry of the solute is optimized in the gas phase with the electronic structure method and basis set specified in the SMXGAUSS input file. In the second step, this gas-phase geometry is optimized in the liquid phase at the same level of theory used in the gas phase, and the corresponding optimized Cartesian coordinates from both the gas and liquid phases are printed to the SMXGAUSS output and summary files. You can determine whether or not the geometry has successfully been optimized in the gas phase by searching for the string:

"Gas-phase optimized coordinates"

and in the liquid phase by searching for the string:

"Liquid-phase optimized coordinates"

in the SMXGAUSS output file.

When the geometry in the liquid-phase does not optimize within the number of steps allotted to the calculation (which is specified by the MaxCycles option to the Opt keyword), the calculation terminates, and the latest set of liquid-phase Cartesian coordinates is printed to the SMXGAUSS summary file. You can determine whether or not the geometry optimization exceeded the number of steps allotted to the calculation by searching for the string:

"Maximum number of geometry optimization steps has been exceeded"

in the SMXGAUSS output file.

To restart failed geometry optimizations, use the `Coordinates=input.pun` (where *input.pun* is the name of the SMXGAUSS summary file created from the previous SMXGAUSS calculation, see *Running SMXGAUSS* above) and run the calculation again.

**Example:** Optimize the geometry of hydrogen sulfide in water solvent using SM5.42 and HF/MIDI!6D. Create an SMXGAUSS input file called h2s.inp containing the following keywords:

```
# HF/MIDI!6D Opt=(MaxCycles=2)
sm5.42
solvent = water
coordinates = h2s.xyz
```

1) Use the command:

*Executable\_Path/smxgX.pl h2s.inp h2s.out*

where *X* is either 1 or 2. The gas-phase geometry will optimize within two steps, but not the liquid-phase geometry, so the calculation will need to be restarted.

2) Search h2s.out for the string "Maximum number of geometry optimization steps has been exceeded " to verify that the geometry is not yet optimized.

3) Create a new input file, named h2s\_2.inp containing the following keywords:

```
# HF/MIDI!6D Opt
sm5.42
solvent = water
coordinates = (h2s.pun)
```

4) Use the command:

*Executable\_Path/smxgX.pl h2s\_2.inp h2s\_2.out*

where *X* is either 1 or 2. The program will find the latest set of liquid-phase coordinates from the previous calculation, so it will skip the geometry optimization in the gas phase.

5) Search h2s\_2.out for the string:

"Liquid-phase optimized coordinates"

to verify that the geometry has optimized in the liquid phase.

## Using a Hessian Matrix for Geometry Optimizations

To facilitate geometry optimizations in the liquid phase, a Hessian calculated at the geometry of the solute in the liquid phase can be used.

**Example:** Optimize the geometry of hydrogen sulfide in water solvent using SM5.42 and HF/MIDI!6D. The name of the input file is calcfc.inp, which contains:

```
# HF/MIDI!6D Opt=(CalcFCSol)
sm5.42
solvent = water
coordinates = h2s.xyz
```

1) Use the command:

*Executable\_Path/smxgX.pl calcfc.inp calcfc.out*

where *X* is either 1 or 2. This calculation first optimizes the structure in the gas phase at the HF/MIDI!6D level, carries out a liquid-phase Hessian calculation on the gas-phase optimized geometry, and then optimizes the geometry in the liquid phase beginning from the gas-phase optimized geometry and the initial Hessian calculated at this geometry.

The CalcFCSol option can also be used when restarting liquid-phase geometry optimizations. In this case, the Hessian calculation is carried out on the latest set of liquid-phase coordinates found in the file specified by the Coordinates keyword.

**Example:** Optimize the geometry of hydrogen sulfide in water solvent using SM5.42 and HF/MIDI!6D. The name of the first SMXGAUSS input file is h2s.inp, the contents of which are:

```
# HF/MIDI!6D Opt=(MaxCycles=2)
sm5.42
solvent = water
coordinates = h2s.xyz
```

1) Use the command:

*Executable\_Path/smxgX.pl h2s.inp h2s.out*

where *X* is either 1 or 2. The geometry will optimize in the gas phase within two steps, but not in the liquid phase. Search the output file for the string "Exceeded number of allowed steps in geometry optimization" to verify that the geometry is not optimized in the liquid phase yet.

2) Create a new input file named h2s\_restart.inp, containing:

```
# HF/MIDI!6D Opt=CalcFCSol  
SM5.42  
Solvent=Water  
Coordinates=h2s.pun
```

water

1) Use the command:

*Executable\_Path/smxgX.pl h2s\_restart.inp h2s\_restart.out*

where *X* is either 1 or 2. The latest set of Cartesian coordinates in the liquid phase is located on the file h2s.pun and these coordinates are the initial coordinates used in this calculation. Because the CalcFCSol option is specified, a Hessian calculation in the liquid phase at these coordinates is carried out first. Then a geometry optimization in the liquid phase is carried out beginning with these coordinates and using the initial liquid-phase Hessian.

The CalcFCGas keyword is used in a similar fashion to CalcFCSol, but it is used to aid geometry optimizations in the gas phase. CalcFCGas and CalcFCSol can be used in the same calculation.

## Performing Geometry Optimizations on Transition States

As mentioned above, a liquid-phase geometry optimization with SMXGAUSS is an automated, two-step procedure. In the first step, the geometry of the solute is optimized in the gas phase with the electronic structure method and basis set specified in the SMXGAUSS input file. In the second step, this gas-phase geometry is optimized in the liquid phase at the same level of theory used in the gas phase, and the corresponding optimized Cartesian coordinates from both the gas and liquid phases are printed to the SMXGAUSS output and summary files.

For transition state geometry optimizations, it is often recommended that a Hessian calculation be performed on the initial gas phase geometry (using CalcFCGas), as well as on the optimized gas phase geometry (using CalcFCSol). For an example of a calculation in which both the CalcFCGas and CalcFCSol keywords are used in the same calculation, see test case test6.inp below. In some cases (e.g., in cases where the user knows that the input geometry is very close to a stationary point, or in cases where very little structural relaxation is expected to occur in the liquid phase) using the CalcFCGas and CalcFCSol keywords may not be required in order for the transition state geometry optimization to run successfully. For an example of a transition state geometry optimization that converges without using either of these keywords, see test case test5.inp below.

### *Special note to users running SMXGAUSS in mode 2.*

SMXGAUSS can be used to optimize transition state geometries with or without first performing Hessian calculations, regardless of whether the program is being run in mode 1 or mode 2. For users running SMXGAUSS in mode 2, it is useful to point out that some versions of GAUSSIAN03 do not allow the user to perform transition state geometry optimizations (via the Opt=TS keyword) without first calculating (or reading in via the input file) force constants generated from an initial Hessian calculation. While testing SMXGAUSS, we discovered that this is true for GAUSSIAN03 revision C.01. Several earlier versions of GAUSSIAN03 that were also tested (revision B.01 and B.05) do not have this limitation (i.e. transition state optimizations *can* be performed without an initial set of force constants). However, regardless of the GAUSSIAN03 revision that is used to run SMXGAUSS in mode 2, SMXGAUSS does not have this limitation (see test5.smxgauss). User's interested in learning more about how SMXGAUSS avoids this limitation should see the file mkgauss.lib that is contained in the distribution of SMXGAUSS.

## Identifying Minima and Transition States with a Hessian Calculation

Hessian calculations can also be used to characterize stationary points as minima or transition states.

**Example:** Optimize the geometry of hydrogen sulfide in water solvent using SM5.42 and HF/MIDI!6D and then characterize it as a minimum via vibrational frequency analysis. The name of the first SMXGAUSS file is h2s\_opt.inp, the contents of which are:

```
# HF/MIDI!6D Opt
sm5.42
solvent = water
coordinates = h2s.xyz
```

1) Use the command:

```
Executable_Path/smxgX.pl h2s_opt.inp h2s_opt.out
```

where *X* is either 1 or 2. Search the output file for the string "Liquid-phase optimized coordinates" to verify that the geometry has been optimized in the liquid phase.

2) Create a new input file named freq.inp, containing:

```
# HF/MIDI!6D Freq
SM5.42
Solvent=Water
Coordinates=h2s_opt.pun
```

3) Use the command:

*Executable\_Path/smxgX.pl freq.inp freq.out*

where *X* is either 1 or 2. Locate the vibrational frequencies and their corresponding normal modes by searching for the string:

"Vibrational frequencies (CM\*\**-1*) and normal modes"

in *freq.out*. For linear molecules, the five frequencies that are smallest in magnitude will almost always correspond to rotational and translational modes. For nonlinear molecules, the six frequencies that are smallest in magnitude will correspond to these modes. The translational and rotational frequencies are printed last, after the vibrational frequencies. Note that when all vibrational frequencies (excluding the five or six from translations and rotations) are real numbers (i.e., when they are all positive), the structure corresponds to a minimum, and when one or more of the vibrational frequencies is imaginary (they will be printed as negative numbers), the structure corresponds to a transition state.

## Test Calculations for SMXGAUSS

This section contains eight test calculations for SMXGAUSS, which are located in the tests directory of the SMXGAUSS distribution. These test jobs are described below.

### test1.inp

#### Input

```
#SM6
B3LYP/6-31+G(d,p)
Solvent=water
Coordinates=h2s.xyz
```

```
SM6/B3LYP/6-31+G(d,p) calculation
of the aqueous solvation free energy
of hydrogen sulfide;
(experimental value = -0.7 kcal/mol)
```

#### Summary of Output

```
##### Summary of SMxGauss calculation #####
Gas-phase energy at B3LYP/6-31+G(D,P) = -399.393411 a.u.
G-S(liq) free energy of system at B3LYP/6-31+G(D,P) = -399.394703 a.u.
Standard-state free energy of solvation = -0.811 kcal/mol
Free energy of cavity-dispersion-solvent structure = 0.020 kcal/mol
Free energy of polarization = -0.918 kcal/mol
Electronic/Nuclear distortion energy = 0.087 kcal/mol
```

#### Description of Output

The standard-state free energy of solvation is calculated to be  $-0.811$  kcal/mol.

This output reports the following:

- i) the expectation value of the energy using the gas-phase optimized wave function, which is  $-399.393411$  hartrees.
- ii) the free energy in solution, which is  $-399.394703$  hartrees.
- iii) the nonbulk electrostatic contribution to the free energy of solvation. This value is calculated to be  $0.020$  kcal/mol.
- iv) the expectation value of the polarization energy, which is calculated by the generalized Born method using the liquid-phase wave function. This value is calculated to be  $-0.918$  kcal/mol.
- v) the distortion energy, which is the change in the energy of the solute upon solvation, i.e., the difference between the liquid-phase energy and the gas-phase energy. This value is calculated to be  $0.087$  kcal/mol.

**test2a.inp****Input**

```
#SM6 Opt
MPW1PW91/6-31G(d)
Solvent=water
Coordinates=h2s.xyz
```

```
SM6/MPW1PW91/6-31G(d) optimization
of hydrogen sulfide in water
```

**Summary of Output**

The gas-phase geometry optimization has completed successfully.

--- Gas-phase optimized coordinates ---

|   |          |           |           |
|---|----------|-----------|-----------|
| S | 0.000000 | 0.000000  | 0.102881  |
| H | 0.000000 | 0.973724  | -0.823047 |
| H | 0.000000 | -0.973724 | -0.823047 |

--- Liquid-phase optimized coordinates ---

|   |          |           |           |
|---|----------|-----------|-----------|
| S | 0.000000 | 0.000000  | 0.103118  |
| H | 0.000000 | 0.972303  | -0.824948 |
| H | 0.000000 | -0.972303 | -0.824948 |

##### Summary of SMxGauss calculation #####

|   |                  |
|---|------------------|
| Gas-phase energy at MPW1PW91/6-31G(D) =               | -399.384306 a.u. |
| G-S(liq) free energy of system at MPW1PW91/6-31G(D) = | -399.386383 a.u. |
| Standard-state free energy of solvation =             | -1.303 kcal/mol  |
| Free energy of cavity-dispersion-solvent structure =  | -0.334 kcal/mol  |
| Free energy of polarization =                         | -1.084 kcal/mol  |
| Electronic/Nuclear distortion energy =                | 0.115 kcal/mol   |

**Description of Output**

Both the gas and liquid-phase optimized coordinates are printed to output. The standard-state free energy of solvation for the liquid-phase optimized geometry is calculated to be  $-1.303$  kcal/mol.

**test2b.inp****Input**

```
#SM6 Freq Solvent=water
MPW1PW91/6-31G(d)
Coordinates=test2a.pun
```

```
Numerical frequency evaluation (liquid-phase)
for the liquid-phase optimized geometry obtained
from test2a.inp
```

**Summary of Output**

----- Vibrational frequencies (CM<sup>-1</sup>) and normal modes -----

|             |   |   | 2769.48 | 2748.97 | 1246.76 | 10.24   |
|-------------|---|---|---------|---------|---------|---------|
|             |   |   | A       | A       | A       | A       |
| 1           | S | X | .00000  | .04097  | .00000  | .00000  |
|             |   | Y | .02970  | .00000  | .00000  | .02108  |
|             |   | Z | -.00029 | .00000  | .00000  | .57722  |
| 2           | H | X | .00000  | -.70651 | .70711  | .00000  |
|             |   | Y | -.47233 | .00000  | .00000  | .01787  |
|             |   | Z | -.52609 | .00000  | .00000  | .57395  |
| 3           | H | X | .00000  | -.70651 | -.70711 | .00000  |
|             |   | Y | -.47234 | .00000  | .00000  | .01864  |
|             |   | Z | .52549  | .00000  | .00000  | .57990  |
| NORM** (-1) |   |   | .00000  | .00000  | .00000  | .00000  |
|             |   |   | 5       | 6       | 7       | 8       |
|             |   |   | -8.30   | -14.49  | -28.14  | -35.77  |
|             |   |   | A       | A       | A       | A       |
| 1           | S | X | .00000  | .60943  | .00000  | .00000  |
|             |   | Y | .57739  | .00000  | .00000  | .00000  |
|             |   | Z | -.02092 | .00000  | -.03198 | .03000  |
| 2           | H | X | .00000  | .56062  | .00000  | .00000  |
|             |   | Y | .57679  | .00000  | .49143  | .52271  |
|             |   | Z | -.02153 | .00000  | .50792  | -.47575 |
| 3           | H | X | .00000  | .56062  | .00000  | .00000  |
|             |   | Y | .57674  | .00000  | -.49142 | -.52268 |
|             |   | Z | -.02025 | .00000  | .50793  | -.47575 |
| NORM** (-1) |   |   | .00000  | .00000  | .00000  | .00000  |

```

          9
        -91.63
          A
1   S      X   .00000
        Y  -.03222
        Z   .00000
2   H      X   .00000
        Y   .51114
        Z  -.48806
3   H      X   .00000
        Y   .51117
        Z   .48806

      NORM** (-1)   .00000

```

### **Description of Output**

The three vibrational frequencies of hydrogen sulfide (in wave numbers) are 2769, 2749, and 1247. Below each frequency is the corresponding normal mode. The last six frequencies listed correspond to rotational and translational modes.

.

## test3.inp

### Input

```
#SM6 Opt=(CalcFCGas) Solvent=water  
B3PW91/MIDIX6D  
Coordinates=h2s.xyz
```

```
SM6/B3PW91/MIDIX6D optimization of hydrogen sulfide  
in water; force constants calculated at initial  
gas-phase geometry to facilitate geometry  
optimization in the liquid phase
```

### Summary of Output

```
##### Summary of SMxGauss calculation #####
```

```
Gas-phase energy at B3PW91/MIDIX6D = -397.475673 a.u.  
G-S(liq) free energy of system at B3PW91/MIDIX6D = -397.477643 a.u.  
Standard-state free energy of solvation = -1.236 kcal/mol  
Free energy of cavity-dispersion-solvent structure = -0.360 kcal/mol  
Free energy of polarization = -0.994 kcal/mol  
Electronic/Nuclear distortion energy = 0.118 kcal/mol
```

### Description of Output

The standard-state free energy of solvation is calculated to be  $-1.236$  kcal/mol.

## test4.inp

### Input

```
#SM6 opt=(CalcFCsol) Solvent=water  
B3PW91/MIDIX6D  
Coordinates=h2s.xyz
```

```
SM6/B3PW91/MIDIX6D optimization  
of hydrogen sulfide in water; liquid-phase  
force constants calculated for the  
optimized gas-phase geometry to facilitate  
geometry optimization in the liquid phase
```

### Summary of Output

```
##### Summary of SMxGauss calculation #####
```

```
Gas-phase energy at B3PW91/MIDIX6D = -397.475677 a.u.  
G-S(liq) free energy of system at B3PW91/MIDIX6D = -397.477643 a.u.  
Standard-state free energy of solvation = -1.234 kcal/mol  
Free energy of cavity-dispersion-solvent structure = -0.361 kcal/mol  
Free energy of polarization = -0.995 kcal/mol  
Electronic/Nuclear distortion energy = 0.122 kcal/mol
```

### Description of Output

The standard-state free energy of solvation is calculated to be  $-1.234$  kcal/mol.

**test5.inp****Input**

```
#SM6 Opt=(TS)
MPW1K/6-31+G(d)
Solvent=water
Coordinates=h2o-oh.xyz
```

```
SM6/MPW1K/6-31+G(d) optimization of the
H2O-OH transition state (CS), in water
```

**Summary of Output**

```
--- Gas-phase optimized coordinates ---
```

|   |           |           |          |
|---|-----------|-----------|----------|
| H | -0.941703 | -1.413748 | 0.000000 |
| O | -0.000420 | -1.242876 | 0.000000 |
| H | 0.047155  | -0.159683 | 0.000000 |
| O | -0.000420 | 1.243564  | 0.000000 |
| H | 0.901275  | 1.567924  | 0.000000 |

```
--- Liquid-phase optimized coordinates ---
```

|   |           |           |          |
|---|-----------|-----------|----------|
| H | -0.930986 | -1.544716 | 0.000000 |
| O | 0.002049  | -1.295690 | 0.000000 |
| H | 0.017537  | -0.288646 | 0.000000 |
| O | 0.002049  | 1.311635  | 0.000000 |
| H | 0.880669  | 1.705800  | 0.000000 |

```
##### Summary of SMxGauss calculation #####
```

|  |                  |
|--|------------------|
| Gas-phase energy at MPW1K/6-31+G(D) =                | -152.193401 a.u. |
| G-S(liq) free energy of system at MPW1K/6-31+G(D) =  | -152.344243 a.u. |
| Standard-state free energy of solvation =            | -94.654 kcal/mol |
| Free energy of cavity-dispersion-solvent structure = | -7.152 kcal/mol  |
| Free energy of polarization =                        | -89.888 kcal/mol |
| Electronic/Nuclear distortion energy =               | 2.386 kcal/mol   |

**Description of Output**

The optimized geometry of the water-hydroxide transition state structure in both the gas and liquid-phases is printed to output. The standard-state free energy of solvation for the liquid-phase structure is calculated to be -94.654 kcal/mol.

**test6.inp****Input**

```
#SM6 Opt=(CalcFCGas,TS,CalcFCSol)
MPW1K/6-31+G(d)
Solvent=water
Coordinates=h2o-oh.xyz
```

```
SM6/MPW1K/6-31+G(d) optimization of the
H2O-OH transition state (CS), in water;
force constants are calculated in both the
gas and liquid-phase to facilitate geometry
optimization
```

**Summary of Output**

```
--- Gas-phase optimized coordinates ---
```

|   |           |           |          |
|---|-----------|-----------|----------|
| H | -0.941716 | -1.413254 | 0.000000 |
| O | -0.000416 | -1.242997 | 0.000000 |
| H | 0.047323  | -0.159670 | 0.000000 |
| O | -0.000416 | 1.243533  | 0.000000 |
| H | 0.901049  | 1.568632  | 0.000000 |

```
--- Liquid-phase optimized coordinates ---
```

|   |           |           |          |
|---|-----------|-----------|----------|
| H | -0.930741 | -1.545884 | 0.000000 |
| O | 0.002026  | -1.295755 | 0.000000 |
| H | 0.016390  | -0.288973 | 0.000000 |
| O | 0.002026  | 1.312185  | 0.000000 |
| H | 0.881937  | 1.703418  | 0.000000 |

```
##### Summary of SMxGauss calculation #####
```

|  |                  |
|--|------------------|
| Gas-phase energy at MPW1K/6-31+G(D) =                | -152.193401 a.u. |
| G-S(liq) free energy of system at MPW1K/6-31+G(D) =  | -152.344242 a.u. |
| Standard-state free energy of solvation =            | -94.655 kcal/mol |
| Free energy of cavity-dispersion-solvent structure = | -7.152 kcal/mol  |
| Free energy of polarization =                        | -89.902 kcal/mol |
| Electronic/Nuclear distortion energy =               | 2.399 kcal/mol   |

**Description of Output**

The optimized geometry of the water-hydroxide transition state structure in both the gas and liquid-phases is printed to output. The standard-state free energy of solvation for the liquid-phase structure is calculated to be -94.655 kcal/mol.

**test7a.inp****Input**

```
#SM6
B3LYP/6-31+G(d,p)
SolK=273
Solvent=water
Coordinates=h2o.xyz
```

```
SM6T/B3LYP/6-31+G(d,p) calculation
of the aqueous solvation free energy
of water at 273 K;
(experimental value = -4.46 kcal/mol)
```

**Summary of Output**

```
##### Summary of SMxGauss calculation at 273 K #####
```

|   |                 |
|---|-----------------|
| Gas-phase energy at B3LYP/6-31+G(D,P) =               | -76.433989 a.u. |
| G-S(liq) free energy of system at B3LYP/6-31+G(D,P) = | -76.449145 a.u. |
| Standard-state free energy of solvation =             | -9.511 kcal/mol |
| Free energy of cavity-dispersion-solvent structure =  | -3.900 kcal/mol |
| Free energy of polarization =                         | -5.845 kcal/mol |
| Electronic/Nuclear distortion energy =                | 0.234 kcal/mol  |

**Description of Output**

**test7b.inp****Input**

```
#SM6
B3LYP/6-31+G(d,p)
SolK=298
Solvent=water
Coordinates=h2o.xyz
```

```
SM6T/B3LYP/6-31+G(d,p) calculation
of the aqueous solvation free energy
of water at 298 K;
(experimental value = -3.94 kcal/mol)
```

**Summary of Output**

```
##### Summary of SMxGauss calculation at 298 K #####
```

```
Gas-phase energy at B3LYP/6-31+G(D,P) = -76.433989 a.u.
G-S(liq) free energy of system at B3LYP/6-31+G(D,P) = -76.448478 a.u.
Standard-state free energy of solvation = -9.092 kcal/mol
Free energy of cavity-dispersion-solvent structure = -3.489 kcal/mol
Free energy of polarization = -5.836 kcal/mol
Electronic/Nuclear distortion energy = 0.233 kcal/mol
```

**Description of Output**

**test7c.inp****Input**

```
#SM6
B3LYP/6-31+G(d,p)
SolK=348
Solvent=water
Coordinates=h2o.xyz
```

```
SM6T/B3LYP/6-31+G(d,p) calculation
of the aqueous solvation free energy
of water at 348 K;
(experimental value = -2.98 kcal/mol)
```

**Summary of Output**

```
##### Summary of SMxGauss calculation at 348 K #####
```

```
Gas-phase energy at B3LYP/6-31+G(D,P) = -76.433989 a.u.
G-S(liq) free energy of system at B3LYP/6-31+G(D,P) = -76.447269 a.u.
Standard-state free energy of solvation = -8.334 kcal/mol
Free energy of cavity-dispersion-solvent structure = -2.750 kcal/mol
Free energy of polarization = -5.815 kcal/mol
Electronic/Nuclear distortion energy = 0.231 kcal/mol
```

**Description of Output**

**test7d.inp****Input**

```
#SM6
B3LYP/6-31+G(d,p)
SolK=373
Solvent=water
Coordinates=h2o.xyz
```

```
SM6T/B3LYP/6-31+G(d,p) calculation
of the aqueous solvation free energy
of water at 373 K;
(experimental value = -2.53 kcal/mol)
```

**Summary of Output**

```
##### Summary of SMxGauss calculation at 373 K #####
```

```
Gas-phase energy at B3LYP/6-31+G(D,P) = -76.433989 a.u.
G-S(liq) free energy of system at B3LYP/6-31+G(D,P) = -76.446721 a.u.
Standard-state free energy of solvation = -7.989 kcal/mol
Free energy of cavity-dispersion-solvent structure = -2.417 kcal/mol
Free energy of polarization = -5.803 kcal/mol
Electronic/Nuclear distortion energy = 0.231 kcal/mol
```

**Description of Output**

## **SCRF Schemes**

The keyword ISCRF determines which SCRF scheme is used for a given calculation. The value of ISCRF is automatically set by SMXGAUSS based on which basis set is used. Currently, ISCRF is set to either 1 or 2. When ISCRF is set to 1, SCRF scheme I is used. This scheme uses the current solution-phase elements of the Mayer bond order matrix at every step of the SCF iterations. In SMXGAUSS, Scheme I is automatically used for all methods that do not use diffuse basis functions, except for SM5.42/HF/cc-pVDZ.

The other SCRF scheme used in SMXGAUSS is called Scheme II (ISCRF=2). This scheme uses elements of the gas-phase Mayer bond order matrix instead of the liquid-phase elements. In SMXGAUSS, Scheme II is automatically used for SM5.42/HF/cc-pVDZ and all methods that use basis sets containing diffuse functions.

In general, both schemes yield very similar results. However, Scheme I does not always converge the SCF for methods using larger basis sets, such as cc-pVDZ or basis sets with diffuse functions, but Scheme II almost always does. Note that geometry optimizations or Hessian calculations cannot be carried out using the MIDI!5D (also called MIDI! or MIDIX) or cc-pVDZ basis sets because analytical free energy gradients are not available for basis sets using spherical harmonic  $d$  and  $f$  functions (or functions of higher angular momentum than  $f$ ).

## Density Functional Methods Recommended for use with CM4 and SM6 in SMXGAUSS

| Pure DFT functionals recommended for use with CM4 and SM6 in SMXGAUSS. |                  |  |
|--|------------------|--|
| Method   | SMXGAUSS Keyword | Reference(s)   |
| BLYP   | BLYP             | A. D. Becke, <i>Phys. Rev. A</i> <b>38</b> , 3098 (1988).<br>C. Lee, W. Yang, and R. G. Parr, <i>Phys. Rev. B</i> <b>37</b> , 785 (1988).<br>B. Miehlich, A. Savin, H. Stoll, and H. Preuss, <i>Chem. Phys. Lett.</i> <b>157</b> , 200 (1989).   |
| BPW91  | BPW91            | A. D. Becke, <i>Phys. Rev. A</i> <b>38</b> , 3098 (1988).<br>K. Burke, J. P. Perdew, and Y. Wang, in <i>Electronic Density Functional Theory: Recent Progress and New Directions</i> , Ed. J. F. Dobson, G. Vignale, and M. P. Das (Plenum, 1998).<br>J. P. Perdew, in <i>Electronic Structure of Solids ' 91</i> , Ed. P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991) 11.<br>J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, <i>Phys. Rev. B</i> <b>46</b> , (1992).<br>J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, <i>Phys. Rev. B</i> <b>48</b> , (1993).<br>J. P. Perdew, K. Burke, and Y. Wang, <i>Phys. Rev. B</i> <b>54</b> , 16533 (1996).            |
| mPWPW91  | MPW000           | C. Adamo and V. Barone, <i>J. Chem. Phys.</i> <b>108</b> , 664 (1998).<br>K. Burke, J. P. Perdew, and Y. Wang, in <i>Electronic Density Functional Theory: Recent Progress and New Directions</i> , Ed. J. F. Dobson, G. Vignale, and M. P. Das (Plenum, 1998)<br>J. P. Perdew, in <i>Electronic Structure of Solids ' 91</i> , Ed. P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991) 11<br>J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, <i>Phys. Rev. B</i> <b>46</b> , (1992).<br>J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, <i>Phys. Rev. B</i> <b>48</b> , (1993).<br>J. P. Perdew, K. Burke, and Y. Wang, <i>Phys. Rev. B</i> <b>54</b> , 16533 (1996). |

| Hybrid DFT functionals recommended for use with CM4 and SM6 in SMXGAUSS. |               |                              |  |
|--|---------------|------------------------------|--|
| Method   | Fraction HFE  | SMXGAUSS Keyword             | Reference(s)   |
| B3LYP  | 0.200         | B3LYP                        | P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, <i>J. Phys. Chem.</i> <b>98</b> , 11623 (1994). |
| B3PW91   | 0.200         | B3PW91                       | A. D. Becke, <i>J. Chem. Phys.</i> <b>98</b> , 5648 (1993).  |
| mPW1PW91   | 0.250         | MPW1PW91 <i>or</i><br>MPW250 | C. Adamo and V. Barone, <i>J. Chem. Phys.</i> <b>108</b> , 664 (1998).   |
| MPW1S  | 0.060         | MPW060                       | B. J. Lynch, Y. Zhao, and D. G. Truhlar, <i>J. Phys. Chem. A</i> <b>107</b> , 1384 (2003).                         |
| MPW1N  | 0.406         | MPW406                       | B. L. Kormos and C. J. Cramer, <i>J. Phys. Org. Chem.</i> <b>15</b> , 712 (2002).                                  |
| MPW1K  | 0.428         | MPW428                       | B. J. Lynch, P. L. Fast, M. Harris and D. G. Truhlar <i>J. Phys. Chem. A</i> <b>104</b> , 4811 (2000).             |
| MPWX   | 0.000 – 0.999 | MPW(000-999)                 |  |

## Available Solvents in the solvent.txt file

Below is a list of the solvents available in the file solvent.txt. A pdf version of this file can be found at <http://comp.chem.umn.edu/solvation/mnsddb.pdf>. Note that each solvent should appear in the SMXGAUSS input exactly as it appears below (except for case, since the input is case-insensitive). If the solvent of interest is not listed, either the Solvent\_Descriptors keyword needs to be used or the solvent name and its descriptors should be added to the solvent.txt file (which is in tab-delimited format).

1,1,1-trichloroethane  
 1,1,2-trichloroethane  
 1,1-dichloroethane  
 1,2,4-trimethylbenzene  
 1,4-dioxane  
 1-bromo-2-methylpropane  
 1-bromopentane  
 1-bromopropane  
 1-butanol  
 1-chloropentane  
 1-chloropropane  
 1-decanol  
 1-fluorooctane  
 1-heptanol

1-hexanol  
1-hexene  
1-hexyne  
1-iodobutane  
1-iodopentene  
1-iodopropane  
1-nitropropane  
1-nonanol  
1-octanol  
1-pentanol  
1-pentene  
1-pentyne  
1-propanol  
2,2,2-trifluoroethanol  
2,2,4-trimethylpentane  
2,4-dimethylpentane  
2,4-dimethylpyridine  
2,6-dimethylpyridine  
2-bromopropane  
2-chlorobutane  
2-heptanone  
2-hexanone  
2-methyl-2propanol  
2-methylpentane  
2-methylpyridine  
2-nitropropane  
2-octanone  
2-pentanone  
2-propanol  
2-propen-1-ol  
3-methylpyridine  
3-pentanone  
4-heptanone  
4-methyl 2-pentanone  
4-methylpyridine  
5-nonanone  
alpha-chlorotoluene  
acetonitrile  
aniline  
anisole  
benzaldehyde  
benzene  
benzonitrile  
benzyl alcohol  
bromobenzene  
bromoethane

bromooctane  
butanal  
butanoic acid  
butanone  
butanonitrile  
butyl ethanoate  
butylamine  
butylbenzene  
carbon disulfide  
carbon tetrachloride  
chlorobenzene  
cis-1,2-dimethylcyclohexane  
cis-decalin  
cyclohexane  
cyclohexanone  
cyclopentane  
cyclopentanol  
cyclopentanone  
decane  
dibromomethane  
dibutyl ether  
dichloromethane  
diethyl ether  
diethyl sulfide  
diethylamine  
diiodomethane  
dimethyl disulfide  
dimethylacetamide  
dimethylformamide  
dimethylpyridine  
dimethylsulfoxide  
dipropylamine  
dodecane  
E-1,2-dichloroethene  
E-2-pentene  
ethanethiol  
ethanoic acid  
ethanol  
ethyl ethanoate  
ethyl methanoate  
ethyl phenyl ether  
ethylbenzene  
ethylene glycol  
fluorobenzene  
formamide  
formic acid

hexadecyl iodide  
hexanoic acid  
iodobenzene  
iodoethane  
iodomethane  
isobutanol  
isopropyl ether  
isopropylbenzene  
isopropyltoluene  
m-cresol  
m-xylene  
mesitylene  
methanol  
methyl benzoate  
methyl ethanoate  
methyl methanoate  
methyl phenyl ketone  
methyl propanoate  
methylbutanoate  
methylcyclohexane  
methylformamide  
n-heptane  
n-hexadecane  
n-hexane  
n-methylaniline  
n-octane  
n-pentane  
nitrobenzene  
nitroethane  
nitromethane  
n-nonane  
o-chlorotoluene  
o-cresol  
o-dichlorobenzene  
o-nitrotoluene  
o-xylene  
p-xylene  
pentadecane  
pentanal  
pentanoic acid  
pentyl ethanoate  
pentylamine  
perfluorobenzene  
phenyl ether  
propanal  
propanoic acid

propanone  
propanonitrile  
propyl ethanoate  
propylamine  
pyridine  
pyrrolidine  
sec-butanol  
tbutylbenzene  
tetrachloroethene  
tetrahydrofuran  
tetrahydrothiophenedioxide  
tetralin  
thiophene  
thiophenol  
toluene  
trans-decalin  
tribromomethane  
tributylphosphate  
trichloroethene  
trichloromethane  
triethylamine  
undecane  
Z-1,2-dichloroethene

## Troubleshooting

Below is a listing of some error messages generated by SMXGAUSS and a brief explanation of why they are printed by the program.

**Error message:** system mopac failed: -1 at /usr/local/g03/g03.c01/g03/bsd/Gau\_External line 53, <INF> line 4.

**Explanation:** SMXGAUSS was not installed properly (mode 2), and must be reinstalled. The absolute path of the location of the smxgauss distribution is not listed before the absolute path of the location of GAUSSIAN03.

**Error message:** SM5.42, SM5.43, or SM6 was not found in input. You must specify one of these options.

**Explanation:** The keyword SM5.42, SM5.43, or SM6 must be specified in the SMXGAUSS input file.

**Error message:** Electronic structure method not found in input. You must specify HF, BPW91, B3LYP, or mPWX, (X=PW91,1PW91,1K,1KK, or fraction HF exchange\*1000.

**Explanation:** The solvation models in SMXGAUSS are used in conjunction with any of the above electronic structure methods, so one of them needs to be specified in the input file. See the section entitled *Basic Keywords* above for appropriate combinations of solvation model, electronic structure method, and basis set.

**Error message:** Basis set not found in input. You must specify MIDI!, MIDI!6D, 6-31G(d), 6-31+G(d), cc-pVDZ, or DZVP.

**Explanation:** The solvation models in SMXGAUSS are used in conjunction with any of the above basis sets, so one of them needs to be specified in the input file. See the section entitled *Basic Keywords* above for appropriate combinations of solvation model, electronic structure method, and basis set.

**Error message:** SM $x$  ( $x = 5.42, 5.43, \text{ or } 6$ ) parameters do not exist for *Level/Basis*. See the SMXGAUSS manual for a listing of methods for which SM $x$  ( $x = 5.42, 5.43, 6$ ) exist.

**Explanation:** The choice of solvation model, electronic structure method, and basis set are inconsistent. See the section entitled *Basic Keywords* for a listing of allowed combinations.

**Error message:** You have requested a calculation that requires analytical gradients, but they are not available for basis sets with spherical harmonic  $d$  and  $f$  functions.

**Explanation:** The solvation models in SMXGAUSS only have analytic free energy gradients for basis sets with Cartesian  $d$  and  $f$ . So whenever MIDI! (MIDIX, MIDIX5D, or MIDI!5D) or cc-pVDZ are used, they can only be used for single-point calculations.

**Error message:** Both Solvent and Solvent\_Descriptors keywords were found in the input. Use only one of them to specify the solvent for your calculation.

**Explanation:** Specify the solvent only once, using either the Solvent keyword or the Solvent\_Descriptors keyword.

**Error message:** Neither the Solvent nor the Solvent\_Descriptors were found in the input file.

**Explanation:** You must specify the solvent with either the Solvent keyword or the Solvent\_Descriptors keyword.

## Platforms

SMXGAUSS version 3.3 has been tested on the following platforms:

| Machine                         | Operating System     | Compiler(s)   | Install File   |
|---------------------------------|----------------------|---|--|
| IBM SP WinterHawk+ nodes        | AIX version 5.1      | XL Fortran version 9.1                              | <i>install.ibm.csh</i>                                   |
| IBM SP NightHawk nodes          | AIX version 5.1      | XL Fortran version 9.1                              | <i>install.ibm.csh</i>                                   |
| IBM pSeries 690 and pSeries 655 | AIX version 5.2      | XL Fortran version 9.1                              | <i>install.ibm.csh</i>                                   |
| Netfinity Linux cluster         | Red Hat Linux 2.4.21 | pgf77 version 5.2.4<br>gnu g77 version 3.2.3        | <i>install.linux.csh</i><br><i>install.linux-g77.csh</i> |
| SGI-Altix, Itanium 2            | Red Hat Linux 2.4.21 | gnu g77 version 3.2.3                               | <i>install.ia64.csh</i>                                  |
| SGI Origin 2000                 | IRIX version 6.5     | MIPSPro version 7.4.1<br>gnu g77 version 3.2.3      | <i>install.irix.csh</i><br><i>install.irix-g77.csh</i>   |
| SunBlade 2000 UltraSparc III    | Solaris 9            | Sun ONE Studio version 7.1<br>gnu g77 version 3.3.1 | <i>install.sun.csh</i><br><i>install.irix-g77.csh</i>    |
| Mac G5 (OS X version 10.4.3)    | Darwin 7.9.0         | gnu g77 version 3.5.0                               | <i>install.darwin.csh</i>                                |

SMXGAUSS version 3.4.1 has been tested in mode 2 with the following versions of GAUSSIAN03:

- GAUSSIAN03, Revision C.01
- GAUSSIAN03, Revision D.01

Prior versions of SMXGAUSS have also been tested in mode 2 with the following versions of GAUSSIAN03:

- GAUSSIAN03, Revision B.01
- GAUSSIAN03, Revision B.05

## Revision History

### **SMXGAUSS—version 1.0 (April 2004)**

**Authors: J. D. Thompson, B. J. Lynch, J. D. Xidos, J. Li, G. D. Hawkins, T. Zhu, Y. Volobuev, M. Dupuis, D. Rinaldi, D. A. Liotard, C. J. Cramer, and D. G. Truhlar**

This version of SMXGAUSS is based on version 4.5 of HONDOPLUS.

This is the first version of SMXGAUSS. SMXGAUSS can be used to carry out SM5.42 and SM5.43 calculations using the appropriate wave functions specified in the Executive Summary.

### **SMXGAUSS—version 2.0 (October 2004)**

**Authors: J. D. Thompson, B. J. Lynch, J. D. Xidos, J. Li, G. D. Hawkins, T. Zhu, Y. Volobuev, M. Dupuis, D. Rinaldi, D. A. Liotard, C. J. Cramer, and D. G. Truhlar**

This version of SMXGAUSS is based on version 4.6 of HONDOPLUS.

Additional parameter sets for the SM5.43 solvation model were added. In particular, the parameters for MPWX/MIDI!, MPWX/MIDI!6D, MPWX/6-31G(d), MPWX/6-31+G(d), and MPWX/6-31+G(d,p), where  $X$  can take on any value between 0 and 60.6, were added.

### **SMXGAUSS—version 3.0 (July 2005)**

**Authors: C. P. Kelly, J. D. Thompson, B. J. Lynch, J. D. Xidos, J. Li, G. D. Hawkins, T. Zhu, Y. Volobuev, M. Dupuis, D. Rinaldi, D. A. Liotard, C. J. Cramer, and D. G. Truhlar**

This version of SMXGAUSS is based on version 4.7 of HONDOPLUS.

Parameter sets for the SM6 solvation model were added. Parameters were added for DFT/MIDI!6D, DFT/6-31G(d), DFT/6-31+G(d), and DFT/6-31+G(d,p), where  $X$  can take on any value between 0 and 99.9.

All of the SM $x$  models can use up to 99.9 for  $X$ , instead of the previous upper limit that was set to 60.6.

Atomic radii are now available for all elements on the periodic table.

**SMXGAUSS–version 3.0.1 (October 2005)**

**Authors: C. P. Kelly, J. D. Thompson, B. J. Lynch, J. D. Xidos, J. Li, G. D. Hawkins, T. Zhu, Y. Volobuev, M. Dupuis, D. Rinaldi, D. A. Liotard, C. J. Cramer, and D. G. Truhlar**

This version of SMXGAUSS is based on version 4.7 of HONDOPLUS.

In SMXGAUSS–version 3.0, a bug in the file named procinput.lib caused the program to stop when liquid-phase Hessian calculations were attempted. This bug has been fixed in SMXGAUSS–version 3.0.1.

**SMXGAUSS–version 3.1 (November 2005)**

**Authors: C. P. Kelly, J. D. Thompson, B. J. Lynch, J. D. Xidos, J. Li, G. D. Hawkins, T. Zhu, Y. Volobuev, M. Dupuis, D. Rinaldi, D. A. Liotard, C. J. Cramer, and D. G. Truhlar**

This version of SMXGAUSS is based on version 4.9 of HONDOPLUS.

This version of SMXGAUSS has been tested on more platforms than previous versions.

A new test suite has been developed that includes test jobs that test the CalcFCGas, CalcFCSol, and TS keywords.

**SMXGAUSS–version 3.2 (December 2005)**

**Authors: C. P. Kelly, J. D. Thompson, B. J. Lynch, J. D. Xidos, J. Li, G. D. Hawkins, T. Zhu, Y. Volobuev, M. Dupuis, D. Rinaldi, D. A. Liotard, C. J. Cramer, and D. G. Truhlar**

If SMXGAUSS is installed under mode 1, the executable is now named smxg1.pl. If installed under mode 2, the executable is named smxg2.pl.

The mode used to run SMXGAUSS (either mode1 or mode2) is printed to the output file.

The ISCRF option (via the override) keyword is no longer supported.

A warning message is printed and the calculation ends if geometry optimizations with either the MIDI! or cc-pVTZ basis sets are attempted.

**SMXGAUSS–version 3.3 (January 2006)**

**Authors: C. P. Kelly, J. D. Thompson, B. J. Lynch, J. D. Xidos, J. Li, G. D. Hawkins, T. Zhu, Y. Volobuev, M. Dupuis, D. Rinaldi, D. A. Liotard, C. J. Cramer, and D. G. Truhlar**

Earlier versions running under mode 1 did not read the charge and multiplicity from punch files. This bug has been fixed in version 3.3.

This version has been tested on a Mac mini G4.

**SMXGAUSS–version 3.4 (February 2006)**

**Authors: A. C. Chamberlin, C. P. Kelly, J. D. Thompson, B. J. Lynch, J. D. Xidos, J. Li, G. D. Hawkins, T. Zhu, Y. Volobuev, M. Dupuis, D. Rinaldi, D. A. Liotard, C. J. Cramer, and D. G. Truhlar**

The parameters for the temperature dependent version of SM6 were included.

The additional keyword SolK was included.

Four additional tests for SolK were included in the test suite (test7a, test7b, test7c and test7d)

The Gau\_External script was modified to allow SMXGAUSS to work with versions D01 and D02 of Gaussian 03

**SMXGAUSS–version 3.4.1 (October 2006)**

**Authors: A. C. Chamberlin, C. P. Kelly, J. D. Thompson, B. J. Lynch, J. D. Xidos, J. Li, G. D. Hawkins, T. Zhu, Y. Volobuev, M. Dupuis, D. Rinaldi, D. A. Liotard, C. J. Cramer, and D. G. Truhlar**

In SMXGAUSS–version 3.4, a bug in the file named intstaller.temp caused the installation to hang up if the user requested to compile the code using mode 2.

**SMXGAUSS–version 3.4.2 (August 2007)**

**Authors: A. C. Chamberlin, C. P. Kelly, J. D. Thompson, B. J. Lynch, J. D. Xidos, J. Li, G. D. Hawkins, T. Zhu, Y. Volobuev, M. Dupuis, D. Rinaldi, D. A. Liotard, C. J. Cramer, and D. G. Truhlar**

In prior versions of SMXGAUSS there was a bug that caused the program to compute incorrect gradients for gas-phase and liquid-phase molecules, this bug has been fixed.

In prior versions of SMXGAUSS there was a bug that caused the program to compute incorrect energies of solvation during geometry optimizations when the ISCRF=2 option was set. This error has been corrected.