EXCITED ELECTRONIC STATES USING GAMESS
LEVELS OF THEORY

• Singles CI
  – All single excitations from RHF ground state
  – Brillioun Theorem: $\langle \Psi_0 | H | \Psi_i^a \rangle = 0$
    • No improvement of ground state
  – Simplest level of theory for excited states
  – Accuracy ~ Hartree-Fock
  – Best for lowest lying excited states
  – Fails for states dominated by double excitations
    • Common for higher excited states
SINGLES CI

• In GAMESS
  – $\text{CONTROL} \ \text{CITYP}=\text{CIS} \ \ldots \ $\text{END}
  – $\text{CIS}$
    • NSTATE=('# of states requested')
    • ISTATE=(choose one)
    • MULT=(spin multiplicity)
    • CISPRP={.T., .F.}
      – Generates properties for ISTATE
      – Requires calculation of density matrix
  – Can do geometry opts using analytic gradients
LEVELS OF THEORY

• CISD
  – All single and double excitations from RHF ground state
  – Much more accurate than CIS
  – Much more time-consuming than CIS
    • Requires \((vv|oo)\) and \((vo|vo)\) integrals
  – Analytic gradients available
    • Very time-consuming
CISD

• In GAMESS
  – $\text{CONTRL CITYP=GUGA ... END}$
  – $\text{CIDRT}$
    • GROUP= (point group or subgroup)
    • IEXCIT=2 (CISD)
      – This will generate all single and double excitations
    • Can reduce the computational effort using
      – NFZV= (# omitted virtuals)
      – Not systematic
LEVELS OF THEORY

• EOM-CC
  – Equations of motion (EOM) coupled cluster
  – Calculates excitation energies directly
    • More accurate than subtracting excited - ground state
  – Much more accurate than CIS
    • Options include EOM-CCSD(T), CR-EOM-CCSD(T)
    • Starting wave function can come from CIS or CISd
      – Small d means identify active space for doubles
  – Much more time-consuming than CIS or CISD
  – No analytic gradients
EOM-CC

• In GAMESS
  – \texttt{$CONTRL\ CCTYP=EOM-CCSD\ \ldots$END}
  – \texttt{$EOMINP$}
    • \texttt{GROUP=} (point group or subgroup)
    • \texttt{MTRIP=} 
      – Method for triples
        » 1=CR-EOMCCSD(T) standard
        » 2=CR-EOMCCSD(T) iterative CISD starting point
        » See manual for other options
    • \texttt{MINIT=} 
      – Initial guess procedure for EOM procedure
        » 1=CISd (see manual for options)
        » 2=CIS
LEVELS OF THEORY

• Multi-reference CI
  – CI on top of MCSCF
    • FOCI (first order CI): All single excitations from each MCSCF determinant
    • SOCI (second order CI): All single & double excitations from each MCSCF determinant
    • Better than CIS or CISD since orbital space is re-optimized in MCSCF step
• In GAMESS
  – Assume MCSCF was done in previous run, orbitals have been checked and read in using $VEC
  – $CONTRL CITYP=GUGA
  – $CIDRT
    • GROUP= (point group or subgroup)
    • FOCl=.T. or SOCl=.T.
COMING TO GAMESS

• Time-dependent density functional theory (TDDFT)
  – Similar approach to EOM-CC
  – Similar level of theory to CIS, except based on DFT
    • Single excitations from Kohn-Sham determinant
    • More accurate than CIS since DFT better than HF
    • Fails for states dominated by double excitations
    • Like DFT, tough to predict success or failure
• Many excited electronic states of various spins
  – Surface crossings are common
    • Different spin states: intersystem crossings
      – Spin-orbit coupling (SOC) can be important
      – Several SOC methods in GAMESS
        » Full all-electron (Breit-Pauli)
        » Partial two-electron (P2E)
        » One-electron $Z_{\text{eff}}$ method
    • Same spin states
      – Born-Oppenheimer breakdown
      – Derivative (vibronic) coupling important
  – Both lead to radiationless transitions
  – Essential processes in photochem, photobiology