# GCHSM

Gaussian Charge distributed Harmonic Solvation Model

## User Manual

## Ver. 1.0.0

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## Abstract

This manual describes how to install, configure, and run GCHSM, a wrapper of PySCF that implements the Gaussian Charge–distributed Harmonic Solvation Model (GC-HSM) for quantum-chemical calculations in solution and gas phase. GC-HSM addresses limitations of the original HSM and enables accurate evaluation of condensed-phase thermodynamic quantities.

## 1. Overview

GCHSM requires an input file to operate. The default filename for this file is "input.inp", and it primarily consists of the following three sections:

- Main section
- Title section
- Geometry section

An empty line is inserted at the end of both the Main and Title sections. Below is an example of an input file for calculating vibrational frequencies for water molecules in solution.

```
%MAIN                                            Main section
CALCTYPE = hess
METHOD     = HF
DFTTYP     = B3LYP-D3BJ
BASIS      = cc-pvdz
HSM        = TRUE
PROJECT    = TRUE
FREQTEMP = 298.15
%END

#vibrational frequency calculation               Title section

%GEOMETRY                                         Geometry section
0 1
O    0.00000000000000    0.00000002290434    0.12533601079751
H    0.00000000000000    0.75867849691627   -0.46855429138676
H    0.00000000000000   -0.75867851982061   -0.46855430941074
%END
```

## 1.1. MAIN section

```
%MAIN                                    Main section
CALCTYPE = hess                          Calculation Details
METHOD    = HF                           Specify Functional
DFTTYP    = B3LYP-D3BJ
BASIS     = cc-pvdz                       Specify Base Functions
HSM       = TRUE                          Perform HSM Calculation
PROJECT   = TRUE
FREQTEMP = 298.15
%END
```

Keyword/option separator is either a half-width space or the Tab key.

| | Option | [Default] | Contents |
|---|---|---|---|
| ✓ | CALCTYPE | [sp] | : Specify the following calculation types: |
| | | | ・sp: Single-point energy calculation |
| | | | ・opt: Structure optimization calculation |
| | | | ・hess: Frequency calculation |
| | | | ・freq: Thermodynamic property evaluation |
| ✓ | METHOD | [DFT] | : Specifies the functional. HF, DFT, and MP2 are supported. |
| ✓ | DFTTYP | [B3LYP] | : Effective only when METHOD=DFT is specified. |
| ✓ | BASIS | [STO-3G] | : Specifies the basis set. |
| ✓ | HSM | [TRUE] | : Performs GC-HSM calculations. |
| | | | When HSM = TRUE, performs calculations in an aqueous solvent environment using: |
| | | | (SCRF = CPCM, ALPHA = 1.2, EPS = 80.1510, ORDER = 17) |
| | | | When HSM = FALSE, performs calculations in the gas phase |
| ✓ | SCRF | [CPCM] | : CPCM and COSMO methods are supported. |
| ✓ | ALPHA | [1.2] | : Specifies the scaling factor for PCM calculations. |
| ✓ | EPS | [80.1510] | : Specifies the solvent's relative dielectric constant. |
| ✓ | ORDER | [17] | : Specifies the Lebedev order. |
| ✓ | PROJECT | [FALSE] | : Indicates whether to project into translational and rotational spaces. |
| ✓ | NE_CAVITY | [PCM] | : Specifies the method for generating cavity surfaces when calculating non-electrostatic terms. For NE_CAVITY = PCM, grid subdivision of cavity spheres is applied. For NE_CAVITY = SES, a polyhedral approximation of cavity spheres is used. |

| ✓ | NE_MODEL | [GAMESS] | : Specifies the method for calculating dispersion and repulsive energy. Only `NE_MODEL=GAMESS` is permitted. Calculation performed according to references [1,2]. |
|---|---|---|---|
| ✓ | NE_DENSITY | [0.997] | : Specifies the density of solvent molecules. |
| ✓ | NE_MOLAR_MASS | [18.01528] | : Specifies the molecular weight of the solvent molecule. |
| ✓ | NE_CAV_MODEL | [SPT] | : Specifies the calculation method for cavity generation energy. `NE_CAV_MODEL=SPT` is only valid and performs calculations based on reference [3]. |
| ✓ | NE_SPT_T | [298.15] | : Specifies temperature for cavitation energy calculation. |
| ✓ | NE_SPT_SIGMA | [1.50] | : Specifies solvent radius. |
| ✓ | NE_SPT_VM | [18.07] | : Specifies solvent molecular volume. |
| ✓ | NE_SPT_ALPHA | [0.000257] | : Specifies the isobaric-isothermal volume coefficient of the solvent. |
| ✓ | NE_SPT_P | [1.0] | : Specifies pressure. |
| ✓ | NE_SPT_PUNIT | [atm] | : Specifies the pressure unit as defined in `NE_SPT_P`. |
| ✓ | FREQTEMP | [298.15] | : Specifies the temperature to use when calculating internal energy and entropy. Multiple temperatures can be specified. |
| ✓ | MOLE | [LINEAR] | : Valid when `CALCTYPE=freq` is specified. Specifies the shape of the numerator. |

## 1.2. Title section

| `#vibrational frequency calculation` | *Title section* |
|---|---|

The Title section is used to append information related to the calculation. Begin with "#".

## 1.3. Geometry section

| `%GEOMETRY` | *Geometry Section* |
|---|---|
| `0 1` | *Charge, Spin Multiplicity* |
| `O   0.00000000000000    0.00000002290434    0.12533601079751` | *Coordinates for Atomic 1* |
| `H   0.00000000000000    0.75867849691627   -0.46855429138676` | *Coordinates for Atomic 2* |
| `H   0.00000000000000   -0.75867851982061   -0.46855430941074` | *Coordinates for Atomic 3* |
| `%END` | |

The Geometry section begins with specifying two integer values: the charge and spin multiplicity of the input structure. After a newline, specify the atomic positions using decimal Cartesian coordinates (in angstroms).

## 2. Output

When submitting a job, two output files are generated: I. input.out and II. freq.out. Notably, I. has the same name as the input file (input.inp).

### 2.1.  input.out

```
~ (omitted)
Execution of GCHSM begun Mon Oct 06 17:10:55 2025


------------------------------------
vibrational frequency calculation
------------------------------------


---------
SYSTEM
---------
Total number of atoms         3
Number of electrons          10
Charge of system              0
Spin multiplicity             1
Number of basis functions    24
Number of occupied orbitals    5


-----------------------
VIBRATION OPTIONS
-----------------------
Projection of trans/rot: ON (nTR = 6)


-----------------------
Computational Details
-----------------------
Method         HF
DFT functional    -
Basis          cc-pvdz
Dispersion     DFT-D3(BJ)/D3


-----------------------
PCM Details
-----------------------
SCRF (PCM)       CPCM
Dielectric       80.1510
vdW scale alpha  1.200
Lebedev order     17



------------------------------------
Non-electrostatic Contributions
------------------------------------

[Surface]
  Kind               : PCM
  Area (Ang.^2)      : 164.930193
  Volume (Ang.^3)    : 192.557609
  Number of surface point : 228
```

Annotations (right-hand labels):

- *Job Submission Date and Time* — Execution of GCHSM begun Mon Oct 06 17:10:55 2025
- *Title Section Output* — vibrational frequency calculation
- *System Information* — SYSTEM
- *Number of Atoms* — Total number of atoms
- *Number of Electrons* — Number of electrons
- *Charge* — Charge of system
- *Spin Multiplicity* — Spin multiplicity
- *Number of Basis Functions* — Number of basis functions
- *Number of Occupied Orbitals* — Number of occupied orbitals
- *Projection status* — Projection of trans/rot: ON (nTR = 6)
- *Computational Parameters* — Computational Details
- *Functional* — Method
- *Basis Set* — Basis
- *Presence of Dispersion* — Dispersion
- *PCM Information* — PCM Details
- *PCM Type* — SCRF (PCM)
- *Relative Permittivity* — Dielectric
- *Scaling Factor* — vdW scale alpha
- *Number of Lebedev Grid Points* — Lebedev order
- *Non-Electrostatic Term Calculation* — Non-electrostatic Contributions
- *Cavity Construction Method* — Kind
- *Surface Area* — Area
- *Volume* — Volume
- *Total Number of Grid Points (or Total Number of Tessellations for SES)* — Number of surface point

```
[Dispersion/Repulsion]
   Model               : GAMESS
   Density             : 3.332768e-02
   E_disp (kcal/mol) : -3.044875
   E_rep   (kcal/mol) :  0.178001
....
[Cavitation]
   Model               : SPT
   G_cav (kcal/mol)  :   2.192535
   H_c     (kcal/mol)  :   0.190439
   T*S_c (kcal/mol)   : -2.002096


Total non-electrostatic energy (kcal/mol): -0.674339


*** Start vibrational frequency calculation ***


-----------------------------
HARMONIC FREQUENCIES
-----------------------------
Mode   Frequency(cm-1)   Note
-------------------------
    1        17.59
    2        23.84
    3        17.76
    4       227.20
    5       365.60
    6       609.25
    7      1664.19
    8      3555.84
    9      3908.11
--------------------------
----------------------------
Thermochemistry at 298.15 K
-----------------------------


Temperature        : 298.15   K
Pressure           : 1.00      atm
Total Mass         : 18.015   Amu


--------------
Internal energy
--------------


E(vib)   :       54.60 kJ/mol          13.05 kcal/mol
E(rot)   :        4.93 kJ/mol           1.18 kcal/mol
E(trans):        3.72 kJ/mol           0.89 kcal/mol
Total E :       63.26 kJ/mol          15.12 kcal/mol


-------
Entropy
-------
S(vib)   :     0.00002 kJ/mol/K
S(rot)   :     0.01436 kJ/mol/K
S(trans):     0.08387 kJ/mol/K
Total S :     0.09826 kJ/mol/K


Execution of GCHSM terminated normally Mon Oct 06 17:10:57 2025
```

Annotations (right column):

- *Dispersion/Repulsive Energy*
- *Computational Algorithm*
- *Density*
- *Dispersion Energy*
- *Repulsive Energy*
- *Cavity Generation Energy*
- *Computational Method*
- *Free Energy*
- *Enthalpy Contribution*
- *Entropy Contribution*
- *Non-electrostatic Energy*
- *Normal Mode Analysis*
- *If imaginary frequencies are present, print "Imag" in the Note field*
- *If any frequency is less than 10 $cm^{-1}$, print "low" in the Note field*
- *Thermodynamic Calculations (Temperature)*
- *Temperature*
- *Pressure*
- *Mass*
- *Internal Energy*
- *Vibration Energy*
- *Rotational Energy*
- *Translational Energy*
- *Total Energy*
- *Entropy*
- *Electronic Entropy*
- *Rotational Entropy*
- *Translational Entropy*
- *Total Entropy*
- *Job completion time*

## 2.2.　freq.out

```
1   31.357883648009
2   81.795728860024
3   75.988009145976
4   382.649803121748
5   309.735845474172
6   442.385022641645
7   1691.249913131260
8   3849.887419632710
9   3963.622756143805
```

The first column contains vibrational mode numbers, and the second column corresponds to vibrational frequencies (in cm$^{-1}$). When CALCTYPE is set to "freq", this file is exclusively used for thermodynamic quantity calculations.

References

[1] F. M. Floris and J. Tomasi, "Evaluation of the dispersion contribution to the solvation energy. A simple computational model in the continuum approximation", *J. Comput. Chem.*, **10**, 616 (1989).

[2] F. M. Floris, J. Tomasi, and J.L.P. Ahuir, "Dispersion and repulsion contributions to the solvation energy: Refinements to a simple computational model in the continuum approximation", *J. Comput. Chem.*, **12**, 784 (1991).

[3] R. A. Pierotti, "A Scaled Particle Theory of Aqueous and Nonaqueous Solutions", *Chem. Rev.*, **76**, 717 (1976).

■HSM review

1. 中井浩巳, "調和溶媒和モデル（HSM）を用いた凝縮系の自由エネルギー計算", *J. Comput. Chem. Jpn.* **16**, 83 (2017).

■HSM theory

2. H. Nakai and A. Ishikawa, "Quantum chemical approach for condensed-phase thermochemistry: Proposal of a harmonic solvation model, *J. Chem. Phys.*, **141**, 174106 (2014).

■GC-HSM theory

3. *In preparation.*

■HSM illustrative applications

4. A. Ishikawa and H. Nakai, "Quantum chemical approach for condensed-phase thermochemistry (II): Applications to formation and combustion reactions of liquid organic molecules", *Chem. Phys. Lett.*, **624**, 6 (2015).

5. M. Okoshi, A. Ishikawa, Y. Kawamura, and H. Nakai, "Theoretical Analysis of the Oxidation Potentials of Organic Electrolyte Solvents", *ECS Electrochem. Lett.*, **4**, A103 (2015).

6. A. Ishikawa and H. Nakai, "Quantum chemical approach for condensed-phase thermochemistry (III): Accurate evaluation of proton hydration energy and standard hydrogen electrode potential", *Chem. Phys. Lett.,* **650**, 159 (2016).

7. A. Ishikawa, M. Kamata, and H. Nakai, "Quantum chemical approach for condensed-phase thermochemistry (IV): Solubility of gaseous molecules", *Chem. Phys. Lett*., **655-656**, 103 (2016).