

AN INTRODUCTION TO GAMESS

See: 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

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 to 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

- $\Psi = e^T \Psi_0$

- Ψ_0 usually is Ψ_{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))
 - $T \approx T_1 + T_2 + T_3$: CCSDT (very expensive)
 - 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

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_{eff}
- RESC
- Averaging over vibrational states

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

- Derivative (vibronic) coupling

- Only MCSCF at present

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
 - 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

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

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 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

• 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

- H₂O: O and 1 H
- NH₃: 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_s, C_{nh}: plane is XY
- C_{nv}: axis is Z

- For C_{infv}, use C_{4v}

- For D_{infh}, use D_{4h}

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

- GAMESS sub-page