

# **AN INTRODUCTION TO GAMESS**

**See: [www.msg.chem.iastate.edu](http://www.msg.chem.iastate.edu)**

# 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
  - Solvent effects

# REACTION PATHS

- Reaction path is least energy path
  - From reactants (R) through TS to products (P)
    - Minimum energy path (MEP)
    - Also called intrinsic reaction coordinate (IRC)
    - Follows steepest descent path from TS to R or P
    - Steepest descent means -gradient
  - IRC = MEP:
    - Confirms connection between R, TS, P
    - Provides first step in study of reaction dynamics

# CORRELATION METHODS

- **Perturbation theory**

- $E = E^{(0)} + E^{(1)} + E^{(2)} + \dots$

- Simplest  $E^{(0)} = E_{\text{HF}}$ : Then,  $E^{(1)} = 0$
    - If series is terminated at second order: MP2
    - Series does not always converge well
      - Best to just stop at MP2 (MP3, MP4 often terrible)
    - MP2 scales as  $N^5$ 
      - Often good compromise between efficiency & accuracy
    - Includes dispersion naturally
    - Often over-binds weak interactions (benzene dimer)

# CORRELATION METHODS

- **Coupled cluster theory**

$$\psi = e^T \psi_0$$

- $\psi_0$  usually is  $\psi_{\text{HF}}$
- $T = \text{cluster operator} = T_1 + T_2 + T_3 + \dots + T_N$
- $T_1 = \text{sum of 1-particle operators} = \sum t_i$  ( $N^4$  scaling)
- $T_2 = \text{sum of 2-particle operators} = \sum \sum [t_{ij} + t_i t_j]$  ( $N^6$  scaling)
- $T_3 = \text{sum of 3-particle operators} = \sum \sum \sum [t_{ijk} + t_i t_{jk} + \dots]$  ( $N^8$ )
- Approximations
- $T \approx T_1 + T_2$ : CCSD (singles (S) + doubles (D)):  $\sim N^6$
- $T \approx T_1 + T_2 + T_3$ : CCSDT (very expensive):  $\sim N^8$
- Common compromise: CCSD(T):  $N^7$  scaling
  - Get triples (T) using perturbation theory (not iterative)

# 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
  - Semi-numerical Hessian
    - MP2, UMP2, ROMP2
  - Fully Numerical Hessian
    - CCSD(T), MRMP2

# 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, FMO

# 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

- MCSCF, MRMP2

# 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)
- Moving to ReaxFF (Goddard)

# USING GAMESS

- **GAMESS runs on**
  - Any UNIX-based system
  - Any Linux-based system
  - Any Macintosh
  - Windows
- **GAMESS can be downloaded 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 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

- **\$CTRL 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)
  - DFTTYP=
    - None (default)
    - xxx Specify name of functional

# USING GAMESS

- **\$CONTROL 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 via equations-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

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

- 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