

# **AN INTRODUCTION TO GAMESS**

# GAMESS

- General Atomic and Molecular Electronic Structure System
- General purpose electronic structure code
- Primary focus is on *ab initio* quantum chemistry calculations
- Also can do
  - Density functional theory calculations
  - Other semi-empirical calculations (AM1, PM3)
  - QM/MM calculations

# OVERVIEW OF GAMESS

- **Types of wavefunctions**
  - Hartree-Fock (RHF, ROHF, UHF, GVB)
  - CASSCF
  - CI, MRCI
  - Coupled cluster methods
  - Second order perturbation theory
    - MP2 (closed shells)
    - ROMP2 (spin-correct open shells)
    - UMP2 (unrestricted open shells)
    - MCQDPT(CASSCF - MRMP2)
  - Localized orbitals (SCF, MCSCF)

# OVERVIEW OF GAMESS

- Types of wavefunctions
  - Fragment Molecular Orbital Theory (FMO)
    - Enables calculations on very large systems
      - Thousands of atoms
    - HF, DFT, MP2 (closed shells)
    - ROMP2 (spin-correct open shells)
    - Coupled Cluster methods
    - MCSCF

# OVERVIEW OF GAMESS

- Energy-related properties
  - Total energy as function of nuclear coordinates (PES): All wavefunction types
  - Analytic energy gradient
    - RHF, ROHF, UHF, MCSCF, CI, DFT
    - MP2, UMP2, ROMP2
  - Analytic hessian
    - RHF, ROHF, TCSCF/GVB
    - MCSCF

# OVERVIEW OF GAMESS

- Energy-related properties (cont'd)
  - Numerical Hessians from finite differences of analytic gradients
  - Fully numerical derivatives for all methods
  - Saddle point (TS) search (requires Hessian)
  - Minimum energy path = Intrinsic reaction coordinate
    - Several IRC options - GS2 (default) is most effective
    - Requires frequency input, gradients along path
    - Follow reaction path from reactants through TS to products
    - Build reaction path Hamiltonian (RPH): dynamics

# OVERVIEW OF GAMESS

- Energy-related properties (cont'd)
  - Dynamic reaction coordinate (DRC)
    - Add kinetic energy to system at any geometry
    - Add photon(s) to any vibrational mode
    - Classical trajectory using QM-derived energies
    - Requires gradients
  - Monte Carlo sampling: find global minimum
  - Molecular dynamics
    - MM only so far

# OVERVIEW OF GAMESS

- Other functionalities

- Spin-orbit coupling

- Any spin states, any number of states
- Full two-electron Breit-Pauli
- Partial two-electron (P2e)-very efficient, accurate
- Semi-empirical one-electron  $Z_{\text{eff}}$
- RESC
- Averaging over vibrational states

- Other relativistic effects: Douglas-Kroll to 3rd order

- Derivative (vibronic) coupling

# OVERVIEW OF GAMESS

- **Interpretive tools**
  - Localized molecular orbitals (LMO)
  - Localized charge distributions (LCD)
  - MCSCF localized orbitals
- **Nuclear and spectroscopic properties**
  - Spin densities at nucleus (ESR)
  - NMR chemical shifts
  - Polarizabilities, hyperpolarizabilities
  - IR and Raman intensities
  - Transition probabilities, Franck-Condon overlaps

# OVERVIEW OF GAMESS

- QM/MM Methods

- Effective fragment potential (EFP) method for

- Cluster studies of liquids
    - Cluster studies of solvent effects
    - Interfaced with continuum methods for study of liquids and solvation in bulk
    - Covalent link for study of enzymes, proteins, materials
    - General model for intermolecular interactions

- SIMOMM: QM/MM method for surface chemistry

- QM part can be any method in GAMESS
    - MM part from Tinker (Jay Ponder - Washington U)

# USING GAMESS

- **GAMESS runs on**
  - Any UNIX-based system
  - Any Linux-based system
  - Any Macintosh
  - Windows-based PC\_GAMESS, WINGAMESS available (distributed by ISU group)
- **GAMESS can be obtained from**
  - [www.msg.chem.iastate.edu](http://www.msg.chem.iastate.edu)
  - License required - no cost

# USING GAMESS

- For Macintosh
  - OSX, same as UNIX/LINUX
- For UNIX/LINUX systems requires script
- Output appears in .log file
- Vectors, coordinates, hessians appear in .dat file
- IRC data, numerical restart data for frequencies appear in .irc file
- Main Monte Carlo output in .irc file

# USING GAMESS

- Input files are modular, arranged in \$groups
- Most common input groups
  - \$SYSTEM: specifies memory, time limit
  - \$CONTRL: specifies basics of calculation
  - \$BASIS: specifies basis set if standard
  - \$DATA: specifies nuclear coordinates, basis set if non-standard
- Other important groups:
  - \$GUESS, \$SCF, \$FORCE, \$HESS, \$VEC, \$IRC, \$VIB

# USING GAMESS

- \$ sign specifying group must be in column 2
- All groups must terminate with \$END (this \$ can be anywhere except column 1)

# USING GAMESS

- **\$SYSTEM** group:
  - TIMLIM=(default=600 min)
  - MWORDS=(default=1)
  - MEMDDI=
    - Only relevant for parallel run
    - Total required memory (divide by number of processors to get memory requested/node)

# USING GAMESS

- **\$CONTRL** group:
  - ICHARG= (specifies charge on system)
  - MULT= (specifies spin multiplicity)
    - 1 for singlet, 2 for doublet, ...
  - EXETYP=
    - Check: checks input for errors
    - Run: actual run
  - UNITS=
    - angstroms (default)
    - bohr

# USING GAMESS

- **\$CONTROL** group:
  - **Runtyp=** (type of run)
    - Energy (single point energy run)
    - Gradient (energy 1st derivative wrt coordinates)
    - Optimize (optimize geometry)
    - Hessian (energy second derivative, vibrational frequencies, thermodynamic properties):  
generates \$HESS group in .dat file)
    - Sadpoint (saddle point search:requires hessian in \$HESS group)
    - IRC (performs IRC calculation: usually requires \$IRC group, \$HESS group)

# USING GAMESS

- **\$CONTROL** group:
  - **scftyp=** (type of wavefunction)
    - RHF
    - ROHF
    - UHF
    - MCSCF
    - GVB
  - **mplevl=**
    - 0 (default, no perturbation theory)
    - 2 (MP2: valid for RHF, ROHF, MCSCF, GVB)

# USING GAMESS

- **\$CONTRL** group:
  - Cctyp=
    - NONE (no coupled cluster, default)
    - CCSD (singles+doubles)
    - CCSD(T) adds perturbative triples to CCSD
      - Most popular method
      - Triples essential for accurate calculations
    - CR-CCL
      - Specialized method to approximate bond-breaking
    - EOM-CCSD, CR-EOM
      - Excited states vi equaitons-of-motion CC

# USING GAMESS

- \$BASIS group:
  - GBASIS=
    - STO
    - N21
    - N31
    - TZV...
  - NGAUSS=(# gaussians for STO, N21, N31)
  - NDFUNC=(# sets of d's on heavy atoms)
  - NPFUNC=(# sets of p's on hydrogens)
  - NFFUNC=(# sets of f's on TM's)

# USING GAMESS

- \$BASIS group:
  - DIFFSP=.T. (diffuse sp functions on heavy atoms)
  - DIFFS=.T. (diffuse s functions on hydrogens)
  - GBASIS=ccn (correlation consistent)
    - n=2,3,4,5,6
  - GBASIS=accn (augmented cc--pVXZ)
  - GBASIS=ccnc (core correlation)
  - GBASIS=acnc (augmented core correlation)
  - GBASIS=MC-DZP, MC-TZP, MC-QZP

# HF WATER

• basis set	#bf	#2-EI (theory)	#2-EI (actual)	CPU time (sec)
• ccd	24	41,472	13863	.1
• cct	58	1,414,562	566,091	.3
• acct	92	8,954,912	3,754,821	1.4
• ccq	115	21,862,578	11,695,586	4.0
• accq	172	109,401,632	64,214,254	19.7

- HF Scales  $\sim N^4$ ,  $n = \#$  basis functions
- $(172/115)^4 = 5.0$ :  $19.7/4.0 = 4.9$

# USING GAMESS

- \$DATA group
  - Title line (will be printed in output)
  - Symmetry group
    - C1
    - CS
    - CNV 2 (C2V), ...
    - Blank line except C1

# USING GAMESS

- **\$DATA** group
  - Symbol Z xcoord ycoord zcoord
    - Symbol = atomic symbol
    - Z = atomic number
    - xcoord,ycoord, zcoord = Cartesian coords
    - Internal coords is another option
  - Repeat this line for each *symmetry unique* atom (see below)
  - Need to specify basis set after each coordinate line if \$BASIS is not present

# USING GAMESS

- **\$DATA group**
  - symmetry unique atoms
    - H<sub>2</sub>O: O and 1 H
    - NH<sub>3</sub>: N and 1 H
  - saves CPU time
    - numerical Hessians only displace symmetry unique atoms
    - Reduces # integrals to be calculated
  - Need to follow conventions in GAMESS manual
    - C<sub>s</sub>, C<sub>nh</sub>: plane is XY
    - C<sub>nv</sub>: axis is Z
  - For C<sub>infv</sub>, use C<sub>4v</sub>
  - For D<sub>infh</sub>, use D<sub>4h</sub>

# USING GAMESS

- **\$GUESS** group
  - Built-in guess (default) works much of the time
  - **GUESS=MOREAD,NORB=xx \$END**
    - Requires \$VEC group (usually from .dat file)
    - NORB=# MO's to be read in
    - Useful when SCF convergence is difficult
    - Necessary for MCSCF, CI

# RUNNING GAMESS

- **Prepare input file**
  - Within UNIX/Linux using vi line editor
  - On Mac or PC using editor of choice
  - Name of file must be xxx.inp
- **Submit job by**
  - `gms xxx -q fred -l xxx.geomopt.log`

# RUNNING GAMESS

- **Output files**
  - .log file appears in directory in which job was submitted
  - .dat file contains basis set, coordinates, orbitals (\$VEC group), gradient (\$grad group), hessian (\$HESS group), depending on type of run
  - .irc file contains \$VIB group (restart for numerical Hessians), \$IRC group
  - Destroy .dat file & .irc file before re-running
    - `rm ~/scr/xxx.dat`

# RUNNING GAMESS

- For more info, see
  - [www.msg.chem.iastate.edu](http://www.msg.chem.iastate.edu)
  - GAMESS sub-page