AN INTRODUCTION TO GAMESS

See: www.msg.chem.iastate.edu
• **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 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

  \[ E = E^{(0)} + E^{(1)} + E^{(2)} + \ldots \]

  • 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 \( \psi_{HF} \)
- \( T = \text{cluster operator} = T_1 + T_2 + T_3 + \ldots + T_N \)
- \( T_1 = \text{sum of 1-particle operators} = \sum t_i \) (\( N^4 \) scaling)
- \( T_2 = \text{sum of 2-particle operators} = \sum \sum [t_{ij} + t_i t_j] \) (\( N^6 \) scaling)
- \( T_3 = \text{sum of 3-particle operators} = \sum \sum \sum [t_{ijk} + t_i t_{jk} + \ldots] \) (\( N^8 \))
- 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 = Intrinsinc 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
• 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
  – 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

• $\texttt{CONTRL}$ group:
  – $\texttt{ICHARG}=\text{ (specifies charge on system)}$
  – $\texttt{MULT}=\text{ (specifies spin multiplicity)}$
    • 1 for singlet, 2 for doublet, …
  – $\texttt{EXETYP}=\text{ }$
    • Check: checks input for errors
    • Run: actual run
  – $\texttt{UNITS}=\text{ }$
    • aangs (default)
    • bohr
• **$\text{CONTRL 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 $\text{HESS group in .dat file}$
    • Sadpoint (saddle point search: requires hessian in $\text{HESS group}$)
    • IRC (performs IRC calculation: usually requires $\text{IRC group, HESS group}$)
USING GAMESS

• **$CONTRL group:**
  – `scftyp=` *(type of wavefunction)*
    • RHF
    • ROHF
    • UHF
    • MCSCF
    • GVB
  – `mplevel=`
    • 0 *(default, no perturbation theory)*
    • 2 *(MP2: valid for RHF, ROHF, MCSCF, GVB)*
  – `DFTTYP=`
    • None *(default)*
    • `xxx` Specify name of functional
$CONTRL$ group:

- $\text{cctyp}=$
  - 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
$BASIS$ 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

• $\text{BASIS group:}$
  – 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 ~ $N^4$, $n =$ # 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
    • $H_2O$: O and 1 H
    • $NH_3$: N and 1 H
  – saves CPU time
    • numerical hessians only displace symmetry unique atoms
    • Reduces # integrals to be calculated
  – Need to follow conventions in GAMEESS 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