

# INTRODUCTION

Quantum chemistry serves as the bridge between theoretical physics and practical chemistry by offering insights into the complex behavior of atoms and molecules at the quantum level. The Hartree-Fock theory is a cornerstone method that provides a systematic framework for understanding electronic structure. It is a fundamental approach in computational chemistry for approximating the wavefunctions and energies of a quantum many-body system. It is a mean-field theory that treats the electron-electron repulsion in an average way, reducing the complicated many-electron problem to a set of effective one-electron equations.

This report aims to provide an in-depth understanding of the computational aspects involved in solving the HF equations, including the theoretical foundations, approximations, and practical considerations.

Additionally, the report explores more complex subjects such as configuration interaction techniques, offering methods for determining correlation energies that go beyond the Hartree-Fock approximation, emphasizing the balance between conceptual clarity and computational feasibility.

# THE ELECTRONIC PROBLEM

Our aim is to solve the non-relativistic, time-independent Schrödinger equation for a molecular system, we need to consider the following components of the Hamiltonian:

- Kinetic energy of electrons
- Kinetic energy of nuclei
- Attractive potential between electrons and nuclei
- Repulsive potential between electrons
- Repulsive potential between nuclei

$$\mathcal{H} = - \sum_{n=1}^N \frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j=1}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}$$

We often find using standard SI units very inconvenient to use so we define Atomic units to make our calculations easy.  $Q = XQ'$  Where X is a conversion factor.

Born-Oppenheimer approximation: Since we know that  $M_{\text{nuclei}} \gg m_e$ , thus nucleus moves very slowly when compared to electron. Therefore we consider KE of nucleus to be zero and PE of Nucleus to be approximately constant.

## ANTISYMMETRY AND SPIN ORBITALS

The wavefunction describing a system of fermions, such as electrons, must be antisymmetric with respect to the exchange of any two particles. This requirement is known as the Pauli Exclusion Principle and is satisfied by constructing Slater determinants from spin orbitals, which are products of spatial orbitals and spin functions (will be discussed later in this report).

- spatial  $\rightarrow$  specifies x, y, z coordinates, orthonormal
- spin  $\rightarrow$  coordinates with spin.
- K spatial orbitals  $\implies$  2K spin orbitals.

## HARTREE PRODUCTS

HPs are simple products of spin orbitals. But these do not incorporate the necessary antisymmetry and exchange correlation effects.

Let  $\Psi(x_1, x_2, \dots, x_N) = \chi_i(x_1)\chi_j(x_2) \dots \chi_k(x_N)$  such that  $\mathcal{H}|\Phi\rangle^{\text{HP}} = \mathcal{E}|\Phi\rangle^{\text{HP}}$  where  $\mathcal{E} = \varepsilon_i + \varepsilon_j + \dots + \varepsilon_k$ , then wavefunction is called *Hartree Product*.

## SLATER DETERMINANTS

Slater determinants on the other hand properly account for the antisymmetric nature of the wavefunction and introduce exchange correlation between parallel-spin electrons.

Slater Determinant is given by the form :

$$\Psi(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(1) & \dots & \chi_N(1) \\ \dots & \dots & \dots \\ \chi_1(N) & \dots & \chi_N(N) \end{vmatrix}$$

rows  $\rightarrow e^-s$           cols  $\rightarrow$  spin orbitals

we also define  $\mathcal{P}(r_1, r_2)dr_1dr_2$  as simultaneous probability of e1 and e2. And it is equal to:

- = 0 for same/parallel spin
- $\neq 1$  for opposite spin

## THE HARTREE-FOCK APPROXIMATIONS

The Hartree-Fock (HF) approximation is based on the variation principle, which states that the best wavefunction within a given functional form will yield the lowest possible energy. By minimizing the energy expectation value with respect to the spin orbitals, the HF equation is obtained.

The HF equation replaces the complicated many-electron problem with an effective one-electron problem, where the electron-electron repulsion is treated in an average way. This is achieved by introducing the Fock operator, which incorporates the electron-electron repulsion through the Coulomb and exchange operators.

Solving the HF equation is an iterative process known as the Self-Consistent Field (SCF) procedure, where an initial guess for the spin orbitals is improved repeatedly until convergence is achieved. The converged HF energy represents

the best possible energy within the single-determinant approximation and the given one-electron basis set.

## THE MINIMAL BASIS $H_2$ MODEL MO-LCAO

$$\begin{aligned}\phi(\mathbf{r} - \mathbf{R}) &= (\zeta^3/\pi)^{1/2} e^{-\zeta|\mathbf{r}-\mathbf{R}|} & \zeta : \text{is orbital exponent} \\ \phi(\mathbf{r} - \mathbf{R}) &= (2\alpha/\pi)^{3/4} e^{-\alpha|\mathbf{r}-\mathbf{R}|^2} & \alpha : \text{is Gaussian orbital exponent}\end{aligned}$$

- $\phi_1$  &  $\phi_2$  can be assumed normalized but not orthogonal  
 $\therefore$  overlap  $S_{12} = \int d\mathbf{r} \phi_1^*(\mathbf{r}) \phi_2(\mathbf{r})$
- $\psi_1 = [2(1 + S_{12})]^{-1/2} (\phi_1 + \phi_2)$  gerade
- $\psi_2 = [2(1 - S_{12})]^{-1/2} (\phi_1 - \phi_2)$  ungerade
- Since only 2 basis functions used therefore we call these minimal basis set.
- In this notation the Hartree-Fock ground state is given by

$$|\Psi_0\rangle = |\psi_1 \bar{\psi}_1\rangle = |1\bar{1}\rangle$$

## EXCITED DETERMINANTS

Total combination  $\binom{2K}{N}$  because we have 2K total spin orbitals and out which N can be occupied.

We take HF ground state as reference state and classify others how they differ from reference state.

All combinations can be classified as HF ground, singlet, doublet, ... , N-tuply excited states.

## OPERATORS AND MATRIX ELEMENTS

### Minimal Basis $H_2$ Matrix Elements

- The Hamiltonian for any two-electron system is

$$\begin{aligned}H &= \left( -\frac{1}{2} \nabla_1^2 - \sum_A \frac{Z_A}{r_{1A}} \right) + \left( -\frac{1}{2} \nabla_2^2 - \sum_A \frac{Z_A}{r_{2A}} \right) + \frac{1}{r_{12}} \\ &= h(1) + h(2) + \frac{1}{r_{12}}\end{aligned}$$

$h(1)$  is a core-Hamiltonian describing KE and PE in the field of the nuclei (the "core").

- $\langle \Psi_0 | \mathcal{O}_1 | \Psi_0 \rangle = \langle 1 | h | 1 \rangle + \langle 2 | h | 2 \rangle.$
- $\langle \Psi_0 | \mathcal{O}_2 | \Psi_0 \rangle = \langle 12 | 12 \rangle - \langle 12 | 21 \rangle.$
- $\langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle = \langle \Psi_0 | \mathcal{O}_1 + \mathcal{O}_2 | \Psi_0 \rangle = \langle 1 | h | 1 \rangle + \langle 2 | h | 2 \rangle + \langle 12 | 12 \rangle - \langle 12 | 21 \rangle$

### Notations for One- and Two-Electron Integrals

- physicists' notation:  $\langle ij | kl \rangle = \langle \chi_i \chi_j | \chi_k \chi_l \rangle = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) r_{12}^{-1} \chi_k(\mathbf{x}_1) \chi_l(\mathbf{x}_2)$   
 $\rightarrow \langle ij | kl \rangle = \langle ji | lk \rangle = \langle kl | ij \rangle^*$   
 $\rightarrow \langle ij || kl \rangle = \langle ij | kl \rangle - \langle ij | lk \rangle = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) r_{12}^{-1} (1 - P_{12}) \chi_k(\mathbf{x}_1) \chi_l(\mathbf{x}_2)$   
 $\rightarrow$  where  $P_{12}$  is an operator which interchanges the coordinates of electron one and two.  
 Note that  $\langle ij || kk \rangle = 0$
- chemists' notation: chemists' notation:  $[ij, kl] = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1) \chi_j(\mathbf{x}_1) r_{12}^{-1} \chi_k^*(\mathbf{x}_2) \chi_l(\mathbf{x}_2)$

### SPIN ORBITALS

$$[i|h|j] = \langle i|h|j \rangle = \int d\mathbf{x}_1 \chi_i^*(\mathbf{x}_1) h(\mathbf{r}_1) \chi_j(\mathbf{x}_1)$$

$$\langle ij | kl \rangle = \langle \chi_i \chi_j | \chi_k \chi_l \rangle = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) r_{12}^{-1} \chi_k(\mathbf{x}_1) \chi_l(\mathbf{x}_2) = [ik | jl]$$

$$[ij | kl] = [\chi_i \chi_j | \chi_k \chi_l] = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1) \chi_j(\mathbf{x}_1) r_{12}^{-1} \chi_k^*(\mathbf{x}_2) \chi_l(\mathbf{x}_2) = \langle ik | jl \rangle$$

$$\langle ij || kl \rangle = \langle y | kl \rangle - \langle ij | lk \rangle = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1) \ell_j^*(\mathbf{x}_2) r_{12}^{-1} (1 - P_{12}) \chi_k(\mathbf{x}_1) \chi_l(\mathbf{x}_2)$$

### SPATIAL ORBITALS

$$(i|h|j) = h_{ij} = (\psi_i|h|\psi_j) = \int d\mathbf{r}_1 \psi_i^*(\mathbf{r}_1) h(\mathbf{r}_1) \psi_j(\mathbf{r}_1)$$

$$(ij | kl) = (\psi_i \psi_j | \psi_k \psi_l) = \int d\mathbf{r}_1 d\mathbf{r}_2 \psi_i^*(\mathbf{r}_1) \psi_j(\mathbf{r}_1) r_{12}^{-1} \psi_k^*(\mathbf{r}_2) \psi_l(\mathbf{r}_2)$$

$$J_{uj} = (ii | jj) \quad \text{Coulomb integrals} \quad K_{ij} = (ij | ji) \quad \text{Exchange integrals}$$

### General Rules for Matrix Elements

Evaluation of the matrix element  $\langle K | \mathcal{O} | L \rangle$  depend on whether  $\mathcal{O}$  is a sum of  $1e^-$  operators ( $\mathcal{O}_\infty$ ) or a sum of  $1e^-s$  operators ( $\mathcal{O}_2$ ) and the value of  $\langle K | \mathcal{O} | L \rangle$  depends on the degree to which  $|K\rangle$  and  $|L\rangle$  differ.

- Case 1: determinants are identical,
- Case 2: the 2 determinants differ by one spin orbital,
- Case 2: the 2 determinants differ by two spin orbitals (To use the rules, the two determinants must first be in maximum coincidence.
- the energy of the HF ground state is

$$E_0 = \langle \Psi_0 | H | \Psi_0 \rangle = \sum_a^N [a|h|a] + \frac{1}{2} \sum_a^N \sum_b^N [aa | bb] - [ab | ba]$$

$$\approx \sum_a^N \langle a|h|a \rangle + \frac{1}{2} \sum_a^N \sum_b^N \langle ab||ab \rangle$$

### Derivation of the Rules for Matrix Elements

Using overlap, orthogonality and permutation operator derivations are carried out. Following are the results obtained:

- Case 1:  $\langle K | \mathcal{O}_1 | K \rangle = \sum_m^N \langle m|h|m \rangle$  &  $\langle K | \mathcal{O}_2 | K \rangle = \frac{1}{2} \sum_m^N \sum_n^N \langle mn||mn \rangle$
- Case 2:  $\langle K | \mathcal{O}_1 | K \rangle = \langle m|h|m \rangle$  &  $\langle K | \mathcal{O}_2 | K \rangle = \sum_n^N \langle mn||pn \rangle$
- Case 3:  $\langle K | \mathcal{O}_1 | K \rangle = 0$  &  $\langle K | \mathcal{O}_2 | K \rangle = \langle mn||pq \rangle$

### Transition from Spin Orbitals to Spatial Orbitals

In spatial wave functions:

- $$[\psi_i|h|\psi_j] = [\psi_i|h|\psi_j] = (\psi_i|h|\psi_j)$$

$$[\psi_i|h|\Psi_j] = [\Psi_i|h|\psi_j] = 0$$
- In general, when only a single bar appears on either side of the two electron integral (e.g.,  $[\psi_i\bar{\psi}_j | \psi_k\psi_l]$ ), this integral vanishes by spin orthogonality. The general reduction is
 
$$[\psi_i\psi_j | \psi_k\psi_l] = [\psi_i\psi_j | \bar{\psi}_k\bar{\psi}_l] = [\bar{\psi}_i\bar{\psi}_j | \psi_k\psi_l] = [\bar{\psi}_i\bar{\psi}_j | \bar{\psi}_k\bar{\psi}_l] = (\psi_i\psi_j | \psi_k\psi_l)$$
- The Hartree-Fock energy of minimal basis H<sub>2</sub> is

$$E_0 = 2(\psi_1|h|\psi_1) + (\psi_1\psi_1 | \psi_1\psi_1) = 2(1|h|1) + (11 | 11)$$

## Coulomb and Exchange Integrals

- The Hartree-Fock energy of a closed-shell ground state is

$$E_0 = 2 \sum_a^{N/2} \langle a|h|a \rangle + \sum_{ab}^{N/2} 2 \langle ab | ab \rangle - \langle ab | ba \rangle = 2 \sum_a h_{aa} + \sum_{ab} 2J_{ab} - K_{ab}$$

- Appearance of exchange integrals in the expression for the energy of a determinant is the result of exchange correlation.

## Pseudo-Classical Interpretation of Determinantal Energies

- An electron (irrespective of its spin) in spatial orbital  $\psi$ , contributes the term  $h_{ii}$ , to the energy.
- Each unique pair of electrons (irrespective of their spin) in spatial orbitals  $\psi_i$  and  $\psi_j$  contributes the term  $J_{ij}$ , and each unique pair of electrons with parallel spins contributes the term  $-K_{ij}$  to the energy. The total energy of the determinant is the sum of all these contributions.

## SECOND QUANTIZATION

In the second quantization formalism the antisymmetry property of the wave function has been transferred onto the algebraic properties of certain operators.

### Creation and Annihilation Operators and Their Anticommutation Relations

- $a_i^\dagger$  creation operator: creates an  $e^-$  in spin orbital  $\chi_i$
- $a_i$  annihilation operator: adjoint of  $a_i^\dagger$ : destroys an  $e^-$  in spin orbital  $\chi_i$
- We cannot create or destroy an  $e^-$  twice
- $a_i^\dagger a_i + a_i a_i^\dagger = 1$  (anticommutation relation)
- The general strategy for evaluating such matrix elements is to move, using the anticommutation relations, the annihilation operators to the right until they operate directly on the vacuum state (  $\langle | \rangle$  ).

## Second-Quantized Operators and Their Matrix Elements

$$\mathcal{O}_1 = \sum_{ij} \langle i|h|j \rangle a_i^\dagger a_j$$
$$\mathcal{O}_2 = \frac{1}{2} \sum_{ijkl} \langle ij | kl \rangle a_i^\dagger a_j^\dagger a_l a_k$$

## SPIN-ADAPTED CONFIGURATIONS

Restricted means that two electrons  $\alpha$  &  $\beta$  are in same spatial orbital.

### Spin Operators

The spin angular momentum of a particle is a vector operator  $\vec{s}$ .

$$s^2 |s, m_s\rangle = s(s+1) |s, m_s\rangle$$
$$s_z |s, m_s\rangle = m_s |s, m_s\rangle$$

Where  $s$  is a quantum number describing the total spin and  $m_s$  is a quantum number describing the  $z$  component of the spin.

Instead of using  $s_x$  and  $s_y$ , it is often more convenient to work with the "step-up" and "step-down" ladder operators,  $s_+$  and  $s_-$ , defined as

$$s_+ = s_x + is_y$$
$$s_- = s_x - is_y$$

(These operators increase or decrease the value of  $m_s$  by 1)

In the usual non-relativistic treatment, since the Hamiltonian does not contain any spin coordinates so both  $\mathcal{S}$  and  $\mathcal{S}_z$  commute with the Hamiltonian.

## Restricted Determinants and Spin-Adapted Configurations

All the  $e^-$  spins are paired in a closed-shell determinant: pure singlet: eigenfunction of  $\mathcal{S}^2$  with eigenvalue zero.

Open-shell determinants are not eigenfunctions of  $\mathcal{S}^2$  except when all the open-shell electrons have parallel spin.



## Unrestricted Determinants

Since the  $1s\alpha$  electron has an exchange interaction with the  $2s\alpha$  electron, whereas the  $1s\beta$  electron does not. The  $2s\alpha$  electron spin "polarizes" the  $1s$  shell. The  $1s\alpha$  and  $1s\beta$  electrons will experience different effective potentials and would "prefer" not to be described by the same spatial function.

Unrestricted determinants are not eigen functions of  $\mathcal{S}^2$ . Moreover, they cannot be spin-adapted by combining a small number of unrestricted determinants as is the case for restricted determinants.

Unrestricted wave functions are commonly used as a first approximation to doublet and triplet states.

Unrestricted determinant is approximately a doublet and an unrestricted wave function is contaminated by higher, not lower, multiplicity components,  $\therefore$  expected value of  $\mathcal{S}^2$  is always too high.

# THE HARTREE-FOCK EQUATIONS

We want to find spin orbitals  $\{\phi_i\}$  which can form a single determinant approximating the ground state of an  $N$ -electron system under Hamiltonian  $H$ .

The equation for the best (Hartree-Fock) spin orbitals is the Hartree-Fock integro-differential equation and given by:

$$h(1)\chi_a(1) + \sum_{b \neq a} \left[ \int d\mathbf{x}_2 |\chi_b(2)|^2 r_{12}^{-1} \right] \chi_a(1) - \sum_{b \neq a} \left[ \int d\mathbf{x}_2 \chi_b^*(2) \chi_a(2) r_{12}^{-1} \right] \chi_b(1) = \varepsilon_a \chi_a(1)$$

## THE COULOMB AND EXCHANGE OPERATORS

**Coulomb Operator:** This operator represents the electrostatic interaction between charged particles/electrons within a system. In the context of HF theory, the Coulomb operator accounts for the repulsion between electrons due to their negative charges.

**Exchange Operator:** The exchange operator arises from the electron exchange symmetry. It reflects the fact that electrons are indistinguishable particles

with antisymmetric wave functions, meaning that the wave function changes sign when the positions of any two electrons are exchanged. In the context of HF theory, it accounts for the quantum mechanical exchange interaction between electrons and is essential for capturing the correct behavior of electron correlation.

The exchange operator is considered non-local, in contrast to the local Coulomb operator, because no simple potential  $\mathcal{K}(x)$  is uniquely defined at a local point in space  $x$ .

$$\begin{aligned}\langle \chi_a(1) | J_b(1) | \chi_a(1) \rangle &= \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_a^*(1) \chi_a(1) r_{12}^{-1} \chi_b^*(2) \chi_b(2) = [aa | bb] \\ \langle \chi_a(1) | K_b(1) | \chi_a(1) \rangle &= \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_a^*(1) \chi_b(1) r_{12}^{-1} \chi_b^*(2) \chi_a(2) = [ab | ba]\end{aligned}$$

## THE FOCK OPERATOR

The Fock operator  $f(1)$  is the sum of a core-Hamiltonian operator  $h(1)$  and an effective one-electron potential operator called the Hartree-Fock potential  $v^{\text{HF}}(1)$ .

$$\begin{aligned}f |\chi_a\rangle &= \varepsilon_a |\chi_a\rangle \\ f(1) &= h(1) + \sum_b J_b(1) - K_b(1) \\ &= h(1) + \sum_b \int d\mathbf{x}_2 \chi_b^*(2) r_{12}^{-1} (1 - P_{12}) \chi_b(2)\end{aligned}$$

The Hartree-Fock equations are really nonlinear equations and will need to be solved by iterative procedures.

## INTERPRETATION OF SOLUTIONS

### Orbital Energies and Koopmans' Theorem

The orbital energies obtained from the HF calculation have physical significance, as described by Koopmans' theorem. The ionization potential (IP) and electron affinity (EA) can be estimated from the orbital energies, although this approximation breaks down for strongly correlated systems.

Although the Fock operator depends functionally on occupied spin orbitals, but once the occupied spin orbitals are known the Fock operator becomes a well-defined Hermitian operator, which will have an infinite number of eigenfunctions.

The matrix representation of the Fock operator in the basis of spin orbital eigenfunctions is diagonal with diagonal elements equal to the orbital energies.

$$\begin{aligned}\varepsilon_a &= \langle a|h|a\rangle + \sum_{b \neq a} \langle ab | ab \rangle - \langle ab | ba \rangle \\ \varepsilon_r &= \langle r|h|r\rangle + \sum_b \langle rb | rb \rangle - \langle rb | br \rangle\end{aligned}$$

The ionization potential of  $|^N \Psi_0\rangle$  for this process is

$$\text{IP} = {}^{N-1}E_c - {}^N E_0$$

where  ${}^{N-1}E_c$  and  ${}^N E_0$  are the expectation values of the energy of the two relevant single determinants.

Orbital energies are generally negative and ionization potentials are positive.

$$\text{IP} = {}^{N-1}E_c - {}^N E_0 = -\varepsilon_c$$

$$\text{EA} = {}^N E_0 - {}^{N+1}E^r = -\varepsilon_r$$

Koopmans' theorem states that ionization potentials can be estimated from orbital energies in a Hartree-Fock calculation.

## Brillouin's Theorem

$$\begin{pmatrix} \langle \Psi_0 | H | \Psi_0 \rangle & \langle \Psi_0 | H | \Psi_a^r \rangle \\ \langle \Psi_a^r | H | \Psi_0 \rangle & \langle \Psi_a^r | H | \Psi_a^r \rangle \end{pmatrix} \begin{pmatrix} c_0 \\ c_a^r \end{pmatrix} = E_0 \begin{pmatrix} c_0 \\ c_a^r \end{pmatrix}$$

The mixing of the two states depends on the off-diagonal element  $\langle \Psi_0 | H | \Psi_a^r \rangle$ .

$$\begin{pmatrix} E_0 & 0 \\ 0 & \langle \Psi_a^r | H | \Psi_a^r \rangle \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = E_0 \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

Brillouin's Theorem states that singly excited determinants  $|\Psi_a^r\rangle$  will not interact directly with a reference Hartree-Fock determinant  $|\Psi_0\rangle$ , i.e.,

$$\langle \Psi_0 | H' | \Psi_a^r \rangle = 0.$$

# RCS HF: THE Roothaan Equations

$$f(1)\psi_j(1) = \varepsilon_j\psi_j(1)$$

## CLOSED-SHELL HARTREE-FOCK: RESTRICTED SPIN ORBITALS

The Roothaan equations provide a practical way to solve the HF equations by expressing the spin orbitals as linear combinations of basis functions. This approach transforms the integro-differential HF equations into a matrix eigenvalue problem, which can be solved numerically.

The Roothaan equations involve the construction of the Fock matrix, which depends on the density matrix and the one-electron and two-electron integrals over the basis functions. The diagonalization of the Fock matrix yields the molecular orbital coefficients and orbital energies.

The closed-shell Fock operator thus has the form:

$$f(\mathbf{r}_1) = h(\mathbf{r}_1) + \sum_a^{N/2} \int d\mathbf{r}_2 \psi_a^*(\mathbf{r}_2) (2 - P_{12}) r_{12}^{-1} \psi_a(\mathbf{r}_2) \quad \text{or, equivalently,}$$

$$f(1) = h(1) + \sum_a^{N/2} 2J_a(1) - K_a(1)$$

The closed-shell expression for orbital energies is:

$$\varepsilon_i = (\psi_i | h | \psi_i) + \sum_b^{N/2} 2(ii | bb) - (ib | bi) = h_{ii} + \sum_b^{N/2} 2J_{ib} - K_{ib}$$

Roothaan Equation is given by  $\sum_v F_{\mu\nu} C_{vi} = \varepsilon_i \sum_v S_{\mu\nu} C_{vi} \quad i = 1, 2, \dots, K$

-  $F_{\mu\nu}$  is the Fock matrix, representing the effective one-electron Hamiltonian in the basis of molecular orbitals.

-  $C_{vi}$  is the coefficient matrix, containing the expansion coefficients of the molecular orbitals in terms of the basis functions.

-  $S_{\mu\nu}$  is the overlap matrix, representing the overlap between different basis functions.

-  $\varepsilon_i$  is the diagonal matrix containing the orbital energies.

As the basis set becomes more and more complete, the expansion leads to more accurate representations of the "exact" molecular orbitals.

The overlap matrix  $S$  (the metric matrix) has elements:

$$S_{\mu\nu} = \int d\mathbf{r}_1 \phi_{\mu}^*(1) \phi_{\nu}(1) \quad 0 \leq |S_{\mu\nu}| \leq 1$$

The Fock matrix  $F$  is the matrix representation of the Fock operator with the set of basis functions  $\{\phi_{\mu}\}$ . It has elements:  $F_{\mu\nu} = \int d\mathbf{r}_1 \phi_{\mu}^*(1) f(1) \phi_{\nu}(1)$

The probability distribution function (charge density) is  $|\psi_a(\mathbf{r})|^2$

$$\rho(\mathbf{r}) = 2 \sum_a^{N/2} \psi_a^*(\mathbf{r}) \psi_a(\mathbf{r}) = \sum_{\mu\nu} P_{\mu\nu} \phi_{\mu}(\mathbf{r}) \phi_{\nu}^*(\mathbf{r})$$

we have defined a density matrix to analyze the bonding patterns and electron distribution in molecules sometimes called, a charge-density bond-order matrix

$$\text{as: } P_{\mu\nu} = 2 \sum_a^{N/2} C_{\mu a} C_{\nu a}^*$$

it provides a quantitative measure of the electron density associated with individual chemical bonds within a molecular system.

### Orthogonalisation of the Basis

If we have a set of functions  $\{\phi_{\mu}\}$  that are not orthogonal, then it will always be possible to find a transformation matrix  $X$  (not unitary) such that a transformed set of functions  $\{\phi'_{\mu}\}$  form an orthonormal set,

$$\phi'_{\mu} = \sum_v X_{v\mu} \phi_v \quad \mu = 1, 2, \dots, K$$

Two ways of orthogonalizing the basis set:

1. First procedure, called symmetric orthogonalization, uses the inverse square root of  $S$  for  $X$  :

$$\mathbf{X} \equiv \mathbf{S}^{-1/2} = \mathbf{U} \mathbf{S}^{-1/2} \mathbf{U}^{\dagger}$$

2. Second way, called canonical orthogonalization, uses the transformation matrix :

$$\mathbf{X} = \mathbf{U} \mathbf{S}^{-1/2}$$

## THE SCF PROCEDURE

Molecular Integrals Calculation:

Before solving the HF equations, the system's Hamiltonian must be constructed.

It involves calculating various integrals over the MOs and AOs, including overlap integrals, KE integrals, nuclear attraction integrals, and e-e repulsion integrals. These integrals form the basis for constructing the Fock matrix.

Self-Consistent Field (SCF) Iteration:

- Initial Guess : An initial guess for the molecular orbitals is required. This can be based on atomic orbitals (e.g., using the LCAO-MO approach)
- Fock Matrix : Using the initial guess for the MOs, the Fock matrix is constructed.
- Diagonalization : The Fock matrix is diagonalized to obtain a new set of MO coefficients.
- Density Matrix : From the MO coefficients, a new density matrix is formed.
- Convergence Check : The SCF procedure iterates by updating the Fock matrix using the new density matrix until convergence is achieved, i.e., energy or the density matrix start changing very negligibly between iterations.

Post-HF Corrections:

- Configuration Interaction (CI) (Discussed later in this report)
- Coupled Cluster (CC)
- Density Functional Theory (DFT)

Basis Set Considerations:

The accuracy of HF calculations depends on the choice of basis set. Larger basis sets can capture electron correlation effects better but the computational cost increases very rapidly.

Cost Calculations:

Let  $N_{\text{bf}}$  be the number of basis functions used in our calculations then,

- Memory for Electron Repulsion Integrals:  

$$M_{\text{eri}} = N_{\text{bf}}^4 \times 8 \times 10^{-6} \text{ MB}$$
- Memory for Fock Matrix:  $M_{\text{fock}} = N_{\text{bf}}^2 \times 8 \times 10^{-6} \text{ MB}$
- Memory for Molecular Orbitals:  $M_{\text{mo}} = N_{\text{bf}} \times N_{\text{occ}} \times 8 \times 10^{-6} \text{ MB}$

(we are assuming that each entry occupy space of 8 bytes, also  $1\text{MB} = 10^6\text{B}$  therefor we are introducing the factor of  $8 \times 10^{-6}$  to convert data to MB)

Currently, only functions of the Slater and Gaussian types are used widely.

Using a null (zero) matrix is the simplest technique to estimate the density matrix  $P$  and is also a very practical way to begin the iteration process. Also a semi-empirical extended Hückel type calculation, with an "effective"  $F$ , is often used for an initial guess at the wave function.

## Expectation Values and Population Analysis

The total electronic energy is:  $E_{\text{tol}} = E_0 + \sum_A \sum_{B>A} \frac{Z_A Z_B}{R_{AB}}$  where

$$E_0 = \frac{1}{2} \sum_{\mu} \sum_v P_{v\mu} (H_{\mu v}^{\text{core}} + F_{\mu v})$$

The dipole moment of a collection of charges is given by :

$$\vec{\mu} = - \sum_{\mu} \sum_v P_{\mu v} (v|\mathbf{r}|\mu) + \sum_A Z_A \mathbf{R}_A$$

$$N = \sum_{\mu} \sum_v P_{\mu v} S_{v\mu} = \sum_{\mu} (\mathbf{PS})_{\mu\mu} = \text{tr } PS$$

Interpret  $PS_{\mu\mu}$  as the number of electrons to be associated with  $\{\phi_{\mu}\}$ . This is called a Mulliken population analysis and the net charge is given by :

$$q_A = Z_A - \sum_{\mu \in A} (\mathbf{PS})_{\mu\mu}$$

## MODEL CALCULATIONS ON $H_2$ AND $HeH^+$

We take two-electron molecules  $H_2$  and  $HeH^+$  as the prototypes for homonuclear and heteronuclear diatomic molecules and perform our calculations.

### The 1s Minimal STO-3G Basis Set

Orbital exponents, typically used in quantum chemistry calculations, are positive numbers greater than zero that dictate the size and shape of basis functions. A larger exponent corresponds to a tighter, more compact function, while a smaller exponent results in a broader, more diffuse function.

At  $r=0$ , the Slater function has a finite slope but the Gaussian function has a zero slope, and at large  $r$ , the Gaussian function decays much more steeply than the Slater function.

Evaluation of integrals with four-centers is very difficult and time/resource consuming with Slater basis functions. In Gaussian, the product of two 1s Gaussian functions, each on different centers is a constant and is a 1s Gaussian function on a third center.

To enhance computational efficiency and accuracy, we employ predetermined linear combinations of individual Gaussian functions, termed contractions, which yield contracted Gaussian functions (CGFs),

$$\phi_{\mu}^{CGF}(\mathbf{r} - \mathbf{R}_A) = \sum_{p=1}^L d_{p\mu} \phi_p^{\text{GF}}(\alpha_{p\mu}, \mathbf{r} - \mathbf{R}_A)$$

By a proper choice of the  $L$ ,  $d_{p\mu}$ , and  $\alpha_{p\mu}$ , the CGF can be made to assume any functional form consistent with the primitive functions used.

If one stretches any bond for which the correct products of dissociation must be represented by open-shell wave functions, then restricted closed shell calculations must necessarily give the wrong limit. Because in restricted calculation both electrons are forced to occupy the same spatial molecular orbital  $\psi_i$ .

STO-3G (example of CGF) basis sets are often used in polyatomic calculations, in preference to evaluating integrals with Slater functions.

## STO-3G $H_2$

We describe restricted closed-shell calculations on the ground state of  $H_2$ .

For a discussion of the SCF results, it is convenient to transform the basic integrals in terms of the  $\{\phi_{\mu}\}$  to corresponding integrals in terms of the functions  $\{\psi_i\}$ .

If one stretches any bond for which the correct products of dissociation must be represented by open-shell wave functions, then restricted closed shell calculations must necessarily give the wrong limit. Because in restricted calculation both electrons are forced to occupy the same spatial molecular orbital  $\psi_i$ .



# CONFIGURATION INTERACTION

The Hartree-Fock method does not capture dynamic correlation, which arises from electron-electron interactions beyond the mean-field approximation.

The RHF method cannot describe the dissociation of molecules into open-shell fragments (eg.,  $H_2 \rightarrow 2H$ ).

Although the unrestricted Hartree-Fock (HF) method provides a qualitatively accurate depiction of dissociation phenomena, the resultant potential energy curves or surfaces are not precise.

These limitation can be addressed by the Configuration Interaction (CI) method, which expands the wavefunction as a linear combination of Slater determinants.

In the CI method, the reference state is typically taken as the HF determinant, and excited determinants are generated by replacing occupied spin orbitals with virtual (unoccupied) spin orbitals. The resulting CI wavefunction can provide a more accurate description of the electronic structure, but the computational cost increases rapidly with the size of the configuration space.

## MULTICONFIGURATIONAL WAVE FUNCTIONS AND THE STRUCTURE OF THE FULL CI MATRIX

The determinant created using the  $N$  lowest energy spin orbitals is denoted as  $|\Psi_0\rangle$ . Besides  $|\Psi_0\rangle$ , there are numerous other  $N$ -electron determinants derived from the  $2K$  spin orbitals

Describing other alternate determinants is convenient by noting their differences from  $|\Psi_0\rangle$ . Thus the set of possible determinants include  $|\Psi_0\rangle$ , the singly excited determinants  $|\Psi_0^r\rangle$  (which differ from  $|\Psi_0\rangle$  in having the spin orbital  $\chi_a$  replaced by  $\chi_r$ ), the doubly excited determinants  $|\Psi_{ab}^{rs}\rangle$ , etc., up to and including  $N$ -tuply excited determinants.

$$\begin{aligned} |\Phi_0\rangle = & c_0 |\Psi_0\rangle + \left(\frac{1}{1!}\right)^2 \sum_{ar} c_a^r |\Psi_a^r\rangle + \left(\frac{1}{2!}\right)^2 \sum_{abrs} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle \\ & + \left(\frac{1}{3!}\right)^2 \sum_{\substack{abc \\ rst}} c_{abc}^{rst} |\Psi_{abc}^{rst}\rangle + \left(\frac{1}{4!}\right)^2 \sum_{\substack{abcd \\ rstu}} c_{abcd}^{rstu} |\Psi_{abcd}^{rstu}\rangle + \dots \end{aligned}$$

There is no mixing of wave functions with different spin (i.e.,  $\langle \Psi_i | \mathcal{H} | \Psi_j \rangle = 0$  if  $|\Psi_i\rangle$  and  $|\Psi_j\rangle$  have different spin).

The energies corresponding to these determinants can be determined by forming the matrix representation of the Hamiltonian in the basis of the N-electron functions of expansion and then finding the eigenvalues of this matrix. This is called the full CI matrix, and the method is referred to as full CI.

The smallest eigenvalue serves as a maximum limit for the ground state energy of the system, while the larger eigenvalues set upper limits for the energies of excited states within the system..

The difference between the lowest eigenvalue ( $\mathcal{E}_0$ ) and the Hartree-Fock energy ( $E_0$ ) obtained within the same one-electron basis is called the basis set correlation energy.

#### Important Observations:

- Brillouin's theorem: all matrix elements of the form  $\langle \Psi_0 | \mathcal{H} | \Psi_0^r \rangle$  are zero. Therefor there is no coupling between the HF ground state and single excitations.
- All matrix elements of the Hamiltonian between Slater determinants which differ by more than 2 spin orbitals are zero.
- As single excitations don't mix directly with  $|\Psi_0\rangle$ , they have a very small effect on the ground state energy. Their effect is not considered zero because they do mix indirectly, but they interact with the doubles which in turn interact with  $|\Psi_0\rangle$ .
- Since the double excitations can mix directly with  $|\Psi_0\rangle$ , it is to be expected that these excitations play an important, and, for small systems, a predominant role in determining the correlation energy.
- A particularly good test of any procedure for calculating ionization potentials is  $N_2$ , since for this molecule Koopmans' theorem predicts the incorrect ordering of the first two ionization potentials. We note that SDCI predicts the correct ordering of the
- A near-Hartree-Fock-limit calculation predicts the wrong sign of the dipole moment of CO. ionization potentials. These results are expected to be close to the SDCI-limit (i.e., SDCI with a complete one-electron basis).

## INTERMEDIATE NORMALIZATION AND AN EXPRESSION FOR THE CORRELATION ENERGY

Two very important properties which help us to solve calculation here are :

$$\langle \Psi_0 | \Phi_0 \rangle = 1 \quad \langle \Psi_0 | H - E_0 | \Phi_0 \rangle = E_{\text{corr}} \quad \langle \Psi_0 | \Phi_0 \rangle = E_{\text{corr}}$$

where we have used the fact that  $|\Phi_0\rangle$  is intermediately normalized.

$$\left\langle \Psi_1^{2\frac{2}{1}} | H | \Psi_0 \right\rangle + c \left\langle \Psi_1^{2\frac{2}{1}} | H - E_0 | \Psi_{11}^{22} \right\rangle = c E_{\text{corr}}$$

Defining

$$2\Delta = \left\langle \Psi_{11}^{22} | H - E_0 | \Psi_{11}^{22} \right\rangle = 2(\varepsilon_2 - \varepsilon_1) + J_{11} + J_{22} - 4J_{12} + 2K_{12}$$

or

$$K_{12} + 2\Delta c = c E_{\text{corr}}$$

The two simultaneous equations can be combined into the matrix equation

$$\begin{pmatrix} 0 & K_{12} \\ K_{12} & 2\Delta \end{pmatrix} \begin{pmatrix} 1 \\ c \end{pmatrix} = E_{\text{corr}} \begin{pmatrix} 1 \\ c \end{pmatrix}$$

To obtain the lowest eigenvalue we solve above eqn for c, and substitute to get  $E_{\text{corr}}$ .

$$c = \frac{K_{12}}{E_{\text{corr}} - 2\Delta} \quad E_{\text{corr}} = \frac{K_{12}^2}{E_{\text{corr}} - 2\Delta} = \Delta - (\Delta^2 + K_{12}^2)^{1/2}$$

## DOUBLY EXCITED CI

A systematic procedure for accomplishing computationally viable scheme is to consider only those configurations which differ from the HF ground state wave function by no more than a predetermined number, say m, of spin orbitals. For example, if m = 4, then one would include single, double, triple, and quadruple excitations in the trial function. For full CI, m would be equal to the number of electrons.

Even for DCI it is not, in general, practical to include all possible double excitations from  $|\Psi_0\rangle$ .

$$E_{\text{corr}} \cong - \sum_{\substack{a < b \\ r < s}} \frac{\langle \Psi_0 | H | \Psi_{ab}^{rs} \rangle \langle \Psi_{ab}^{rs} | H | \Psi_0 \rangle}{\langle \Psi_{ab}^{rs} | H - E_0 | \Psi_{ab}^{rs} \rangle} = \sum_{\substack{a < b \\ r < s}} E_{\text{corr}} \begin{pmatrix} rs \\ ab \end{pmatrix}$$

## NATURAL ORBITALS AND THE ONE-PARTICLE REDUCED DENSITY MATRIX

The set of natural orbitals, introduced by P.-O. Löwdin , forms a one-electron basis for which the CI expansion is more rapidly convergent than it is with the Hartree-Fock basis.

If we are interested only in the probability of finding an electron in  $d\mathbf{x}_1$  at  $\mathbf{x}_1$ , independent of where the other electrons are, then we must average over all space-spin coordinates of the other electrons, i.e., integrate over  $\mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_N$  to obtain  $\rho(\mathbf{x}_1)$  is called the reduced density function for a single electron in an  $N$  electron system.

$$\rho(\mathbf{x}_1) = N \int d\mathbf{x}_2 \cdots d\mathbf{x}_N \Phi(\mathbf{x}_1, \dots, \mathbf{x}_N) \Phi^*(\mathbf{x}_1, \dots, \mathbf{x}_N)$$

The one-particle reduced density matrix (1-RDM) provides a useful way to extract information about the electronic structure from the many-electron wavefunction. The diagonal elements of the 1-RDM represent the electron densities, while the off-diagonal elements describe the coherence between different spin orbitals.

The 1-RDM can be used to calculate various properties, such as the total electron density, dipole moments, and orbital populations. It also plays a crucial role in the development of reduced density matrix functional theory (RDMFT), which aims to circumvent the limitations of traditional density functional theory (DFT) by working directly with the 1-RDM.

The matrix  $\gamma(\mathbf{x}_1, \mathbf{x}'_1)$ , which depends on two continuous indices, is called the first-order reduced density matrix or alternatively, the one-electron reduced density matrix or simply the one-matrix.

$$\gamma(\mathbf{x}_1, \mathbf{x}'_1) = N \int d\mathbf{x}_2 \cdots d\mathbf{x}_N \Phi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \Phi^*(\mathbf{x}'_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$$

The elements of the orthonormal set in which  $\gamma$  is diagonal are called natural spin orbitals.

## TRUNCATED CI

Truncated CI involves limiting the size of the CI expansion by including only a subset of the most important configurations.

A number of factors can be used to determine the truncation, including limiting the number of excited determinants, picking configurations according to their contribution to the total electronic energy, or restricting the excitation level (e.g., only including single and double excitations). So we have to compromise between computational cost and accuracy

# CONCLUSIONS

The HF theory provides a fundamental starting point for understanding and computing the electronic structure of molecular systems. Even though it has limitations in capturing dynamic correlation effects, still it serves as a crucial building block for more advanced methods, such as configuration interaction, coupled cluster theory, and density functional theory.

The computational aspects discussed in this report, including the formulation of the HF equations, basis set considerations, and practical implementation details, are essential for understanding and applying the HF method in computational chemistry calculations.

The computational cost of HF calculations scales roughly as  $N^4$  with respect to the system size, where  $N$  is the number of basis functions or occupied orbitals. This steep increasing limits the applicability of HF theory to relatively small systems, but at the same time it is motivating the development of more efficient methods for larger molecules and extended systems.