

# Tentative Program

## I. OVERVIEW

1. Modern methods of computational chemistry (MM, ab initio, DFT and Hybrid methods).
2. Introduction to the Emerson Center's facilities

## II. Molecular mechanics and Molecular Dynamic

3. Molecular mechanics and Molecular Dynamic methods
4. Applications and Practical sessions on Problem solving.

## III. Transition Metal Chemistry and Catalysis

5. Computational approaches to the Transition Metal Chemistry
6. Computational Catalysis (including Organic, Inorganic and Enzymatic)
7. Practical sessions on Problem solving.

## IV. Small Molecules and Excited State Studies

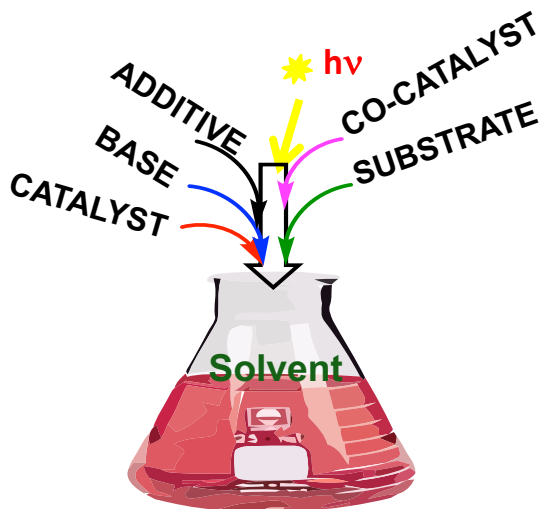
8. Overview Methodology
9. Application to Spectroscopy, problem solving.
10. Application to Radical Chemistry, problem solving.

## Advantages:

Provides atomistic level understandings of catalysis, guides experiments, may lead to designing of more efficient, cost-effective and novel catalytic processes

## Disadvantages:

It is a model and may not include all real-time contributors into the understanding.



Complexity is to characterize something with many parts where those parts interact with each other in multiple ways.

Complex systems present problems both in mathematical modeling and philosophical foundations.

The study of complex systems requires multi-disciplinary and truly collaborative approaches.

***Man possesses the ability to imitate the workings of Nature".*** 3<sup>rd</sup> century, AD **Zosimos:**

***Join and truly collaborative experimental and computational efforts will lead to more dramatic and novel findings.***

# OVERVIEW Computational Modeling

## Computational Modeling

Quantum Mechanical Approach

Molecular Mechanical Approach  
Amber, UFF, MM etc.

Hybrid Approaches:  
QM/MM and ONIOM

Ab Initio Approach

Density Functional Approach

- Hartree-Fock (HF)
- Electron Correlation
- Basis Sets
- Effective Core Potentials

- Kohn-Sham theorem



Hybrid Density Functional: **B3LYP, BLYP, M06, etc.**

# Ab Initio (from first principles) Approaches

To get the  $E_{\text{tot}}$  and  $\Psi$ : Solve the Schrodinger eq. for frozen nuclei  
(the Born-Oppenheimer approximation)

Time dependent  
(the wave equation):

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

Time independent (stationary solutions or *eigenfunctions* of  $\mathbf{H}$ ):

$$\mathbf{H} \Psi_l(r) = E_l \Psi_l(r), \text{ for } l=1, 2, \dots$$

where:

$$\mathbf{H} = \mathbf{T} + \mathbf{N}_e - E_{\text{el}}$$

is the Hamiltonian operator of the system

# Quantum Chemical Calculations:

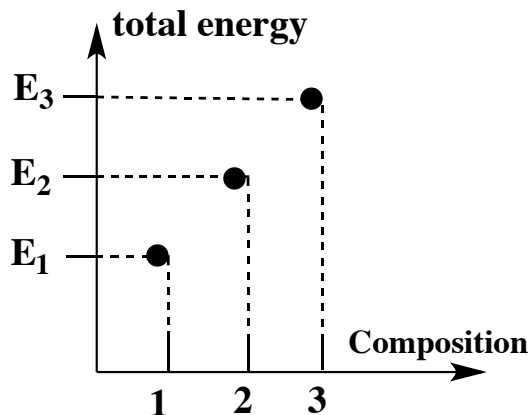
What is necessary ?

$$H\Psi_I = E_I\Psi_I$$

- H** Energy operator → Method  
The Hamiltonian defines everything about the system

Results are:

- $E_I$**  Total Energy for state  $I$   
 **$\Psi_I$**  Wavefunction for state  $I$  is a probabilistic description of electronic motion for a given geometry, charge and spin state



In Ab initio approaches:  
"Composition" is a Wavefunction

In DFT approaches:  
"Composition" is a Density

# Hartree-Fock (HF) Approximation.

For many-electron systems, it is impossible exactly solve the Schrodinger eq. Therefore, some approximations are necessary. The **Hartree-Fock** and **Roothaan** approximations are among the most popular approximations.

**Hartree-Fock (HF) Approximation.** - This is an approximation to the Hamiltonian **H**:

$$\mathbf{H} \Rightarrow \mathbf{F} = \mathbf{T} + \mathbf{N}_e + \mathbf{V}^{\text{HF}}$$

Where  $\mathbf{V}^{\text{HF}}$  – is the average potential experienced by the  $i$ -th electron due to the presence of the other electrons. *The essence of the HF approximation is to replace the complicated many-electron problem by a one-electron problem in which electron-electron repulsion is treated in an average way.*

$\mathbf{V}^{\text{HF}}$  depends from the wavefunction of  $i$ -th electron, so **HF** eq should be solved ONLY by Self-Consistent-Field (SCF) technique.

- **RHF (restricted Hartree-Fock)** method use the same orbitals for  $\alpha$ -spin and  $\beta$ -spin.
- **UHF (unrestricted Hartree-Fock)** method use different orbitals for  $\alpha$ -spin and  $\beta$ -spin.

# Configuration Interaction (CI) approach

Provides eigenvalues (as  $E_{\text{HF}} + E_{\text{corr}}$ ) and MULTI-determinant (Multi-Slater determinant) based wavefunction:

$$\Psi_{\text{CI}}(1,2, \dots, N) = \sum_{i=1}^m c_i \psi_i(1,2, \dots, N)$$

## Popular ab initio methods

<b>HF</b>	-	Hartree-Fock
<b>MP2</b>	-	Moller-Plesset Second order
<b>MP3</b>	-	Moller-Plesset Third order
<b>MP4 (SDQ)</b>	-	Moller-Plesset fourth order (and also includes S, D and Q Excitations)
<b>MP4 (SDTQ)</b>	-	Adds triple excitations
<b>CISD</b>	-	Configuration Interaction
<b>QCISD</b>	-	Quadratic CI
<b>CCSD</b>	-	Coupled-cluster method
<b>CASSCF</b>	-	Complete Active Space-SCF

$$H\Psi = E\Psi$$

**H** Energy operator  $\rightarrow$  Method

**$\Psi$**  Wavefunction is a functional description of molecular system with a given geometry, charge, spin state, etc...

The **N electron wavefunction**  $\Psi(1,2, \dots, N)$  is constructed from the MO's and spin functions. The simplest such wavefunction which satisfies the Pauli exclusion or the anti-symmetry principle is a determinantal wave function. (Slater determinant = SD)

$$\Psi_0(1,2, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1) & \psi_2(1) & \psi_3(1) & \cdots & \psi_N(1) \\ \psi_1(2) & \psi_2(2) & \psi_3(2) & \cdots & \psi_N(2) \\ \vdots & \vdots & \vdots & & \vdots \\ \psi_1(N) & \psi_2(N) & \psi_3(N) & \cdots & \psi_N(N) \end{vmatrix}$$

$\begin{array}{c} \uparrow \psi_N \\ \vdots \\ \uparrow \psi_3 \\ \uparrow \downarrow \psi_2 \\ \uparrow \psi_1 \end{array}$

where  $\psi_i(\nu) = \phi_i(\nu)\alpha(\nu)$  or  $\psi_i(\nu) = \phi_i(\nu)\beta(\nu)$ ,  
 $\phi_i(\nu)$  is the spatial molecular orbital,

$\psi_i(\nu)$  describes spin-orbital,  
 $\alpha(\nu)$  or  $\beta(\nu)$  is the spin function

### Roothaan approximation:

$$\varphi_i = \sum C_{mi} \chi_m \quad \chi_m - \text{ is Atomic Orbital (or basis function)}$$

Combining of **HF** and **R**-approximations will give us **Hartree-Fock-Roothaan** eq.

$$FC = EC$$

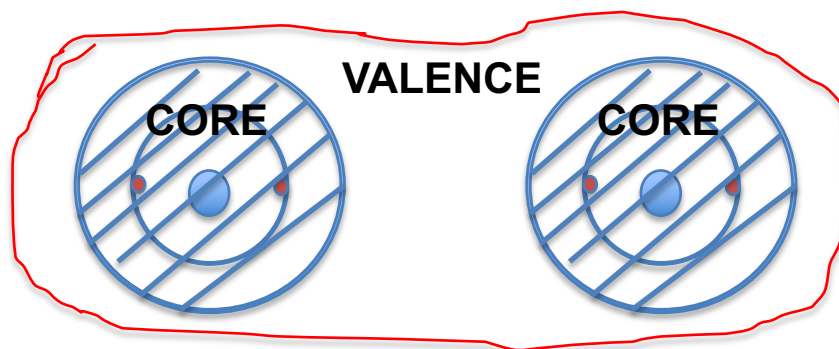
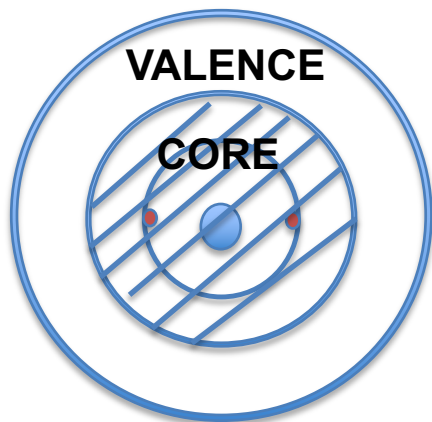
So, we should know F and C (coefficient matrix) to get Total Energy and Wavefunction.





Since basis sets can be interpreted as restriction of each electron to a particular region of space, larger basis sets impose fewer constraints of electrons, and more accurately approximate exact molecular orbital: Thus, accuracy of the calculations improves via increasing the basis sets to HF limit:

**Minimal Basis Set < Double-Zeta < Triple-Zeta < ..... HF basis limit**



There are mixed approach too: To use minimal basis set for inner-shells, but double-, triple-, ... zeta basis sets for valence shells (electrons). This approach called – “split-valence” basis sets: 3-21G, 6-31G etc.

### Various options for Basis Set specification

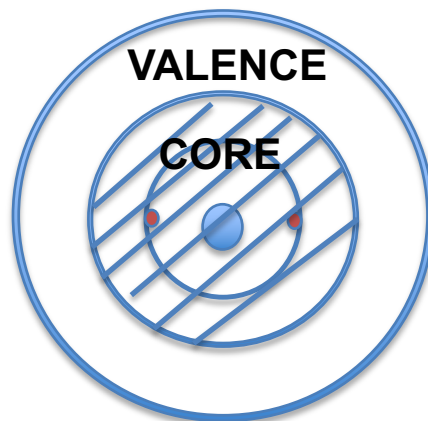
The following basis sets are stored internally in the *Gaussian* program.

**STO-3G;            3-21G;            6-21G;            4-31G;            6-31G;    6-311G**  
**D95V;            AND MORE .....**



# Effective Core Potential (ECP) Method

Ex. Pt (78-el) atom:  $(1s)^2(2s)^2 \dots (5s)^2(5p)^6(5d)^9(6s)^1$



**Effective core potential (ECP) method** allows to replace core electrons by an effective potential, thus reducing # of electrons & # of basis functions.

Parameters for potential are fitted to reproduce the results of full electron calculations for atoms and diatomics.

Disadvantage of ECP = additional approximation

Advantage of ECP = less expensive

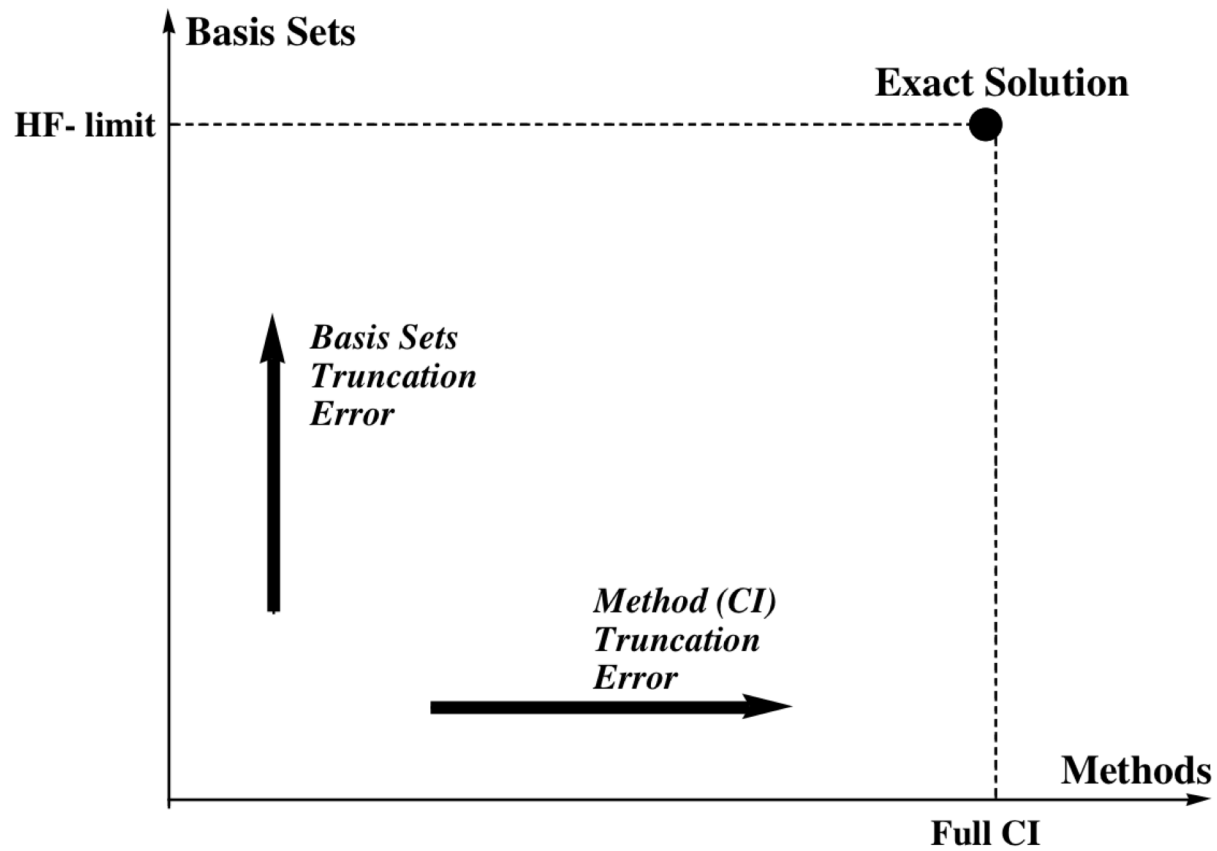
# Effective Core Potential (ECP) Method

Additional merit of ECP: **ECP can incorporate the relativistic effect.**

1s electrons are very close to nucleus. Kinetic energy of 1s electrons is very large.  
high speed - relativistic. Have to use relativistic QM.

## • Practical ECP and associated basis set

- Hay-Wadt (Los Alamos) ECP: LANL2DZ, LANL3DZ, etc..
- Stevens / Basch / Krauss ECP CEP-431, etc
- Stuttgart ECP SDD



# Density functional Methods (DFT)

Schrödinger equation of  $N$  electron system involves  $3N$  variables.

$$H(1,2, \dots, N) \Psi (1,2, \dots, N) = E \Psi (1,2, \dots, N)$$

“electron density”  $\rho =$  probability density of finding an electron at position  $\mathbf{r} = (x,y,z)$

$$\rho(\mathbf{r}) = \rho(x,y,z) = N \int \Psi^*(1,2, \dots, N) \Psi(1,2, \dots, N) dx_2 \cdots dx_N$$

$$\int \rho(\mathbf{r}) d\mathbf{r} = N \text{ (total \# of electrons)}, \quad d\mathbf{r} = \text{volume element}$$

## • Hohenberg-Kohn Theorems

1. For a non-degenerate ground state,

$\rho(\mathbf{r})$  determines potential  $V(\mathbf{r})$ , where  $\mathbf{r}$  involves 3 variables  $(x,y,z)$ .

2. Once we know the potential  $V(\mathbf{r})$ , we have Hamiltonian  $H$  and can determine the ground state energy  $E_0$  by *variational principle*.

$$V(\mathbf{r}) \rightarrow E_0$$

- Energy is a *functional* of  $\rho(\mathbf{r})$ :  $E[\rho] = T[\rho] + V_{ne}[\rho] + V_{ee}[\rho]$



# Exact Electronic Hamiltonian = Kinetic + Nuclear-Electron + Electr-Electr

Orbital Approaches

Density Approach

1. **Hartree-Fock:** Replace the complicated many-electron problem by a one-electron problem in which many-electron repulsion is treated in an average way

2. Hartree-Fock Equation

3.  $E_{\text{elec}} = E_{\text{kin}} + E_{\text{NE}} + E_{\text{J}} + E_{\text{HF}}(\text{XC})$

4.  $E_{\text{HF}}(\text{XC}) = E_{\text{HF}}(\text{X})$ , No correlation

1. **Hohenberg-Kohn:** Ground-state molecular energy, wavefunction of the molecules with a non-degenerate ground state are uniquely determined by the ground electron probability density.

2. Kohn-Sham equation

3.  $E_{\text{elec}} = E_{\text{kin}} + E_{\text{NE}} + E_{\text{J}} + E_{\text{DFT}}(\text{XC})$

4.  $E_{\text{DFT}}(\text{XC}) = E_{\text{DFT}}(\text{X}) + E_{\text{DFT}}(\text{C})$



★  $E_{\text{hybrid}}(\text{X}) = C_{\text{HF}} E_{\text{HF}}(\text{X}) + C_{\text{DFT}} E_{\text{DFT}}(\text{X})$