

Computational Chemistry  
Semester II M.Sc Chemistry  
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AB INITIO METHODS

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# Ab initio methods in computational chemistry

- ❑ "Ab Initio" means "from the beginning"
- ❑ This name is given to computations which are derived directly from theoretical principles, with no inclusion of experimental data
- ❑ Most of the time this is referring to an approximate quantum mechanical calculation.
- ❑ The approximations made are usually mathematical approximations, such as using a simpler functional form for a function or getting an approximate solution to a differential equation.
- ❑ The most common type of ab initio calculation is the '**Hartree Fock**' calculation in which the primary approximation is called the **central field approximation**



# A review of Hartree Fock Calculations

# THE WAY TO HF CALCULATIONS

SWE

1 D box

3 D box

Hydrogen  
Atom

Variation &  
Perturbation

Hartree and  
Hartree Fock  
Methods

# Self Consistent Field Concept

- ▶ An important unsolved problem in quantum mechanics is how to deal with indistinguishable, interacting particles like electrons
- ▶ If particles interact, that interaction must be in the Hamiltonian.
- ▶ So until we know where the particles are, we can't write down the Hamiltonian, but until we know the Hamiltonian, we can't tell where the particles are.
- ▶ SCF is an iterative method used to calculate the molecular orbitals with maximum possible accuracy

# Hartree's Method

- ▶ According to Hartree's self-consistent-field (SCF) model of the atom, the motion of each electron in the effective field of the  $N-1$  others is governed by a one-particle Schrödinger equation.
- ▶ It follows that the electrons are *independent*, and interact only via the mean-field Coulomb potential
- ▶ the electrons feel the averaged field of all the other electrons in the system.
- ▶ We assume the wavefunction can be written as a Hartree product:

$$\Psi(r_1 + r_2) = \Psi_1(r_1)\Psi_2(r_2)$$

- ▶ The individual one-electron wavefunctions,  $\Psi_1$  &  $\Psi_2$  are called molecular orbitals.
- ▶ This form of the wavefunction does not allow for instantaneous interactions of the electrons.
- ▶ Instead, the electrons feel the averaged field of all the other electrons in the system.
- ▶ The Hartree form of the wavefunction is sometimes called the **independent electron approximation**.

# Pauli's Exclusion Principle

- ▶ Total wavefunction must be antisymmetric with respect to the interchange of electron coordinates
- ▶ The Pauli Principle is a consequence of antisymmetry
- ▶ *The Hartree wavefunction is not antisymmetric*
- ▶ Fock modified the Hartree's Equation by adding the concept of antisymmetry and formulated the Hartree- Fock Equation

# Hartree Fock Equation

- ▶ The antisymmetrized wavefunction is called the Hartree-Fock wavefunction.
- ▶ It can be written as a Slater determinant
- ▶ This ensures the electrons are indistinguishable and are therefore associated with every orbital
- ▶ The HF wavefunction is an antisymmetric wavefunction written in terms of the one-electron Molecular Orbitals.



▶ The Schrodinger wave equation  $\hat{H}\Psi = E\Psi$

▶ The Hamiltonian is made up of energy terms

$$\hat{H} = \hat{T}_n + \hat{T}_e + \hat{V}_{nn} + \hat{V}_{ne} + \hat{V}_{ee}$$

➤ HF theory is the simplest wavefunction-based method

▶ It relies on the following approximations:


*The Born-Oppenheimer approximation*

*The independent electron approximation*


*The Linear Combination of Atomic Orbitals Approximation (LCAO)*


# Central Field Approximation

- ❑ The Coulombic electron-electron repulsion is not specifically taken into account. It's net effect is included in the calculation
- ❑ This is a variational calculation, meaning that the approximate energies calculated are all equal to or greater than the exact energy
- ❑ The energies from HF calculations are always greater than the exact energy and tend to a limiting value called the Hartree Fock limit.

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- ❑ The second approximation in HF calculations is that the wave function must be described by some functional form, which is only known exactly for a few one electron systems.
  - ❑ Because of this approximation, most HF calculations give a computed energy greater than the Hartree Fock limit
  - ▶ A number of types of calculations begin with a HF calculation then correct for the explicit electron-electron repulsion, referred to as correlation.

Eg -Moller-Plesset perturbation theory, Configuration Interaction (CI) etc

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- ▶ *The first step in computational chemistry is the calculation of the molecular orbitals (MOs) for a given molecule.*
  - ▶ If we can calculate the MOs for a molecule, then we can know lots of things about the molecule, including
    - energy
    - electron density
    - electrostatic potential
    - transition state
    - frequency

- 
- ▶ A molecular-orbital theory calculation is a ***mathematical expression of an electron in a molecule.***
  - ▶ Although there are many types of molecular-orbital functions, here we will only look at the **Slater Type Orbitals** (STOs) and the **Gaussian Type Orbitals** (GTOs).

# STO & GTO

- ▶ STOs require more calculating, which takes tremendous amounts of time, however their calculations have been found to be more accurate than GTOs. On the other hand, GTOs, although less accurate, are much faster to calculate than STOs.
- ▶ By adding several GTOs, we can mimic the STOs accuracy. As the number of GTOs used increased, the better they were able to model the STO equation.
- ▶ When using GTOs to model STOs, the new equations are given a new name. They are identified as STO-nG equations where n is a constant that represents the number of GTOs used. For instance, two common equations are the **STO-3G** and the **STO-6G** in which **3** and **6** GTOs are used respectively.

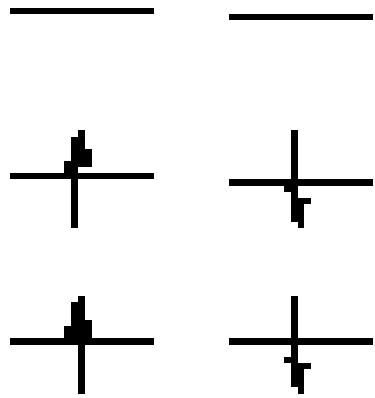
# HF calculations overview

Advantages	Disadvantages
<i>The Born-Oppenheimer approximation</i>	Electronic Correlation
<i>The independent electron approximation</i>	Consequence: Calculated energy is always higher than true energy
Central Field Theory	The calculated value can only reach a minimum energy up to <b>Hartree Fock Limit</b> , which is in turn higher than the true energy
<i>The Linear Combination of Atomic Orbitals approximation (LCAO)</i>	<i>The integrodifferential equations are thereby transformed into algebraic equations (Roothaan's equations) for the expansion coefficients</i>

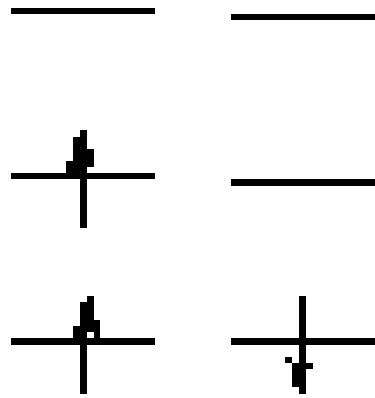
# Roothaan equations

- ▶ The Roothaan equations are strictly the equations for a closed-shell Restricted Hartree-Fock
- ▶ Numerically much easier than integro-differential equations

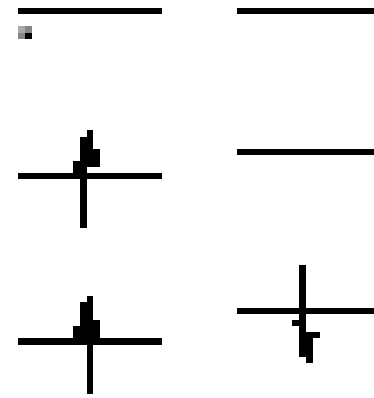




RHF



ROHF



UHF

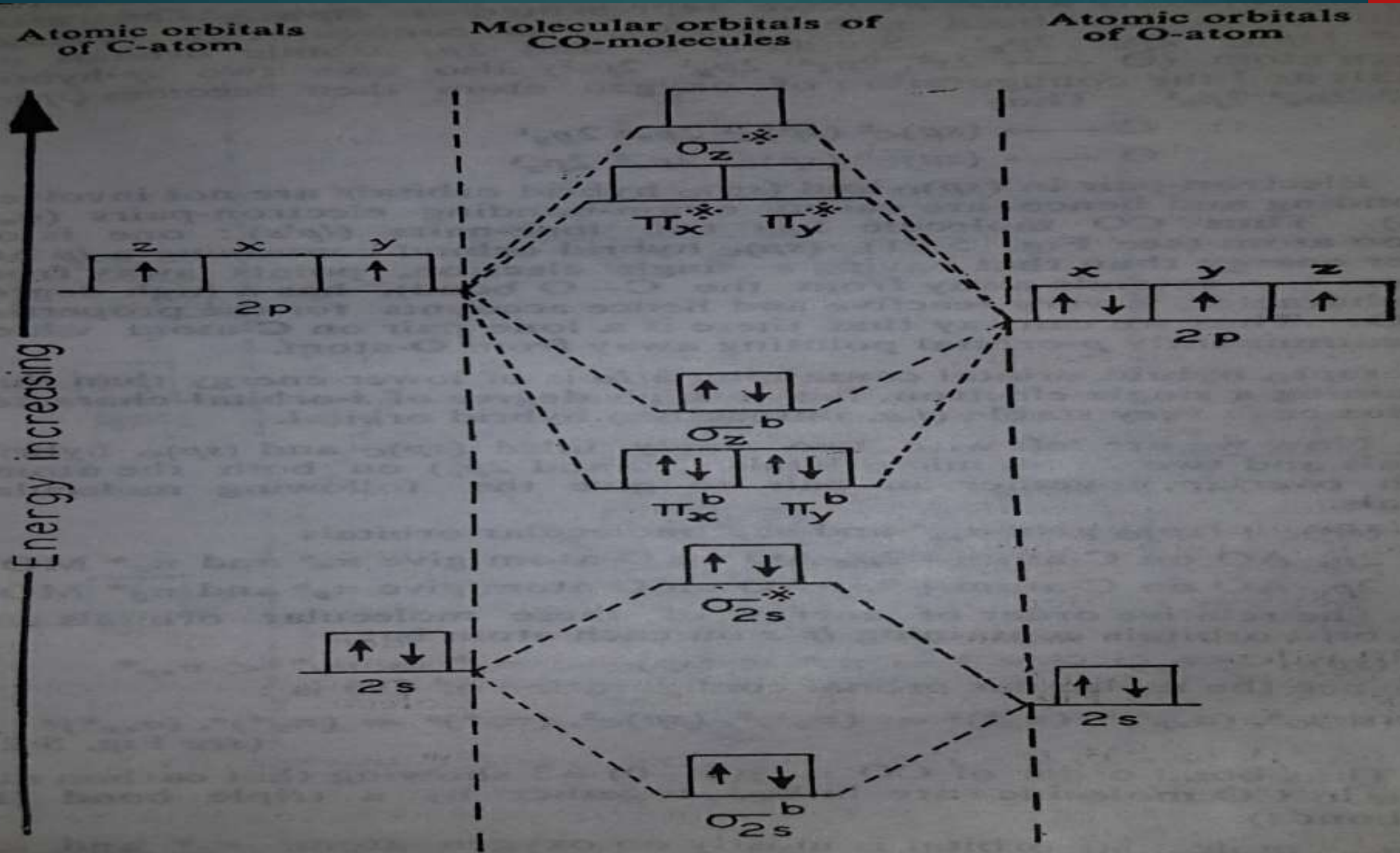


Fig. 5-20. Molecular orbital energy level diagram (drawn not to scale) of CO molecule.