Introduction to Computational Chemistry

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Outline

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What is Computational Chemistry

- **Computational Chemistry** is a branch of chemistry that uses computer science to assist in solving chemical problems.
- Incorporates the results of theoretical chemistry into efficient computer programs.
- Application to single molecule, groups of molecules, liquids or solids.
- Calculates the structure and properties of interest.
- Computational Chemistry Methods range from
  1. Highly accurate (*Ab-initio*,DFT) feasible for small systems
  2. Less accurate (semi-empirical)
  3. Very Approximate (Molecular Mechanics) large systems

Theoretical Chemistry: broadly can be divided into two main categories

1. Static Methods $\Rightarrow$ Time-Independent Schrödinger Equation
   - Quantum Chemical/*Ab Initio* /Electronic Structure Methods
   - Molecular Mechanics
2. Dynamical Methods $\Rightarrow$ Time-Dependent Schrödinger Equation
   - Classical Molecular Dynamics
   - Semi-classical and *Ab-Initio* Molecular Dynamics

- *Ab Initio* meaning "from first principles" methods solve the Schrödinger equation and does not rely on empirical or experimental data.
- Begining with fundamental and physical properties, calculate how electrons and nuclei interact.
- The Schrödinger equation can be solved exactly only for a few systems
  - Particle in a Box
  - Rigid Rotor
  - Harmonic Oscillator
  - Hydrogen Atom
- For complex systems, *Ab Initio* methods make assumptions to obtain approximate solutions to the Schrödinger equations and solve it numerically.
- "Computational Cost" of calculations increases with the accuracy of the calculation and size of the system.

What can we predict with *Ab Initio* methods?

- Molecular Geometry: Equilibrium and Transition State
- Dipole and Quadrupole Moments and polarizabilities
- Thermochemical data like Free Energy, Energy of reaction.
- Potential Energy surfaces, Barrier heights
- Reaction Rates and cross sections
- Ionization potentials (photoelectron and X-ray spectra) and Electron affinities
- Frank-Condon factors (transition probabilities, vibronic intensities)
- Vibrational Frequencies, IR and Raman Spectra and Intensities
- Rotational spectra
- NMR Spectra
- Electronic excitations and UV-VIS spectra
- Electron density maps and population analyses
- Thermodynamic quantities like partition function

Ab Initio Theory

- Born-Oppenheimer Approximation: Nuclei are heavier than electrons and can be considered stationary with respect to electrons. Also know as "clamped nuclei" approximations and leads to idea of potential surface
- Slater Determinants: Expand the many electron wave function in terms of Slater determinants.
- Basis Sets: Represent Slater determinants by molecular orbitals, which are linear combination of atomic-like-orbital functions i.e. basis sets

Born-Oppenheimer Approximation

- Solve time-independent Schrödinger equation

$$\hat{H}\Psi = E\Psi$$

- For many electron system:

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2}\sum_{\alpha}\frac{\nabla_\alpha^2}{M_\alpha}}_{\hat{T}_n} \underbrace{- \frac{\hbar^2}{2m_e}\sum_i \nabla_i^2}_{\hat{T}_e} + \underbrace{\underbrace{\sum_{\alpha>\beta}\frac{e^2 Z_\alpha Z_\beta}{4\pi\epsilon_0 R_{\alpha\beta}}}_{\hat{V}_{nn}} \underbrace{- \sum_{\alpha,i}\frac{e^2 Z_\alpha}{4\pi\epsilon_0 R_{\alpha i}}}_{\hat{V}_{en}} + \underbrace{\sum_{i>j}\frac{e^2}{4\pi\epsilon_0 r_{ij}}}_{\hat{V}_{ee}}}_{\hat{V}}$$

- The wave function $\Psi(R, r)$ of the many electron molecule is a function of nuclear (R) and electronic (r) coordinates.
- Motion of nuclei and electrons are coupled.
- However, since nuclei are much heavier than electrons, the nuclei appear fixed or stationary.

- Born-Oppenheimer Approximation: Separate electronic and nuclear motion:

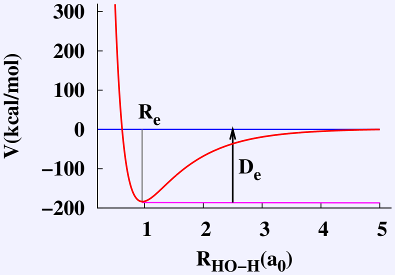
$$\Psi(R, r) = \psi_e(r; R)\psi_n(R)$$

- Solve electronic part of Schrödinger equation

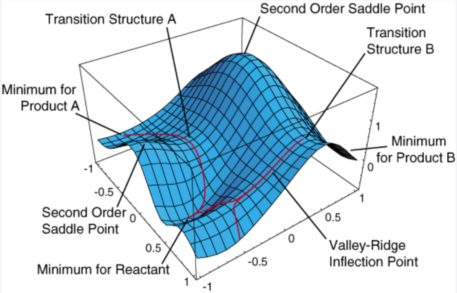
$$\hat{H}_e\psi_e(r; R) = E_e\psi_e(r; R)$$

- BO approximation leads to the concept of potential energy surface

$$V(R) = E_e + V_{nn}$$



- The potential energy surface (PES) is multi-dimensional ($3N-6$ for non-linear molecule and $3N-5$ for linear molecule)
- The PES contains multiple minima and maxima.
- Geometry optimization search aims to find the global minimum of the potential surface.
- Transition state or saddle point search aims to find the maximum of this potential surface, usually along the reaction coordinate of interest.



Picture taken from Bernard Schlegel's course slide at http://www.chem.wayne.edu/∼hbs/chm6440/

Wavefunction Methods

- The electronic Hamiltonian (in atomic units, $\hbar, m_e, 4\pi\epsilon_0, e = 1$) to be solved is

$$\hat{H}_e = -\frac{1}{2}\sum_i \nabla_i^2 - \sum_{\alpha,i}\frac{Z_\alpha}{R_{i\alpha}} + \sum_{i>j}\frac{1}{r_{ij}} + \sum_{\alpha>\beta}\frac{Z_\alpha Z_\beta}{R_{\alpha\beta}}$$

- Calculate electronic wave function and energy

$$E_e = \frac{\langle \psi_e \mid \hat{H}_e \mid \psi_e \rangle}{\langle \psi_e \mid \psi_e \rangle}$$

- The total electronic wave function is written as a Slater Determinant of the one electron functions, i.e. molecular orbitals, MO's

$$\psi_e = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_2(1) & \cdots & \phi_N(1) \\ \phi_1(2) & \phi_2(2) & \cdots & \phi_N(2) \\ \cdots & \cdots & \cdots & \cdots \\ \phi_1(N) & \phi_2(N) & \cdots & \phi_N(N) \end{vmatrix}$$

- MO's are written as a linear combination of one electron atomic functions or atomic orbitals (AO's)

$$\phi_i = \sum_{\mu=1}^{N} c_{\mu i}\chi_\mu$$

$c_{\mu i} \Rightarrow$ MO coefficients
$\chi_\mu \Rightarrow$ atomic basis functions.

- Obtain coefficients by minimizing the energy via Variational Theorem.
- Variational Theorem: Expectation value of the energy of a trial wavefunction is always greater than or equal to the true energy

$$E_e = \langle \psi_e \mid \hat{H}_e \mid \psi_e \rangle \geq \varepsilon_0$$

- Increasing $N \Rightarrow$ Higher quality of wavefunction $\Rightarrow$ Higher computational cost

The most popular classes of ab initio electronic structure methods:

- Hartree-Fock methods
  - Hartree-Fock (HF)
    - Restricted Hartree-Fock (RHF): singlets
    - Unrestricted Hartree-Fock (UHF): higher multiplicities
    - Restricted open-shell Hartree-Fock (ROHF)
- Post Hartree-Fock methods
  - Møller-Plesset perturbation theory (MPn)
  - Configuration interaction (CI)
  - Coupled cluster (CC)
- Multi-reference methods
  - Multi-configurational self-consistent field (MCSCF)
  - Multi-reference configuration interaction (MRCI)
  - n-electron valence state perturbation theory (NEVPT)
  - Complete active space perturbation theory (CASPTn)

Hartree-Fock

1. Wavefunction is written as a single determinant
$$\Psi = det(\phi_1, \phi_2, \cdots \phi_N)$$
2. The electronic Hamiltonian can be written as
$$\hat{H} = \sum_i h(i) + \sum_{i>j} v(i,j)$$
where $h(i) = -\frac{1}{2}\nabla_i^2 - \sum_{i,\alpha} \frac{Z_\alpha}{r_{i\alpha}}$ and $v(i,j) = \frac{1}{r_{ij}}$
3. The electronic energy of the system is given by:
$$E = \langle \Psi | \hat{H} | \Psi \rangle$$
4. The resulting HF equations from minimization of energy by applying of variational theorem:
$$\hat{f}(x_1)\chi_i(x_1) = \varepsilon_i \chi_i(x_1)$$
where ε_i is the energy of orbital χ_i and the Fock operator f, is defined as
$$\hat{f}(x_1) = \hat{h}(x_1) + \sum_j \left[\hat{J}_j(x_1) - \hat{K}_j(x_1)\right]$$

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1. $\hat{J}_j \Rightarrow$ Coulomb operator $\Rightarrow$ average potential at x due to charge distribution from electron in orbital χ_i defined as

$$\hat{J}_j(x_1)\chi_i(x_1) = \left[\int \frac{\chi_j^*(x_2)\chi_j(x_2)}{r_{12}} dx_2\right] \chi_i(x_1)$$

2. $\hat{K}_j \Rightarrow$ Exchange operator $\Rightarrow$ Energy associated with exchange of electrons $\Rightarrow$ No classical interpretation for this term.

$$\hat{K}_j(x_1)\chi_i(x_1) = \left[\int \frac{\chi_j^*(x_2)\chi_i(x_2)}{r_{12}} dx_2\right] \chi_j(x_1)$$

3. The Hartree-Fock equation are solved numerically or in a space spanned by a set of basis functions (Hartree-Fock-Roothan equations)

$$\chi_i = \sum_{\mu=1}^{K} C_{\mu i}\tilde{\chi}_\mu \qquad S_{\mu\nu} = \int dx_1 \tilde{\chi}_\mu^*(x_1)\tilde{\chi}_\nu(x_1)$$

$$\sum_\nu F_{\mu\nu}C_{\nu i} = \varepsilon_i \sum_\nu S_{\mu\nu}C_{\nu i} \qquad F_{\mu\nu} = \int dx_1 \tilde{\chi}_\mu^*(x_1)\hat{f}(x_1)\tilde{\chi}_\nu(x_1)$$

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon}$$

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1. The Hartree-Fock-Roothan equation is a pseudo-eigenvalue equation
2. $\mathbf{C}$'s are the expansion coefficients for each orbital expressed as a linear combination of the basis function.
3. Note: $\mathbf{C}$ depends on $\mathbf{F}$ which depends on $\mathbf{C} \Rightarrow$ need to solve self-consistently.
4. Starting with an initial guess orbitals, the HF equations are solved iteratively or self consistently (Hence HF procedure is also known as self-consistent field or SCF approach) obtaining the best possible orbitals that minimize the energy.

SCF procedure

1. Specify molecule, basis functions and electronic state of interest
2. Form overlap matrix $\mathbf{S}$
3. Guess initial MO coefficients $\mathbf{C}$
4. Form Fock Matrix $\mathbf{F}$
5. Solve $\mathbf{FC} = \mathbf{SC}\varepsilon$
6. Use new MO coefficients $\mathbf{C}$ to build new Fock Matrix $\mathbf{F}$
7. Repeat steps 5 and 6 until $\mathbf{C}$ no longer changes from one iteration to the next.

What are Post Hartree-Fock Methods

1. In Hartree-Fock theory, electron motions of independent of each other i.e. uncorrelated.
2. However, this is not true. For two electrons with same spin $|\Psi_1(r_1)\alpha(\omega_1)\Psi_2(r_2)\alpha(\omega_2)\rangle$, the probability of finding electron 1 at r_1 and electron 2 at r_2

$$
\begin{aligned}
P(r_1, r_2)dr_1dr_2 = \frac{1}{2}\Big(&|\Psi_1(r_1)|^2|\Psi_2(r_2)|^2 + |\Psi_1(r_2)|^2|\Psi_2(r_1)|^2 \\
&- [\Psi_1^*(r_1)\Psi_2(r_1)\Psi_2^*(r_2)\Psi_1(r_2) \\
&+ \ \Psi_2^*(r_1)\Psi_1(r_1)\Psi_1^*(r_2)\Psi_2(r_2)]\Big)\, dr_1dr_2
\end{aligned}
$$

   Now $P(r_1, r_1) = 0 \Rightarrow$ No two electrons with same spins can be at the same place $\Rightarrow$ "Fermi hole"
3. Same-spin electrons are correlated while different spin electrons are not.
4. Energy difference between HF energy and the true energy is the correlation energy

$$E_{corr} = E_0 - E_{HF}$$

- Methods that improve the Hartree-Fock results by accounting for the correlation energy are known as **Post Hartree-Fock methods**
- The starting point for most Post HF methods is the Slater Determinant obtain from Hartree-Fock Methods.
- **Configuration Interaction (CI) methods**: Express the wavefunction as a linear combination of Slater Determinants with the coeffcients obtained variationally

$$|\Psi\rangle = \sum_I c_I |\Psi_I\rangle$$

- **Many Body Perturbation Theory**: Treat the HF determinant as the zeroth order solution with the correlation energy as a pertubation to the HF equation.

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}'; \varepsilon_i = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \cdots$$
$$|\Psi_i\rangle = |\Psi_i^{(0)}\rangle + \lambda |\Psi_i^{(1)}\rangle + \lambda^2 |\Psi_i^{(2)}\rangle \cdots$$

- **Coupled Cluster Theory**:The wavefunction is written as an exponential ansatz

$$|\Psi\rangle = e^{\hat{T}} |\Psi_0\rangle$$

where $|\Psi_0\rangle$ is a Slater determinant obtained from HF calculations and $\hat{T}$ is an excitation operator which when acting on $|\Psi_0\rangle$ produces a linear combination of excited Slater determinants.

Scaling Behavior	Method(s)
N^4	HF
N^5	MP2
N^6	MP3, CISD, CCSD, QCISD
N^7	MP4, CCSD(T), QCISD(T)
N^8	MP5, CISDT, CCSDT
N^9	MP6
N^{10}	MP7, CISDTQ, CCSDTQ

- N = Number of Basis Functions

Density Functional Theory

- Density Functional Theory (DFT) is an alternative to wavefunction based electronic structure methods of many-body systems such as Hartree-Fock and Post Hartree-Fock.
- In DFT, the ground state energy is expressed in terms of the total electron density.

$$\rho_0(r) = \langle \Psi_0 | \hat{\rho} | \Psi_0 \rangle$$

- We again start with Born-Oppenheimer approximation and write the electronic Hamiltonian as

$$\hat{H} = \hat{F} + \hat{V}_{ext}$$

where $\hat{F}$ is the sum of the kinetic energy of electrons and the electron-electron interaction and $\hat{V}_{ext}$ is some external potential.

- Modern DFT methods result from the Hohenberg-Kohn theorem
  1. The external potential V_{ext}, and hence total energy is a unique functional of the electron density $\rho(r)$

$$\text{Energy} = \frac{\langle \Psi \mid \hat{H} \mid \Psi \rangle}{\langle \Psi \mid \Psi \rangle} \equiv E[\rho]$$

  2. The ground state energy can be obtained variationally, the density that minimizes the total energy is the exact ground state density

$$E[\rho] > E[\rho_0], \text{if } \rho \neq \rho_0$$

- If density is known, then the total energy is:

$$E[\rho] = T[\rho] + V_{ne}[\rho] + J[\rho] + E_{nn} + E_{xc}[\rho]$$

where

$$E_{nn}[\rho] = \sum_{A>B} \frac{Z_A Z_B}{R_{AB}} \qquad V_{ne}[\rho] = \int \rho(r) V_{ext}(r) dr$$

$$J[\rho] = \frac{1}{2} \int \frac{\rho(r_1)\rho(r_2)}{r_{12}} dr_1 dr_2$$

- If the density is known, the two unknowns in the energy expression are the kinetic energy functional $T[\rho]$ and the exchange-correlation functional $E_{xc}[\rho]$
- To calculate $T[\rho]$, Kohn and Sham introduced the concept of Kohn-Sham orbitals which are eigenvectors of the Kohn-Sham equation

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{eff}}(r)\right)\phi_i(r) = \varepsilon_i\phi_i(r)$$

  Here, ε_i is the orbital energy of the corresponding Kohn-Sham orbital, ϕ_i, and the density for an "N"-particle system is

$$\rho(r) = \sum_i^N |\phi_i(r)|^2$$

- The total energy of a system is

$$E[\rho] = T_s[\rho] + \int dr\, v_{\text{ext}}(r)\rho(r) + V_H[\rho] + E_{\text{xc}}[\rho]$$

- T_s is the Kohn-Sham kinetic energy which is expressed in terms of the Kohn-Sham orbitals as

$$T_s[\rho] = \sum_{i=1}^{N} \int dr\ \phi_i^*(r) \left(-\frac{1}{2}\nabla^2 \right) \phi_i(r)$$

  v_{ext} is the external potential acting on the interacting system (at minimum, for a molecular system, the electron-nuclei interaction), V_H is the Hartree (or Coulomb) energy,

$$V_H = \frac{1}{2} \int drdr'\ \frac{\rho(r)\rho(r')}{|r - r'|}$$

  and E_{xc} is the exchange-correlation energy.

- The Kohn-Sham equations are found by varying the total energy expression with respect to a set of orbitals to yield the Kohn-Sham potential as

$$v_{\text{eff}}(r) = v_{\text{ext}}(r) + \int \frac{\rho(r')}{|r - r'|} dr' + \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(r)}$$

  where the last term $v_{\text{xc}}(r) \equiv \dfrac{\delta E_{\text{xc}}[\rho]}{\delta \rho(r)}$ is the exchange-correlation potential.

- The exchange-correlation potential, and the corresponding energy expression, are the only unknowns in the Kohn-Sham approach to density functional theory.
- There are many ways to approximate this functional E_{xc}, generally divided into two separate terms

$$E_{\mathrm{xc}}[\rho] = E_{\mathrm{x}}[\rho] + E_{\mathrm{c}}[\rho]$$

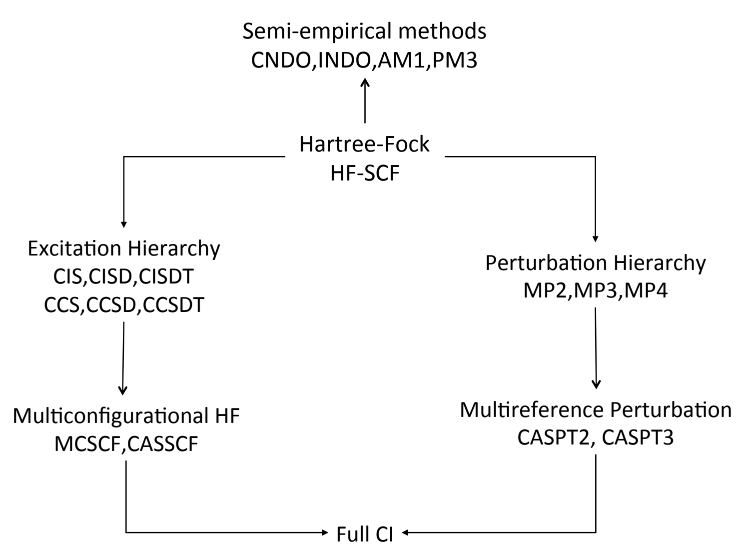
  where the first term is the exchange functional while the second term is the correlation functional.
- Quite a few research groups have developed the exchange and correlation functionals which are fit to empirical data or data from explicity correlated methods.
- Popular DFT functionals (according to a recent poll)
  - PBE0 (PBEPBE), B3LYP, PBE, BP86, M06-2X, B2PLYP, B3PW91, B97-D, M06-L, CAM-B3LYP
  - `http://www.marcelswart.eu/dft-poll/index.html`
  - `http://www.ccl.net/cgi-bin/ccl/message-new?2011+02+16+009`

Semi-empirical Methods

- Semi-empirical quantum methods:
  - Represents a middle road between the mostly qualitative results from molecular mechanics and the highly computationally demanding quantitative results from *ab initio* methods.
  - Address limitations of the Hartree-Fock claculations, such as speed and low accuracy, by omitting or parametrizing certain integrals
- integrals are either determined directly from experimental data or calculated from analytical formula with *ab initio* methods or from suitable parametric expressions.
- Integral approximations:
  - Complete Neglect of Differential Overlap (CNDO)
  - Intermediate Neglect of Differential Overlap (INDO)
  - Neglect of Diatomic Differential Overlap (NDDO) (Used by PM3, AM1, ...)

Semi-empirical methods are fast, very accurate when applied to molecules that are similar to those used for parametrization and are applicable to very large molecular systems.

Heirarchy of Methods



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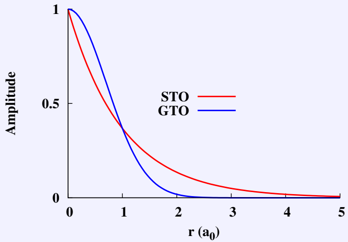
- Slater type orbital (STO) or Gaussian type orbital (GTO) to describe the AO's

$$\chi^{\mathrm{STO}}(r) = x^l y^m z^n e^{-\zeta r}$$
$$\chi^{\mathrm{GTO}}(r) = x^l y^m z^n e^{-\xi r^2}$$

where $L = l + m + n$ is the total angular momentun and ζ, ξ are orbital exponents.



Why STO

- Correct cups at $r \to 0$
- Desired decay at $r \to \infty$
- Correctly mimics H orbitals
- Natural Choice for orbitals
- Computationally expensive to compute integrals and derivatives.

Why GTO

- Wrong behavior at $r \to 0$ and $r \to \infty$
- Gaussian $\times$ Gaussian = Gaussian
- Analytical solutions for most integrals and derivatives.
- Computationally less expensive than STO's

Pople family basis set

1. Minimal Basis: STO-nG
   - Each atom optimized STO is fit with n GTO's
   - Minimum number of AO's needed
2. Split Valence Basis: 3-21G,4-31G, 6-31G
   - Contracted GTO's optimized per atom.
   - Valence AO's represented by 2 contracted GTO's
3. Polarization: Add AO's with higher angular momentum (L)
   - 3-21G* or 3-21G(d),6-31G* or 6-31G(d),6-31G** or 6-31G(d,p)
4. Diffuse function: Add AO with very small exponents for systems with diffuse electron densities
   - 6-31+G*, 6-311++G(d,p)

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Correlation consistent basis set

- Family of basis sets of increasing sizes.
- Can be used to extrapolate basis set limit.
- cc-pVDZ: Double Zeta(DZ) with d's on heavy atoms, p's on H
- cc-pVTZ: triple split valence with 2 sets of d's and 1 set of f's on heavy atom, 2 sets of p's and 1 set of d's on H
- cc-pVQZ, cc-pV5Z, cc-pV6Z
- can be augmented with diffuse functions: aug-cc-pVXZ (X=D,T,Q,5,6)

Pseudopotentials or Effective Core Potentials

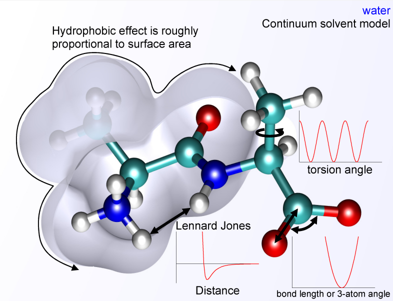
- All Electron calculations are prohibitively expensive.
- Only valence electrons take part in bonding interaction leaving core electrons unaffected.
- Effective Core Potentials (ECP) a.k.a Pseudopotentials describe interactions between the core and valence electrons.
- Only valence electrons explicitly described using basis sets.
- Pseudopotentials commonly used
  - Los Alamos National Laboratory: LanL1MB and LanL2DZ
  - Stuttgard Dresden Pseudopotentials: SDDAll can be used.
  - Stevens/Basch/Krauss ECP's: CEP-4G,CEP-31G,CEP-121G
- Pseudopotential basis are "ALWAYS" read in pairs
  - Basis set for valence electrons
  - Parameters for core electrons

Molecular Mechanics

- The potential energy of all systems in molecular mechanics is calculated using force fields.
- Molecular mechanics can be used to study small molecules as well as large biological systems or material assemblies with many thousands to millions of atoms.
- All-atomistic molecular mechanics methods have the following properties:
  - Each atom is simulated as a single particle
  - Each particle is assigned a radius (typically the van der Waals radius), polarizability, and a constant net charge (generally derived from quantum calculations and/or experiment)
  - Bonded interactions are treated as "springs" with an equilibrium distance equal to the experimental or calculated bond length
- The exact functional form of the potential function, or force field, depends on the particular simulation program being used.

General form of Molecular Mechanics equations

$$
\begin{aligned}
E &= E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} + E_{\text{vdW}} + E_{\text{elec}} \\
&= \frac{1}{2}\sum_{\text{bonds}} K_b (b - b_0)^2 && \text{Bond} \\
&+ \frac{1}{2}\sum_{\text{angles}} K_\theta (\theta - \theta_0)^2 && \text{Angle} \\
&+ \frac{1}{2}\sum_{\text{dihedrals}} K_\phi \left[1 + \cos(n\phi)\right]^2 && \text{Torsion} \\
&+ \sum_{\text{nonbonds}} \left\{ \begin{array}{ll} \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] & \text{van der Waals} \\ + \frac{q_1 q_2}{Dr} & \text{Electrostatics} \end{array} \right.
\end{aligned}
$$



Picture taken from
http://en.wikipedia.org/wiki/Molecular_mechanics

QM/MM

- What do we do if we want simulate chemical reaction in large systems?
- Quantum Mechanics(QM): Accurate, expensive ($\mathcal{O}(N^4)$), suitable for small systems.
- Molecular Mechanics(MM): Approximate, does not treat electrons explicitly, suitable for large systems such as enzymes and proteins, cannot simulate bon breaking/forming

- Methods that combine QM and MM are the solution.
- Such methods are called Hybrid QM/MM methods.
- The basic idea is to partition the system into two (or more) parts
  1. The region of chemical interest is treated using accurate QM methods eg. active site of an enzyme.
  2. The rest of the system is treated using MM or less accurate QM methods such as semi-empirical methods or a combination of the two.

$$\hat{H}_{\text{Total}} = \hat{H}_{\text{QM}} + \hat{H}_{\text{MM}} + \hat{H}^{\text{int}}_{\text{QM}-\text{MM}}$$

ONIOM: Divide the system into a real (full) system and the model system. Treat the model system at high and low level. The total energy of the system is given by

$$E = E(low, real) + E(high, model) - E(low, model)$$

Empirical Valence Bond: Treat any point on a reaction surface as a combination of two or more valence bond structures

$$H(\mathbf{R}, \mathbf{r}) = \begin{vmatrix} H_{11}(\mathbf{R}, \mathbf{r}) & H_{12}(\mathbf{R}, \mathbf{r}) \\ H_{21}(\mathbf{R}, \mathbf{r}) & H_{22}(\mathbf{R}, \mathbf{r}) \end{vmatrix}$$

Effective Fragment Potential: Divide a large system into fragments and perform *ab initio* or DFT calculations of fragments and their dimers and including the Coulomb field from the whole system.

Why Molecular Dynamics?

- Electronic Structure Methods are applicable to systems in gas phase under low pressure (vaccum).
- Majority of chemical reactions take place in solution at some temperature with biological reactions usually at specific pH's.
- Calculating molecular properties taking into account such environmental effects which can be dynamical in nature are not adequately described by electronic structure methods.

Molecular Dynamics

- Generate a series of time-correlated points in phase-space (a trajectory).
- Propagate the initial conditions, position and velocities in accordance with Newtonian Mechanics. $\mathbf{F} = m\mathbf{a} = -\nabla V$
- Fundamental Basis is the **Ergodic Hypothesis**: the average obtained by following a small number of particles over a long time is equivalent to averaging over a large number of particles for a short time.

Molecular Dynamics Theory

- Solve the time-dependent Schrödinger equation

$$\imath\hbar\frac{\partial}{\partial t}\Psi(\mathbf{R},\mathbf{r},t) = \hat{H}\Psi(\mathbf{R},\mathbf{r},t)$$

with

$$\Psi(\mathbf{R},\mathbf{r},t) = \chi(\mathbf{R},t)\Phi(\mathbf{r},t)$$

and

$$\hat{H} = -\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + \underbrace{\frac{-\hbar^2}{2m_e}\nabla_i^2 + V_{n-e}(\mathbf{r},\mathbf{R})}_{H_e(\mathbf{r},\mathbf{R})}$$

- Obtain coupled equations of motion for electrons and nuclei: Time-Dependent Self-Consistent Field (TD-SCF) approach.

$$\imath\hbar\frac{\partial\Phi}{\partial t} = \left[-\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 + \langle\chi|V_{n-e}|\chi\rangle\right]\Phi$$

$$\imath\hbar\frac{\partial\chi}{\partial t} = \left[-\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + \langle\Phi|H_e|\Phi\rangle\right]\chi$$

- Define nuclear wavefunction as

$$\chi(\mathbf{R}, t) = A(\mathbf{R}, t) \exp\left[iS(\mathbf{R}, t)/\hbar\right]$$

where A and S are real.

- Solve the time-dependent equation for nuclear wavefunction and take classical limit ($\hbar \to 0$) to obtain

$$\frac{\partial S}{\partial t} + \sum_I \frac{\hbar^2}{2M_I}(\nabla_I S)^2 + \langle \Phi | H_e | \Phi \rangle = 0$$

an equation that is isomorphic with the Hamilton-Jacobi equation with the classical Hamilton function given by

$$\mathcal{H}(\{\mathbf{R}_I\}, \{\mathbf{P}_I\}) = \sum_I \frac{\hbar^2}{2M_I}\mathbf{P}_I^2 + V(\{\mathbf{R}_I\})$$

where

$$\mathbf{P}_I \equiv \nabla_I S \qquad \text{and} \qquad V(\{\mathbf{R}_I\}) = \langle \Phi | H_e | \Phi \rangle$$

- Obtain equations of nuclear motion from Hamilton's equation

$$\frac{d\mathbf{P}_I}{dt} = -\frac{d\mathcal{H}}{d\mathbf{R}_I} \Rightarrow M\ddot{\mathbf{R}}_I = -\nabla_I V$$

$$\frac{d\mathbf{R}_I}{dt} = \frac{d\mathcal{H}}{d\mathbf{P}_I}$$

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- Replace nuclear wavefunction by delta functions centered on nuclear position to obtain

$$i\hbar\frac{\partial\Phi}{\partial t} = H_e(\mathbf{r}, \{\mathbf{R}_I\})\Phi(\mathbf{r}; \{\mathbf{R}_I\}, t)$$

- This approach of simultaneously solving the electronic and nuclear degrees of freedom by incorporating feedback in both directions is known as **Ehrenfest Molecular Dynamics**.
- Expand Φ in terms of many electron wavefunctions or determinants

$$\Phi(\mathbf{r}; \{\mathbf{R}_I\}, t) = \sum_i c_i(t)\Phi_i(\mathbf{r}; \{\mathbf{R}_I\})$$

  with matrix elements

$$H_{ij} = \langle\Phi_i|H_e|\Phi_j\rangle$$

- Inserting Φ in the TDSE above, we get

$$\imath\hbar\dot{c}_i(t) = c_i(t)H_{ii} - \imath\hbar\sum_{I,i}\dot{\mathbf{R}}_I\mathbf{d}_I^{ij}$$

  with non-adiabtic coupling elements given by

$$\mathbf{d}_I^{ij}(\mathbf{R}_I) = \langle\Phi_i|\nabla_I|\Phi_j\rangle$$

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- Upto this point, no restriction on the nature of Φ_i i.e. adiabatic or diabatic basis has been made.
- Ehrenfest method rigorously includes non-adiabtic transitions between electronic states within the framework of classical nuclear motion and mean field (TD-SCF) approximation to the electronic structure.
- Now suppose, we define $\{\Phi_i\}$ to be the adiabatic basis obtained from solving the time-independent Schrödinger equation,

$$H_e(\mathbf{r}, \{\mathbf{R}_I\})\Phi_i(\mathbf{r}; \{\mathbf{R}_I\}) = E_i(\{\mathbf{R}_I\})\Phi_i(\mathbf{r}; \{\mathbf{R}_I\})$$

- The classical nuclei now move along the adiabatic or Born-Oppenheimer potential surface. Such dynamics are commonly known as **Born-Oppenheimer Molecular Dynamics** or BOMD.
- If we restrict the dynamics to only the ground electronic state, then we obtain ground state BOMD.
- If the Ehrenfest potential $V(\{\mathbf{R}_I\})$ is approximated to a global potential surface in terms of many-body contributions $\{v_n\}$.

$$V(\{\mathbf{R}_I\}) \approx V_e^{approx}(\mathbf{R}) = \sum_{I=1}^{N} v_1(\mathbf{R}_I) + \sum_{I>J}^{N} v_2(\mathbf{R}_I, \mathbf{R}_J) + \sum_{I>J>K}^{N} v_3(\mathbf{R}_I, \mathbf{R}_J, \mathbf{R}_K) + \cdots$$

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- Thus the problem is reduced to purely classical mechanics once the $\{v_n\}$ are determined usually Molecular Mechanics Force Fields. This class of dynamics is most commonly known as **Classical Molecular Dynamics**.
- Another approach to obtain equations of motion for ab-initio molecular dynamics is to apply the Born-Oppenheimer approximation to the full wavefunction $\Psi(\mathbf{r}, \mathbf{R}, t)$

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_k \chi(\mathbf{R}, t)\Phi_k(\mathbf{r}; \mathbf{R}(t))$$

where

$$H_e\Phi_k(\mathbf{r}; \mathbf{R}(t)) = E_k(\mathbf{R}(t))\Phi_k(\mathbf{r}; \mathbf{R}(t))$$

- Assuming that the nuclear dynamics doesn not change the electronic state, we arrive at the equation of motion for nuclear wavefunction

$$\imath\hbar\frac{\partial}{\partial t}\chi(\mathbf{R}, t) = \left[\sum_I -\frac{\hbar^2}{2M_I}\nabla_I^2 + E_k(\mathbf{R})\right]\chi(\mathbf{R}, t)$$

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- The Lagrangian for this system is given by.

$$\mathcal{L} = \hat{T} - \hat{V}$$

- Corresponding Newton's equation of motion are then obtained from the associated Euler-Lagrange equations,

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{\mathbf{R}}_I} = \frac{\partial \mathcal{L}}{\partial \mathbf{R}_I}$$

- The Lagrangian for ground state BOMD is

$$\mathcal{L}_{\text{BOMD}} = \sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 - \min_{\Phi_0} \langle \Phi | H_e | \Phi \rangle$$

and equations of motions

$$M_I \ddot{\mathbf{R}}_I = \frac{d}{dt}\frac{\partial \mathcal{L}_{\text{BOMD}}}{\partial \dot{\mathbf{R}}_I} = \frac{\partial \mathcal{L}_{\text{BOMD}}}{\partial \mathbf{R}_I} = -\nabla_I \min_{\Phi_0} \langle \Phi | H_e | \Phi \rangle$$

Extended Lagrangian Molecular Dynamics (ELMD)

Extend the Lagrangian by adding kinetic energy of fictitious particles and obtain their equation of motions from Euler-Lagrange equations.

Molecular Orbitals: $\{\phi_i\}$

Density Matrix: $P_{\mu\nu} = \sum_i c^*_{\mu i} c_{\nu i}$

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Car-Parrinello Molecular Dynamics (CPMD)

CPMD and NWCHEM

$$\mathcal{L}_{\text{CPMD}} = \sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \sum_i \frac{1}{2} \mu_i \langle \dot{\phi}_i | \dot{\phi}_i \rangle - \langle \Phi_0 | H_e | \Phi_0 \rangle + \text{constraints}$$

R. Car and M. Parrinello, Phys. Rev. Lett. 55 (22), 2471 (1985)

Atom centered Density Matrix Propagation (ADMP)

Gaussian 03/09

$$\mathcal{L}_{\text{ADMP}} = \frac{1}{2} \text{Tr}(\mathbf{V}^T \mathbf{M} \mathbf{V}) + \frac{1}{2} \mu \text{Tr}(\dot{\mathbf{P}} \dot{\mathbf{P}}) - E(\mathbf{R}, \mathbf{P}) - \text{Tr}[\mathbf{\Lambda}(\mathbf{P}\mathbf{P} - \mathbf{P})]$$

H. B. Schlegel, J. M. Millam, S. S. Iyengar, G. A. Voth, A. D. Daniels, G. E. Scuseria, M. J. Frisch, J. Chem. Phys. 114, 9758 (2001)

curvy-steps ELMD (csELMD)

Q-Chem

$$\mathcal{L}_{\text{csELMD}} = \sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \frac{1}{2} \mu \sum_{i<j} \dot{\Delta}_{ij} - E(\mathbf{R}, \mathbf{P}); \quad \mathbf{P}(\lambda) = e^{\lambda \Delta} \mathbf{P}(0) e^{-\lambda \Delta}$$

J.M. Herbert and M. Head-Gordon, J. Chem. Phys. 121, 11542 (2004)

- Electronic energy obtained from
  - Molecular Mechanics ⇒ Classical Molecular Dynamics
    1. LAMMPS
    2. NAMD
    3. Amber
    4. Gromacs
  - Ab-Initio Methods ⇒ Quantum or Ab-Initio Molecular Dynamics
    1. Born-Oppenheimer Molecular Dynamics: Gaussian, GAMESS
    2. Extended Lagrangian Molecular Dynamics: VASP, CPMD, Gaussian (ADMP), NWCHEM(CPMD), QChem (curvy-steps ELMD)
    3. Time Dependent Hartree-Fock and Time Dependent Density Functional Theory: Gaussian, GAMESS, NWCHEM, QChem
    4. Multiconfiguration Time Dependent Hartree(-Fock), MCTDH(F)
    5. Non-Adiabatic and Ehrenfest Molecular Dynamics, Multiple Spawning, Trajectory Surface Hopping
    6. Quantum Nuclei: QWAIMD(Gaussian), NEO(GAMESS)

Classical Molecular Dynamics

- Advantages
  1. Large Biological Systems
  2. Long time dynamics
- Disadvantages
  1. Cannot describe Quantum Nuclear Effects

Ab Initio and Quantum Dynamics

- Advantages
  1. Quantum Nuclear Effects
- Disadvantages
  1. $\sim$ 100 atoms
  2. Full Quantum Dynamics ie treating nuclei quantum mechanically: less than 10 atoms
  3. Picosecond dynamics at best

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Software	QB	Eric	Louie	Oliver	Painter	Poseidon	Philip	Tezpur
Amber	✓	✓	✓	✓	✓	✓	✓	✓
Desmond	✓							
DL_Poly	✓	✓	✓	✓	✓	✓	✓	✓
Gromacs	✓	✓	✓	✓	✓	✓	✓	✓
LAMMPS	✓	✓	✓	✓	✓	✓	✓	✓
NAMD	✓	✓	✓	✓	✓	✓		✓
OpenEye	✓	✓	✓	✓	✓	✓	✓	✓
CPMD	✓	✓	✓	✓	✓	✓		✓
GAMESS	✓	✓	✓	✓	✓	✓	✓	✓
Gaussian		✓	✓	✓	✓		✓	✓
NWCHEM	✓	✓	✓	✓	✓	✓		✓
Piny_MD	✓	✓	✓	✓	✓	✓	✓	✓

Software	Bluedawg	Ducky	Lacumba	Neptune	Zeke	Pelican	Pandora
Amber		✓	✓			✓	
Gromacs	✓	✓	✓	✓	✓	✓	
LAMMPS	✓	✓	✓	✓	✓	✓	
NAMD	✓	✓	✓	✓	✓		
CPMD	✓	✓	✓	✓	✓		
Gaussian	✓	✓	✓		✓	✓	
NWCHEM	✓	✓	✓	✓	✓	✓	
Piny_MD	✓	✓	✓	✓	✓	✓	

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- Commercial Software: Q-Chem, Jaguar,CHARMM
- GPL/Free Software: ACES, ABINIT, Octopus
- **http://en.wikipedia.org/wiki/Quantum_chemistry_computer_programs**
- **http://www.ccl.net/chemistry/links/software/index.shtml**
- **http://www.redbrick.dcu.ie/~noel/linux4chemistry/**

Job Types and Keywords

Job Type	Gaussian	GAMESS	NWCHEM
	# keyword	runtyp=	task
Energy	sp	energy	energy
Force	force	gradient	gradient
Geometry optimization	opt	optimize	optimize
Transition State	opt=ts	sadpoint	saddle
Frequency	freq	hessian	frequencies, freq
Potential Energy Scan	scan	surface	✓
Excited State	✓	✓	✓
Reaction path following	irc	irc	✓
Molecular Dynamics	admp, bomd	drc	dynamics, Car-Parrinello
Population Analysis	pop	pop	✓
Electrostatic Properties	prop	✓	✓
Molecular Mechanics	✓	✓	✓
Solvation Models	✓	✓	✓
QM/MM	oniom	✓	qmmm

Molecular Dynamics Calculations

- Gaussian:
  - BOMD: Born-Oppenheimer Molecular Dynamics
  - ADMP: Atom centered Density Matrix Propagation (an extended Lagrangian Molecular Dynamics similar to CPMD) and ground state BOMD
- GAMESS:
  - DRC: Direct Dynamics, a classical trajectory method based on "on-the-fly" ab-initio or semi-empirical potential energy surfaces
- NWCHEM:
  - Car-Parrinello: Car Parrinello Molecular Dynamics (CPMD)
  - DIRDYVTST: Direct Dynamics Calculations using POLYRATE with electronic structure from NWCHEM

Related HPC Tutorials

- Fall Semester

Introduction to Gaussian/Electronic Structure Methods

- Spring Semester

Introduction to Computational Chemistry: Molecular Dynamics

April 27^{th}

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Useful Links

- Amber:http://ambermd.org
- Desmond:http://www.deshawresearch.com/resources_desmond.html
- DL_POLY:http://www.cse.scitech.ac.uk/ccg/software/DL_POLY
- Gromacs:http://www.gromacs.org
- LAMMPS:http://lammps.sandia.gov
- NAMD:http://www.ks.uiuc.edu/Research/namd
- CPMD: http://www.cpmd.org
- GAMESS: http://www.msg.chem.iastate.edu/gamess
- Gaussian: http://www.gaussian.com
- NWCHEM: http://www.nwchem-sw.org
- PINY_MD:http://homepages.nyu.edu/~mt33/PINY_MD/PINY.html
- Basis Set: https://bse.pnl.gov/bse/portal

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Further Reading

- David Sherill's Notes at Ga Tech:
  `http://vergil.chemistry.gatech.edu/notes/index.html`
- Mark Tuckerman's Notes at NYU:
  `http://www.nyu.edu/classes/tuckerman/quant.mech/index.html`
- Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory, A. Szabo and N. Ostlund
- Introduction to Computational Chemistry, F. Jensen
- Essentials of Cmputational Chemistry - Theories and Models, C. J. Cramer
- Exploring Chemistry with Electronic Structure Methods, J. B. Foresman and A. Frisch
- Ab Initio Molecular Dynamics: Theory and Implementation, D. Marx and J. Hutter`http://www.theochem.ruhr-uni-bochum.de/research/marx/marx.pdf`
- Molecular Modeling - Principles and Applications, A. R. Leach
- Computer Simulation of Liquids, M. P. Allen and D. J. Tildesley

♦ Modern Electronic Structure Theory, T. Helgaker, P. Jorgensen and J. Olsen (Highly advanced text, second quantization approach to electronic structure theory)

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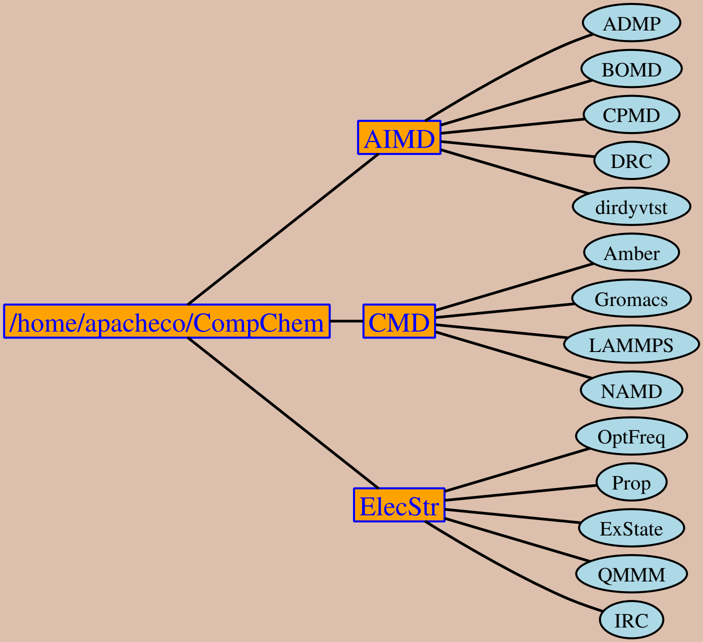
On LONI Linux Systems



- Site specific license
  1. Gaussian 03 and 09
     - LSU Users: Eric
     - Latech Users: Painter, Bluedawg
  2. Gaussian 03
     - ULL Users: Oliver, Zeke
     - Tulane Users: Louie, Ducky
     - Southern Users: Lacumba
  3. UNO Users: No License
- Add +gaussian-03/+gaussian-09 to your .soft file and resoft
- If your institution has license to both G03 and G09, have only one active at a given time.

Example Job submission script on Intel x86

```
#!/bin/tcsh
#PBS -A your_allocation
# specify the allocation. Change it to your allocation
#PBS -q checkpt
# the queue to be used.
#PBS -l nodes=1:ppn=4
# Number of nodes and processors
#PBS -l walltime=1:00:00
# requested Wall-clock time.
#PBS -o g03_output
# name of the standard out file to be "output-file".
#PBS -j oe
# standard error output merge to the standard output file.
#PBS -N g03test
# name of the job (that will appear on executing the qstat command).

# setup g03 variables
source $g03root/g03/bsd/g03.login
set NPROCS=`wc -l $PBS_NODEFILE |gawk '//{print $1}'`
setenv GAUSS_SCRDIR /scratch/$USER
# cd to the directory with Your input file
cd ~apacheco/g03test
# Change this line to reflect your input file and output file
g03 < g03job.inp  > g03job.out
```

Linda Access

```
set NODELIST = ( -vv -nodelist '"' `cat $PBS_NODEFILE` '"' -mp 4)
setenv GAUSS_LFLAGS " $NODELIST "
g03l < g03job.inp  > g03job.out
```

Example Job submission script on P5

```
#!/bin/tcsh
# @ account_no = your_allocation
# @ requirements = (Arch == "Power5")
# @ environment = LL_JOB=TRUE ;  MP_PULSE=1200
# @ job_type = parallel
# @ node_usage = shared
# @ wall_clock_limit = 12:00:00
# @ initialdir = /home/apacheco/g03test
# @ class = checkpt
# @ error = g03_$(jobid).err
# @ queue

# setup g03 variables
source $g03root/g03/bsd/g03.login
# setup and create Gaussian scratch directory
setenv GAUSS_SCRDIR /scratch/default/$USER
mkdir -p $GAUSS_SCRDIR
# cd to the directory with Your input file
cd ~apacheco/g03test
# Change this line to reflect your input file and output file
g03 < g03job.inp  > g03job.out
```

Sample Input

```
%chk=h2o-opt-freq.chk
%mem=512mb
%NProcShared=4

#p b3lyp/6-31G opt freq

H2O OPT FREQ B3LYP

0 1
O
H 1 r1
H 1 r1 2 a1

r1 1.05
a1 104.5
```

Input Description

```
checkpoint file
amount of memory
number of smp processors
blank line
Job description
blank line
Job Title
blank line
Charge Multiplicity
Molecule Description
 Z-matrix format
 with variables
blank line
 variable value

blank line
```

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- Add +gamess-12Jan2009R1-intel-11.1 (on Queenbee) to your .soft and resoft

Job submission script

```
#!/bin/bash
#PBS -A your_allocation
#PBS -q checkpt
#PBS -l nodes=1:ppn=4
#PBS -l walltime=00:10:00
#PBS -j oe
#PBS -N gamess-exam1

export WORKDIR=$PBS_O_WORKDIR
export NPROCS=`wc -l $PBS_NODEFILE | gawk '//{print $1}'`
export SCRDIR=/work/$USER/scr
if [ ! -e $SCRDIR ]; then mkdir -p $SCRDIR; fi
rm -f $SCRDIR/*

cd $WORKDIR
rungms h2o-opt-freq 01 $NPROCS h2o-opt-freq.out  $SCRDIR
cp -p $SCRDIR/$OUTPUT $WORKDIR/
```

Sample Input

```
 $CONTRL SCFTYP=RHF RUNTYP=OPTIMIZE
   COORD=ZMT NZVAR=0 $END
 $STATPT OPTTOL=1.0E-5 HSSEND=.T. $END
 $BASIS GBASIS=N31 NGAUSS=6
   NDFUNC=1 NPFUNC=1 $END
 $DATA
H2O OPT
Cnv 2

O
H 1 rOH
H 1 rOH 2 aHOH

rOH=1.05
aHOH=104.5
 $END
```

Input Description

```
Job control data

geometry search control
6-31G** basis set

molecular data control
Title
Symmetry group and axis

molecule description in
   z-matrix


variables

end molecular data control
```

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- Add +nwchem-5.1.1-intel-11.1-mvapich-1.1 (on Queenbee) to your .soft and resoft

Job submission script

```
#!/bin/sh
#
#PBS -q checkpt
#PBS -M apacheco@cct.lsu.edu
#PBS -l nodes=1:ppn=4
#PBS -l walltime=0:30:00
#PBS -V
#PBS -o nwchem_h2o.out
#PBS -e nwchem_h2o.err
#PBS -N nwchem_h2o

export EXEC=nwchem
export EXEC_DIR=/usr/local/packages/nwchem-5.1-mvapich-1.0-intel-10.1/bin/LINUX64/
export WORK_DIR=$PBS_O_WORKDIR
export NPROCS=`wc -l $PBS_NODEFILE |gawk '//{print $1}'`

cd $WORK_DIR
mpirun_rsh -machinefile $PBS_NODEFILE -np $NPROCS $EXEC_DIR/$EXEC \
  $WORK_DIR/h2o-opt-freq.nw >& $WORK_DIR/h2o-opt-freq.nwo
```

Sample Input

```
title "H2O"
echo
charge 0
geometry
zmatrix
O
H 1 r1
H 1 r1 2 a1
variables
r1 1.05
a1 104.5
end
end
basis noprint
 * library 6-31G
end
dft
 XC b3lyp
 mult 1
end
task dft optimize
task dft energy
task dft freq
```

Input Description

```
Job title
echo contents of input file
charge of molecule
geometry description in
z-matrix format




variables used with values



end z-matrix block
end geometry block
basis description


dft calculation options




job type
```

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