

AN INTRODUCTION TO QUANTUM CHEMISTRY

Mark S. Gordon
Iowa State University



OUTLINE

- Theoretical Background in Quantum Chemistry
- Overview of GAMESS Program
- Applications



QUANTUM CHEMISTRY

- In principle, solve Schrödinger Equation
- Not possible for many-electron atoms or molecules due to many-body problem
- Requires two *levels* of approximation

FIRST APPROXIMATION

- Born-Oppenheimer Approximation
 - Assumes we can study behavior of electrons in a field of *frozen nuclei*
 - Correct H:
 - $H_{\text{exact}} = T_{\text{el}} + V_{\text{el-el}} + T_{\text{nuc}} + V_{\text{nuc-nuc}} + V_{\text{el-nuc}}$
 - $V_{\text{el-nuc}}$ = electron-nucleus cross term: not separable, so fix nuclear positions
 - $H_{\text{approx}} = T_{\text{el}} + V_{\text{el-el}} + V_{\text{el-nuc}} = H_{\text{el}}$

FIRST APPROXIMATION

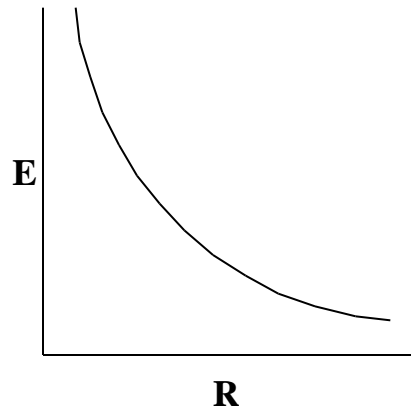
- **Born-Oppenheimer Approximation**
 - Assumes we can study behavior of electrons in a field of *frozen nuclei*
 - Usually OK in ground electronic state: Assumes electronic and nuclear motions are independent: not really true.
 - More problematic in excited states, where different surfaces may cross: gives rise to *non-adiabatic* (vibronic) interactions.



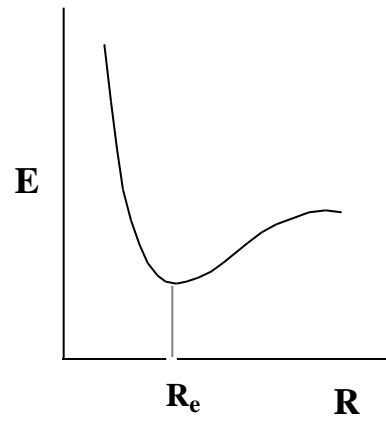
FIRST APPROXIMATION

- **Born-Oppenheimer Approximation**
 - Solve electronic Schrödinger equation at successive (frozen) nuclear configurations
 - For a diatomic molecule (e.g, H₂), Born-Oppenheimer Approximation yields potential energy (PE) *curve*: energy as a function of inter-nuclear distance, R.
 - Bound curve: minimum at finite R
 - Repulsive curve: No stable molecular structure





Repulsive Curve



Bound Curve

FIRST APPROXIMATION

- **Born-Oppenheimer Approximation**
 - Diatomic Molecules: number of points on PE curve determined by number of values of R
 - Polyatomic molecules more complicated:
 - Usually many more coordinates ($3N-6$)
 - generate Potential Energy *Surface* (*PES*)
 - Required number of points increases exponentially with number of atoms



SECOND APPROXIMATION

- Electronic Hamiltonian:
- $H = T_{\text{el}} + V_{\text{el-nuc}} + V_{\text{el-el}}$
- $V_{\text{el-el}}$ not separable:
- Requires orbital approximation
 - Independent particle model: assumes each electron moves in its own *orbital*: ignores *correlation* of behavior of an electron with other electrons
 - Can lead to serious problems



ORBITAL APPROXIMATION

$$\text{hp} = \psi_1(1) \psi_2(2) \dots \psi_N(N)$$

- Hartree product (hp) expressed as a product of spinorbitals $\Psi = \prod_i \psi_i$
- $\psi_i = \phi_i \alpha_i$ = space orbital, $\alpha_i = \text{spin function} (\uparrow, \downarrow)$
- Ignoring repulsions and parametrizing leads to
 - Hückel, extended Hückel Theory
 - Tight Binding Approximation
 - Can be very useful for extended systems

ORBITAL APPROXIMATION

- Recover electron repulsion by using
 - Orbital wave function (approximation)
 - Correct Hamiltonian
- Leads to *Variational Principle*:
 - $\langle E \rangle = \langle \psi | \hat{H} | \psi \rangle \geq E_{\text{exact}}$
 - Using exact Hamiltonian provides an upper bound
 - Can systematically approach the exact energy

ORBITAL APPROXIMATION

- Pauli Principle requires antisymmetry:
 - Wavefunction must be antisymmetric to exchange of any two electrons
 - Accomplished by the antisymmetrizer \hat{A}
- For closed shell species (all electrons paired) antisymmetric wavefunction can be represented by a “Slater determinant” of spinorbitals:

$$= \hat{A} \psi_{\text{hp}} = \left| \begin{array}{c} \psi_1(1) \\ \psi_2(2) \\ \dots \\ \psi_N(N) \end{array} \right|$$

ORBITAL APPROXIMATION

- For more complex species (one or more open shells) antisymmetric wavefunction must be expressed as a linear combination of Slater determinants
- Optimization of the orbitals (minimization of the energy with respect to all orbitals), based on the Variational Principle) leads to:

HARTREE-FOCK METHOD

- Optimization of orbitals leads to
 - $F \psi_i = \epsilon_i \psi_i$
 - $F =$ Fock operator $= h_i + \sum_j \psi_j (2J_j - K_j)$ for closed shells
 - $\psi_i =$ optimized orbital
 - $\epsilon_i =$ orbital energy

HARTREE-FOCK METHOD

- Closed Shells: Restricted Hartree-Fock (RHF)
- Open Shells: Two Approaches
 - Restricted open-shell HF (ROHF)**
 - Wavefunction is proper spin eigenfunction: $S(S+1)$
 - Most orbitals are doubly occupied
 - $= | \underset{1}{\uparrow} \underset{1}{\downarrow} \underset{2}{\uparrow} \underset{2}{\downarrow} \cdots \underset{n}{\uparrow} \underset{n}{\downarrow} \underset{n+1}{\uparrow} \underset{n+2}{\downarrow} \cdots |$

HARTREE-FOCK METHOD

- **Second Approach for Open Shells**
 - Unrestricted HF (UHF)
 - Different orbitals for different spins (,)
 - Wavefunction is not a proper spin eigenfunction
 - Can often get “spin contamination”: spin expectation value that is significantly different from the correct value
 - Indicator that wavefunction may not be reliable

HARTREE-FOCK METHOD

- Closed Shells: Restricted Hartree-Fock (RHF)
- Open Shells
 - Restricted open-shell HF (ROHF)**
 - Unrestricted HF (UHF)
- HF assumes molecule can be described by a simple Lewis structure
- Must be solved iteratively (SCF)

LCAO APPROXIMATION

$$\psi = \sum_{\mu} C_{\mu} \chi_{\mu}$$

- χ_{μ} are AO's: "basis functions"
- C_{μ} are expansion coefficients
- Approximation to Hartree-Fock
 - **FC = Sc**
 - Still solve iteratively for C_{μ} and ϵ_i

LCAO APPROXIMATION

$$= \sum_{\mu} C_{\mu i}$$

- Increase # AO's - approach exact HF
- Requires complete (infinite) basis μ
- Computational effort increases $\sim N^4$
 - Double # AO's, effort goes up by factor of 16!
 - Need to balance accuracy with CPU time, memory

COMMON BASIS SETS

- **Minimal basis set**
 - One AO for each orbital occupied in atom
 - 1s for H, 1s,2s,2p for C, 1s,2s,2p,3s,2p for Si
 - Often reasonable geometries for simple systems
 - Poor energy-related quantities, other properties
- **Double zeta (DZ) basis set**
 - Two AO's for each occupied orbital in atom
 - Better geometries, properties, poor energetics

COMMON BASIS SETS

- Double zeta plus polarization (DZP)
 - Add polarization functions to each atom
 - 1p for H, 2d for C, 3d for Si, 3f for Ti
 - Smallest reasonable basis for correlated calcs
- Triple zeta plus polarization (TZV)
- Diffuse functions for:
 - Anions
 - Weakly bound species (H-bonding, VDW)

TYPES OF BASIS FUNCTIONS

- Slater/exponential functions: e^{-r}
 - Closest to H-atom solutions
 - Required integrals don't have closed form
- Gaussian functions: $\exp(-r^2)$
 - Required integrals have closed form
 - Less accurate than exponential functions
- Solution: systematic linear combinations of gaussians

POPLE BASIS SETS

- **6-31G**
 - Each inner shell AO is combination of 6 gaussians
 - Valence region split into inner & outer regions
 - Inner valence expanded in 3 gaussians
 - Outer valence represented by single gaussian
- **6-31++G(d,p)adds**
 - d functions on each heavy atom
 - p functions on each H
 - Diffuse functions on all atoms (++)

DUNNING BASIS SETS

- **Correlation consistent basis sets**
 - Range from double zeta plus polarization to hextuple zeta plus polarization plus diffuse
 - Best choice for very accurate studies
 - Best choice for weakly bound species

LIMITATIONS OF HF METHOD

- Correlation error: motion of electrons not correlated due to independent particle model
- Geometries often reliable
- Energies generally *not* reliable
- Improvements can come from:
 - Perturbation Theory
 - Variational Principle

IMPROVEMENTS TO HF METHOD

- Perturbation theory:MP2, MP4,...
 - Based on adding successive improvements to both wavefunction and energy
 - *In principle*, leads to exact result, but perturbation must be small
 - Hartree-Fock-based perturbation theory originally due to Moller & Plesset (MP); popularized by Pople and Bartlett (MBPT)

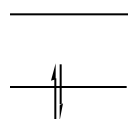
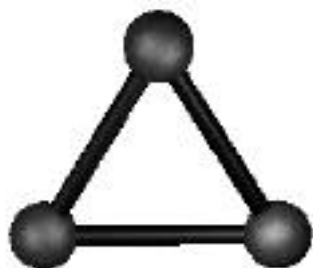
PERTURBATION THEORY

- Computationally efficient
- Often does not converge
 - MP2 often gives better results than MP3, MP4, ...
- Not appropriate if compound is not well described by a simple Lewis structure
- Computational effort $\sim N^5$ (MP2), N^6 (MP4)

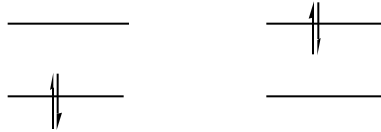
PERTURBATION THEORY

- Alternative is coupled cluster (CC) theory
- Wavefunction is written as
 - $\Psi = \Psi_0 e^T = \Psi_0 (1 + T + T^2 + T^3 + \dots)$
 - Ψ_0 may be HF
 - $T = \text{cluster operator} = T_1(1e) + T_2(2e) + T_3(3e) + \dots$
 - Most popular is CCSD(T)
 - Includes singles, doubles, perturbative triples
 - Scales $\sim N^7$

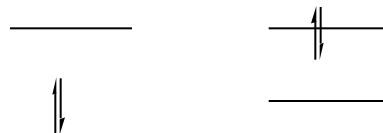
WHAT DO WE DO IF OUR
SYSTEM CANNOT BE WELL
REPRESENTED BY A SINGLE
SIMPLE LEWIS STRUCTURE?



, well separated



significant diradical character
both wavefunctions important



"pure" diradical: two wavefunctions
make equal contributions

IMPROVEMENTS TO HF METHOD

- Variational Principle

- Configuration Interaction ($\sim N^7$)

- $\Psi = \Psi_{\text{HF}} + \Psi_{\text{S}} + \Psi_{\text{D}} + \Psi_{\text{T}} + \dots$

- S = all single excitations
 - D = all double excitations, ...
 - Löwdin (1955): *Complete* CI gives exact wavefunction for the given atomic basis
 - Complete CI generally impossible for any but smallest atoms and diatomic molecules, due to the number of configurations involved
 - Orbitals not re-optimized in CI

IMPROVEMENTS TO HF METHOD

- For near-degeneracies, critical to re-optimize the orbitals
- Called MC (Multi-configurational) SCF
 - Configurations included in MCSCF defined by “active space”:
 - Those orbitals and electrons involved in process
 - Include all configurations generated by distributing active electrons among active orbitals
 - Called complete active space (CAS)SCF

MCSCF

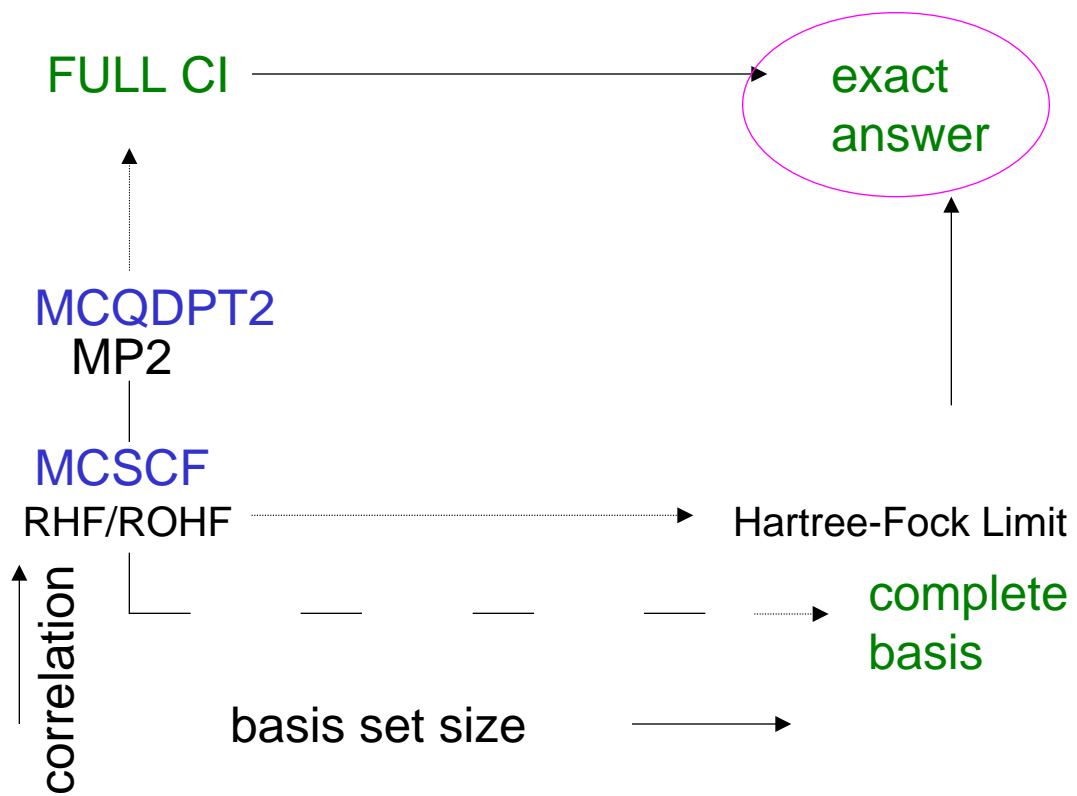
- Usually scales $\sim N^{5-6}$, but can be worse
- Necessary for
 - Diradicals
 - Unsaturated transition metals
 - Excited states
 - Often transition states
- CASSCF accounts for near-degeneracies
- Still need to correct for rest of electron correlation: “dynamic correlation”

MULTI-REFERENCE METHODS

- **Multi-reference CI: MRCI**
 - CI from set of MCSCF configurations
 - Most commonly stops at singles and doubles
 - MR(SD)CI
 - Very demanding
 - ~ impossible to go past 14 electrons in 14 orbitals
- **Multi-reference perturbation theory**
 - More efficient than MRCI
 - Not usually as accurate as MRCI

SUMMARY OF METHODS

- **Perturbation theory**
 - Efficient
 - Size-consistent
 - Often ill-behaved (e.g., non-convergent)
 - Inappropriate for complex species
- **Variation Theory**
 - Systematic and accurate
 - Convergent to correct answer
 - Very CPU-intensive



POTENTIAL ENERGY SURFACES

- Usually very complex - lots of atoms
- Most interesting are
 - Stationary points (minima, transition states)
 - Minimum energy paths (MEP=IRC) connecting minima via transition state (TS)
 - Trajectories starting from stationary points
- Requires
 - Energy first derivatives (gradients)
 - Energy second derivatives (hessians)

LET'S TAKE A BREAK!

FINANCIAL SUPPORT

- Air Force Office of Scientific Research
- National Science Foundation
- DoD CHSSI Software Development
- Ames Laboratory
- DoD HPC Grand Challenge Program