

## Preface

**Hartree-Fock** (HF) is an *ab initio* quantum chemical method for approximating the solution to the many-electron Schrödinger equation. It is an **independent particle model**—meaning that the many-electron problem is recast into a series of independent single-electron problems. HF is often referred to as a **mean field theory** because each electron interacts electrostatically with the average charge distribution of the other  $N - 1$  electrons. The HF method can be used to calculate the electronic structure of atoms and serves as the rigorous foundation for molecular orbital (MO) theory as it involves the linear combination of atomic orbitals (LCAO). As such, it provides an approximate description of bonding in molecules which is central to exploring chemical reactions. Much of the groundwork for advanced chemical theory and computational electronic structure methods is rooted in the simple, but powerful HF approximation.

## Variational Method

Within the “standard” interpretation of quantum mechanics, we posit that the wavefunction  $\Psi$  represents the state of a system and encapsulates all information about said system prior to measurement. Naturally, we would want to determine how  $\Psi$  is constructed if we wish to obtain observable properties of a quantum system.

Let’s begin with a trial wavefunction  $\tilde{\Psi}$  to simulate the exact ground state wavefunction  $\Psi_0$ , the lowest eigenstate of the Hamiltonian  $\hat{H}$ . We can express our trial state vector as a linear combination of basis vectors:

$$|\tilde{\Psi}\rangle = \sum_i c_i |\phi_i\rangle \quad (1)$$

Provided that  $\tilde{\Psi}$  is normalized, the square modulus of each expansion coefficient should sum to 1:

$$\langle\tilde{\Psi}|\tilde{\Psi}\rangle = \sum_i |c_i|^2 = 1 \quad (2)$$

The set of basis vectors in Hilbert space  $\{|\phi_i\rangle\} \in \mathcal{H}$  are chosen to be orthonormal  $\langle\phi_i|\phi_j\rangle = \delta_{ij}$  and satisfy the completeness relation (also known as the **resolution of the identity**):

$$\sum_i |\phi_i\rangle \langle\phi_i| = \mathbb{1} \quad (3)$$

In practice, we’ll need to truncate the basis set and use a finite expansion that is, *per se*, “approximately complete”. At this point, one may compute the expectation value for the

total energy of the system using the trial wavefunction. However, the **variational principle** states that the expectation value for the energy of an approximate ground state wavefunction  $\tilde{E}$  is always greater than or equal to the expectation value for the energy of the true ground state wavefunction  $E_0$  (*vide infra*).

### The Variational Theorem:

$$\frac{\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle}{\langle \tilde{\Psi} | \tilde{\Psi} \rangle} \geq E_0 \quad (4)$$

*Provisional Conditions:*

$$\{|\phi_i\rangle\} \in \mathcal{H} \quad \langle \phi_i | \phi_j \rangle = \delta_{ij} \quad \sum_i |\phi_i\rangle \langle \phi_i| = \mathbf{1}$$

$$|\tilde{\Psi}\rangle = \sum_i c_i |\phi_i\rangle \quad \langle \tilde{\Psi} | \tilde{\Psi} \rangle = \sum_i |c_i|^2 = 1$$

*Proof:*

$$\langle \hat{H} - E_0 \rangle = \frac{\langle \tilde{\Psi} | \hat{H} - E_0 | \tilde{\Psi} \rangle}{\langle \tilde{\Psi} | \tilde{\Psi} \rangle} \quad (5)$$

$$= \frac{\langle \sum_i c_i \phi_i | \hat{H} - E_0 | \sum_i c_j \phi_j \rangle}{\langle \sum_i c_i \phi_i | \sum_i c_j \phi_j \rangle} \quad (6)$$

$$= \frac{\sum_{ij} c_i^* c_j \langle \phi_i | \hat{H} - E_0 | \phi_j \rangle}{\sum_{ij} c_i^* c_j \langle \phi_i | \phi_j \rangle} \quad (7)$$

$$= \frac{\sum_{ij} c_i^* c_j \langle \phi_i | \hat{H} | \phi_j \rangle - \sum_{ij} c_i^* c_j \langle \phi_i | E_0 | \phi_j \rangle}{\sum_{ij} c_i^* c_j \langle \phi_i | \phi_j \rangle} \quad (8)$$

$$= \frac{\sum_{ij} c_i^* c_j \langle \phi_i | E_j | \phi_j \rangle - \sum_{ij} c_i^* c_j \langle \phi_i | E_0 | \phi_j \rangle}{\sum_{ij} c_i^* c_j \langle \phi_i | \phi_j \rangle} \quad (9)$$

$$= \frac{\sum_{ij} c_i^* c_j E_j \langle \phi_i | \phi_j \rangle - \sum_{ij} c_i^* c_j E_0 \langle \phi_i | \phi_j \rangle}{\sum_{ij} c_i^* c_j \langle \phi_i | \phi_j \rangle} \quad (10)$$

$$= \frac{\sum_{ij} c_i^* c_j E_j \delta_{ij} - \sum_{ij} c_i^* c_j E_0 \delta_{ij}}{\sum_{ij} c_i^* c_j \delta_{ij}} \quad (11)$$

$$= \frac{\sum_i c_i^* c_i E_i - \sum_i c_i^* c_i E_0}{\sum_i c_i^* c_i} \quad (12)$$

$$= \frac{\sum_i c_i^* c_i (E_i - E_0)}{\sum_i c_i^* c_i} \quad (13)$$

$$= \frac{\sum_i |c_i|^2 (E_i - E_0)}{\sum_i |c_i|^2} \quad (14)$$

The terms  $\sum_i |c_i|^2$  and  $(E_i - E_0)$  are necessarily positive. Thus,

$$\frac{\sum_i |c_i|^2 (E_i - E_0)}{\sum_i |c_i|^2} \geq 0 \quad (15)$$

Recall  $\sum_i |c_i|^2 = 1$  and that  $E_i = \tilde{E}$  because it is the energy of the approximate ground state wavefunction  $\tilde{\Psi}$ .

$$(\tilde{E} - E_0) \geq 0 \quad (16)$$

$$\tilde{E} \geq E_0 \quad (17)$$

It follows that the energy of any trial wavefunction  $\tilde{E}$  is always an upper bound to the exact ground state energy  $E_0$ .

$$\frac{\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle}{\langle \tilde{\Psi} | \tilde{\Psi} \rangle} \geq E_0 \quad (18)$$

■

## Hartree Product

We must now find an approach, an *ansatz*, to build a wavefunction that describes the entire system of electrons. One may choose to approximate the wavefunction as a product of independent one-electron orbitals. This construction is known as a **Hartree product**.

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_n) = \psi(\mathbf{r}_1) \psi(\mathbf{r}_2) \psi(\mathbf{r}_3) \dots \psi(\mathbf{r}_n) \quad (19)$$

However, there are some problems with taking this approach. Firstly, we assume that the electrons do not interact with each other. More explicitly, we ignore electron-electron repulsion. Although the Schrödinger equation is now separable, a significant portion of electron correlation is left out. Additionally, we do not account for electrons being identical particles. Elementary particles, such as the electron, are said to be **indistinguishable**. We can index the orbitals for the sake of numerical counting, but we can't classically assign labels to individual electrons as the uncertainty principle disallows us from following specific quantum particles. This concept must be included in order to capture the correct physics.

## Antisymmetry Principle

Electrons are fermions. They abide by Fermi-Dirac statistics which specify energy level occupation rules for spin  $1/2$  particles. This differs from the behavior of integer spin particles (bosons), in which an unlimited number of them may occupy a single state (i.e. Bose-Einstein condensate). Following the Pauli exclusion principle, electrons with the same quantum numbers may not occupy the same state. This idea actually emerges from the more fundamental concept, the **antisymmetry principle**.

**The Antisymmetry Principle:** *Electronic wavefunctions must be anti-symmetric with respect to the interchange of any two electrons.* Let us start with a wavefunction describing a system with just two electrons. If we swap the spin-spatial coordinates for each electron,  $\mathbf{x}_1$  and  $\mathbf{x}_2$ , then the result is the same wavefunction with a phase factor of  $-1$ .

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = -\Psi(\mathbf{x}_2, \mathbf{x}_1) \quad (20)$$

For bosons, the result is the same except with a phase factor of  $+1$ . In other words, the wavefunction remains symmetric under the exchange of any two bosons.

## Slater Determinant

We need to define a wavefunction *ansatz* to satisfy both indistinguishability and the anti-symmetry principle. Using our two electron example, we can use the following wavefunction:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} [\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_1(\mathbf{x}_2)\chi_2(\mathbf{x}_1)] \quad (21)$$

Notice that this form resembles that of a matrix determinant:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) \end{vmatrix} \quad (22)$$

$\chi$  is a spin-orbital that is a function of space and spin  $\rightarrow \mathbf{x} = (\mathbf{r}, \omega)$ . The coordinates of both dimensional types are separable:

$$\chi(\mathbf{x}) = \psi(\mathbf{r})\sigma(\omega) \quad (23)$$

$\psi(\mathbf{r})$  and  $\sigma(\omega)$  are spatial and spin parts of the wavefunction respectively. The spin part can take on the up  $\alpha(\omega)$  or down  $\beta(\omega)$  spin configuration.

We can confirm that this is a usable representation by allowing two electrons to be in the same orbital (i.e. let  $\chi_1 = \chi_2$ ).  $\Psi(\mathbf{x}_1, \mathbf{x}_2)$  goes to zero if this happens. It follows that the probability of two electrons occupying the same state goes to zero. This result is consistent with Pauli exclusion. We can generalize suitable wavefunction expressions for  $N$  electrons with the so-called **Slater determinant** (SD).

**The Slater Determinant:** *Anti-symmetric wavefunctions for atoms and molecules can be generated using a normalized determinantal structure.*

$$|\Psi\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix} \quad (24)$$

The normalization factor  $1/\sqrt{N!}$  ensures that the total probability density over all space is unity  $\rightarrow \langle\Psi|\Psi\rangle = 1$ . Moving across columns increases the orbital index whereas moving down rows increases the particle index—both to the extent of  $N$  electrons. The SD can be written in shorthand as a product of diagonals:

$$|\Psi\rangle = |ijk \cdots n\rangle \quad (25)$$

The letters  $i, j, k, \dots, n$  correspond to the set of spin-orbitals  $\{\chi_i\}$  with arbitrary spin.

Let's do an example. If we have 3 electrons in 3 spin-orbitals, there are 3! pairwise permutations that can be performed. In quantum mechanics, we use the **permutation operator**  $\hat{\mathcal{P}}_{ij}$  to swap two different indices corresponding to orbitals or electron coordinates. It is linear, unitary, Hermitian, and idempotent.  $\hat{\mathcal{P}}_{ij}$  has the following properties:

$$[\hat{\mathcal{P}}_{ij}, \hat{H}] = 0 \quad \hat{\mathcal{P}}_{ij}^2 = \hat{\mathcal{P}}_{ij} = \mathbf{1} \quad (26)$$

For an odd number of permutations (an anti-symmetric operation), we get a prefactor of  $-1$  and, for an even number of permutations (a symmetric operation), we get  $+1$ . Let's show this. Consider the SD:

$$|\Psi\rangle = |123\rangle \quad (27)$$

Perform every combination of pairwise exchange:

$$|\Psi\rangle = |123\rangle = -|132\rangle = |312\rangle = -|321\rangle = |231\rangle = -|213\rangle \quad (28)$$

Write out the SD:

$$|\Psi\rangle = \frac{1}{\sqrt{6}} [\chi_1(1)\chi_2(2)\chi_3(3) - \chi_1(1)\chi_2(3)\chi_3(2) + \chi_1(3)\chi_2(1)\chi_3(2) - \chi_1(3)\chi_2(2)\chi_3(1) + \chi_1(2)\chi_2(3)\chi_3(1) - \chi_1(2)\chi_2(1)\chi_3(3)] \quad (29)$$

## Molecular Hamiltonian

We're in a good spot. We now have a proper way to express a many-electron wavefunction. We can compute a wide assortment of properties pertaining to our  $N$  electron system of interest. In particular, we can determine the total energy of any molecule. To do that, we'll need a **Hamiltonian operator** that corresponds to all the kinetic and potential energies of the molecular system  $\rightarrow \hat{H} = \hat{T}_{elec} + \hat{T}_{nuc} + \hat{V}_{elec} + \hat{V}_{nuc}$ . In the time-independent framework, we are concerned with finding stationary states. We shall use our non-relativistic, time-independent Hamiltonian to calculate the expectation value for the total energy.

**The Molecular Hamiltonian:**

$$\hat{H} = - \sum_{i=1}^{N_{elec}} \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{A=1}^{N_{nuc}} \frac{\hbar^2}{2M_A} \nabla_A^2 - \sum_{i=1}^{N_{elec}} \sum_{A=1}^{N_{nuc}} \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} + \sum_{i=1}^{N_{elec}} \sum_{j>i}^{N_{elec}} \frac{e^2}{4\pi\epsilon_0 r_{ij}} + \sum_{A=1}^{N_{nuc}} \sum_{B>A}^{N_{nuc}} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}} \quad (30)$$

Defining constants and variables:

- $\hbar$  is the reduced Planck constant
- $m_e$  is the mass of an electron
- $\nabla^2$  is the Laplacian operator
- $M_A$  is the mass of a nucleus
- $Z_A$  is the atomic number of a nucleus
- $r_{iA} = |r_i - R_A|$  is the distance between an electron and nucleus
- $r_{ij} = |r_i - r_j|$  is the distance between two electrons
- $R_{AB} = |R_A - R_B|$  is the distance between two nuclei
- $k_e^{-1} = 4\pi\epsilon_0$  is the inverse of the Coulomb constant
- $e$  is the elementary charge of a proton (+) or an electron (-)

We can simplify this expression further by setting  $\hbar = m_e = k_e^{-1} = e = 1$ . By doing this we begin working in **atomic units**. We now have:

$$\hat{H} = - \sum_{i=1}^{N_{elec}} \frac{1}{2} \nabla_i^2 - \sum_{A=1}^{N_{nuc}} \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^{N_{elec}} \sum_{A=1}^{N_{nuc}} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N_{elec}} \sum_{j>i}^{N_{elec}} \frac{1}{r_{ij}} + \sum_{A=1}^{N_{nuc}} \sum_{B>A}^{N_{nuc}} \frac{Z_A Z_B}{R_{AB}} \quad (31)$$

The molecular wavefunction depends on the positions of the electrons and nuclei. The mass of a nucleus is many times greater than the mass of an electron (i.e.  $\rightarrow M_A \gg m_e$ ). Because kinetic energy is inversely proportional to mass, we can say that the nuclei move at vastly different timescales than electrons. The nuclei considered to be motionless with respect to the electrons! Therefore we can separate the molecular wavefunction into electronic and nuclear parts:

$$\Psi_{mol}(\mathbf{r}_i, \mathbf{R}_i) = \Psi_{elec}(\mathbf{r}_i; \mathbf{R}_i) \Psi_{nuc}(\mathbf{R}_i) \quad (32)$$

This invocation is known as the **Born-Oppenheimer approximation**. Note that the electronic wavefunction only depends parametrically on the nuclear coordinates. Moving forward, we will just work with  $\Psi_{elec}$ . Since the nuclei appear fixed, we can simplify the Hamiltonian further. The nuclear-nuclear repulsion term  $V_{NN}$  remains constant for each stationary state and can be added to the total energy later on.

$$\hat{H} = - \sum_{i=1}^{N_{elec}} \frac{1}{2} \nabla_i^2 - \sum_{A=1}^{N_{nuc}} \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^{N_{elec}} \sum_{A=1}^{N_{nuc}} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N_{elec}} \sum_{j>i}^{N_{elec}} \frac{1}{r_{ij}} + \sum_{A=1}^{N_{nuc}} \sum_{B>A}^{N_{nuc}} \frac{Z_A Z_B}{R_{AB}} \quad (33)$$

$\nearrow 0$   
 $\nearrow V_{NN}$

We now have what is known as the electronic Hamiltonian plus  $V_{NN}$ :

$$\hat{H} = \underbrace{- \sum_{i=1}^{N_{elec}} \frac{1}{2} \nabla_i^2}_{\hat{T}_{elec}} - \underbrace{\sum_{i=1}^{N_{elec}} \sum_{A=1}^{N_{nuc}} \frac{Z_A}{r_{iA}}}_{\hat{V}_{elec}^{(1)}} + \underbrace{\sum_{i=1}^{N_{elec}} \sum_{j>i}^{N_{elec}} \frac{1}{r_{ij}}}_{\hat{V}_{elec}^{(2)}} + \underbrace{V_{NN}}_{\hat{V}_{nuc}} \quad (34)$$

$\hat{H}$  then becomes the sum of the electronic kinetic term  $\hat{T}_{elec}$ , the electron-nucleus attraction term  $\hat{V}_{elec}^{(1)}$ , the electron-electron repulsion term  $\hat{V}_{elec}^{(2)}$ , and the nuclear-nuclear repulsion term  $\hat{V}_{nuc}$ .



## Pople Notation

Probably the most onerous aspect of reading quantum chemistry literature is understanding the index conventions. We will use the **Pople notation** going forward. We use Greek letters ( $\mu, \nu, \lambda, \dots$ ) to denote functions in the atomic orbital (AO) basis  $\chi_\mu$  and Latin letters ( $i, j, k, \dots$ ) to denote functions in the molecular orbital (MO) basis  $\phi_p$ . For example:

$$\chi_\mu \rightarrow |\mu\rangle \qquad |\phi_p\rangle \rightarrow |p\rangle \qquad (35)$$

Typically, ( $i, j, k, \dots$ ) are reserved for occupied MOs and ( $p, q, r, \dots$ ) correspond to all general MOs. The letters ( $a, b, c, \dots$ ) are often used to unoccupied or virtual MOs. These conventions are usually upheld, but may not be depending on the kind of literature.

Take  $|p\rangle$ , an MO written as a LCAO:

$$|p\rangle = \sum_{\mu} c_{\mu p} |\mu\rangle \qquad (36)$$

We can choose an AO basis set  $\{|\mu\rangle\}$  that is normalized (or normalizable) but not necessarily orthogonal. We generally don't know the set of MO coefficients  $\{c_{\mu i}\}$  to describe a set of orthonormal MOs  $\{|p\rangle\}$ .

## Basis Representation

Now, just what are the functional forms of  $\{|\mu\rangle\}$ ? For periodic systems, we can choose a basis of plane waves of the following form:

$$\phi_{\mathbf{G}}(r) = \frac{1}{\sqrt{\Omega}} e^{i\vec{G}\cdot\vec{r}} \qquad (37)$$

where  $\vec{r}$  is lattice position vector,  $\vec{G}$  is the reciprocal lattice vector, and  $\Omega$  is the unit cell volume. For finite systems such as molecules, we can choose to use a basis of localised Gaussian-type functions:

$$\phi_{abc}^{GTO}(x, y, z) = N x^a y^b z^c e^{-\zeta r^2} \qquad (38)$$

or Slater-type functions:

$$\phi_{abc}^{STO}(x, y, z) = N x^a y^b z^c e^{-\zeta r} \qquad (39)$$

where  $x, y, z$  are the components of the position vector,  $N$  is the normalization constant, orbital angular momentum  $L$  is defined by  $a + b + c$ , and  $\zeta$  controls how tight (large  $\zeta$ ) or diffuse (small  $\zeta$ ) the function is. Although Slater-type functions help properly model the exponential decay of AOs/MOs at long range and capture the correct “cusp” behavior as electrons closely approach other particles, they can take a long time to numerically integrate. Most Slater-type basis sets (e.g. STO-nG) are actually mimicked by a combination of Gaussian functions. Almost all molecular quantum chemistry software use basis sets constructed out of atom-centered Gaussians.

## Integrals

Let’s look at how we go about solving  $\langle \Psi | \hat{H} | \Psi \rangle$ . Recall the electronic Hamiltonian:

$$\hat{H} = - \sum_i^{N_{elec}} \frac{1}{2} \nabla_i^2 - \sum_{i,A}^{N_{elec}} \frac{Z_A}{r_{iA}} + \sum_{i>j}^{N_{elec}} \frac{1}{r_{ij}} \quad (40)$$

Again, we can add the nuclear-nuclear repulsion energy  $V_{NN}$  at the end. Now, for example, consider a SD for two electrons written as  $|ij\rangle$ . We can write the expectation value for the total energy of the state defined by  $|ij\rangle$  as:

$$\langle \Psi | \hat{H} | \Psi \rangle = \langle ij | - \sum_i^{N_{elec}} \frac{1}{2} \nabla_i^2 - \sum_{i,A}^{N_{elec}} \frac{Z_A}{r_{iA}} + \sum_{i>j}^{N_{elec}} \frac{1}{r_{ij}} | ij \rangle \quad (41)$$

We can employ the **interchange theorem** because, in our case, summation and integration commute. This lets us move summation terms in and out of integral arguments (i.e. bra-kets).

Let’s have a look at the kinetic energy term:

$$\langle ij | - \sum_i^{N_{elec}} \frac{1}{2} \nabla_i^2 | ij \rangle \quad (42)$$

Expand the SDs out:

$$\left( \frac{1}{\sqrt{2}} \right) \left( \frac{1}{\sqrt{2}} \right) \left( -\frac{1}{2} \right) \sum_i^{N_{elec}} [\langle ij | \nabla_i^2 | ij \rangle - \langle ji | \nabla_i^2 | ij \rangle + \langle ji | \nabla_i^2 | ji \rangle - \langle ij | \nabla_i^2 | ji \rangle] \quad (43)$$

The Laplacian operator  $\nabla^2$  is a one-electron operator involved in one-electron integrals. It is an operator for a single particle observable and does not “know” anything about orbitals with an index different from its own. The  $1/\sqrt{2}$  factors are the normalization constants from  $\langle ij |$  and  $|ij\rangle$ .

**One-Electron Integrals:** *Example—setting up an expectation value expression for the kinetic energy using a two-electron SD.* Now let us operate solely on one of the electrons. We can partition the terms as follows:

Term 1:

$$\left(-\frac{1}{4}\right) [\langle i(1)j(2) | \nabla_1^2 | i(1)j(2) \rangle] = \left(-\frac{1}{4}\right) \langle i(1) | \nabla_1^2 | i(1) \rangle \langle \cancel{j(2)} | \cancel{j(2)} \rangle^1 \quad (44)$$

$$= \left(-\frac{1}{4}\right) \langle i(1) | \nabla_1^2 | i(1) \rangle \quad (45)$$

Term 2:

$$\left(-\frac{1}{4}\right) [-\langle j(1)i(2) | \nabla_1^2 | i(1)j(2) \rangle] = \left(\frac{1}{4}\right) \langle j(1) | \nabla_1^2 | i(1) \rangle \langle \cancel{i(2)} | \cancel{j(2)} \rangle^0 \quad (46)$$

$$= 0 \quad (47)$$

Term 3:

$$\left(-\frac{1}{4}\right) [\langle j(1)i(2) | \nabla_1^2 | j(1)i(2) \rangle] = \left(-\frac{1}{4}\right) \langle j(1) | \nabla_1^2 | j(1) \rangle \langle \cancel{i(2)} | \cancel{i(2)} \rangle^1 \quad (48)$$

$$= \left(-\frac{1}{4}\right) \langle j(1) | \nabla_1^2 | j(1) \rangle \quad (49)$$

Term 4:

$$\left(-\frac{1}{4}\right) [-\langle i(1)j(2) | \nabla_1^2 | j(1)i(2) \rangle] = \left(\frac{1}{4}\right) \langle i(1) | \nabla_1^2 | j(1) \rangle \langle \cancel{j(2)} | \cancel{i(2)} \rangle^0 \quad (50)$$

$$= 0 \quad (51)$$

Since we're working with an orthonormal set of MOs, the "single-bar" integrals  $\langle i|j \rangle$  and  $\langle j|i \rangle$  will go to zero while the integrals left over from the action of the Laplacian  $\langle i|i \rangle$  and  $\langle j|j \rangle$  will go to one. So then,

$$\langle ij | -\frac{1}{2} \nabla_1^2 | ij \rangle = \left(-\frac{1}{4}\right) [\langle i(1) | \nabla_1^2 | i(1) \rangle + \langle j(1) | \nabla_1^2 | j(1) \rangle] \quad (52)$$

Similarly, the expressions for the kinetic energy operator acting on the second electron are written as:

$$\langle ij | -\frac{1}{2} \nabla_2^2 | ij \rangle = \left(-\frac{1}{4}\right) [\langle i(2) | \nabla_2^2 | i(2) \rangle + \langle j(2) | \nabla_2^2 | j(2) \rangle] \quad (53)$$

Because electrons are indistinguishable, the integrals  $\langle i(1) | \nabla_1^2 | i(1) \rangle$  and  $\langle i(2) | \nabla_2^2 | i(2) \rangle$  are equal, as are the integrals  $\langle j(1) | \nabla_1^2 | j(1) \rangle$  and  $\langle j(2) | \nabla_2^2 | j(2) \rangle$ .

The kinetic energy operator and the electron-nucleus attraction operator are factored into what is commonly known as the **core Hamiltonian**:

$$\hat{h} = - \sum_i^{N_{elec}} \frac{1}{2} \nabla_i^2 - \sum_{i,A}^{N_{elec}} \frac{Z_A}{r_{iA}} \quad (54)$$

Now, how do we deal with the two-electron integrals? The action of the Coulomb operator  $1/r_{ij}$  relies on the distances between occupied orbitals. We can sandwich the operator between two SDs to yield the following:

$$\langle ij | \sum_{i>j}^{N_{elec}} \frac{1}{r_{ij}} | ij \rangle \quad (55)$$

The sum of all pairwise interactions runs over the indices where  $i \neq j$ .

**Two-Electron Integrals:** *Example—setting up an expectation value expression for the electron-electron repulsion energy using a two-electron SD.*

$$\langle ij | \frac{1}{r_{12}} | ij \rangle \quad (56)$$

Expand determinants:

$$\left( \frac{1}{\sqrt{2}} \right) \left( \frac{1}{\sqrt{2}} \right) \left[ \underbrace{\langle ij | \frac{1}{r_{12}} | ij \rangle + \langle ji | \frac{1}{r_{12}} | ji \rangle}_{\text{same}} - \underbrace{\langle ij | \frac{1}{r_{12}} | ji \rangle - \langle ji | \frac{1}{r_{12}} | ij \rangle}_{\text{same}} \right] \quad (57)$$

Since the distance between  $i$  and  $j$  is the same as the distance between  $j$  and  $i$ , equivalent terms will emerge:

$$\left( \frac{1}{2} \right) \left[ 2 \langle ij | \frac{1}{r_{12}} | ij \rangle - 2 \langle ij | \frac{1}{r_{12}} | ji \rangle \right] \quad (58)$$

Simplifying further:

$$\underbrace{\langle ij | \frac{1}{r_{12}} | ij \rangle}_{\text{Coulomb } \mathcal{J}} - \underbrace{\langle ij | \frac{1}{r_{12}} | ji \rangle}_{\text{Exchange } \mathcal{K}} \quad (59)$$

We are left with two terms—Coulomb  $\mathcal{J}$  and exchange  $\mathcal{K}$ . The operator hats are dropped since they now represent expectation values. Both terms are usually referred to as **electron repulsion integrals** (ERIs) or four-center two-electron integrals. Together, they are expressed as a “double-bar” integral:

$$\sum_{i>j}^{N_{elec}} \langle ij || ij \rangle \quad (60)$$

The Coulomb operator  $\hat{\mathcal{J}}$  corresponds to the classical electrostatic repulsion between charged particles. Its action best represented by its operation on an arbitrary spin-orbital  $\chi_i(\mathbf{x}_1)$  :

$$\hat{\mathcal{J}}_j(\mathbf{x}_1) |\chi_i(\mathbf{x}_1)\rangle = \langle \chi_j(\mathbf{x}_2) | \frac{1}{r_{12}} | \chi_j(\mathbf{x}_2) \rangle |\chi_i(\mathbf{x}_1)\rangle \quad (61)$$

$$= \int \left[ \chi_j^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_j(\mathbf{x}_2) d\mathbf{x}_2 \right] \chi_i(\mathbf{x}_1) \quad (62)$$

This gives the average potential that the electron in orbital  $\chi_i$  with coordinates  $\mathbf{x}_1$  “feels” due to the charge density generated by  $\chi_j$  with coordinates  $\mathbf{x}_2$ . One could say that  $\hat{\mathcal{J}}$  is an *effective* one-electron operator because each electron becomes an independent particle interacting with a mean field generated by all other  $N - 1$  electrons. In a simple mathematical sense, we can solve for the total expectation value for the Coulomb potential by integrating over all possible coordinates for the electrons at play:

$$\langle \chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2) | \hat{\mathcal{J}} | \chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2) \rangle = \langle \chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2) | \frac{1}{r_{12}} | \chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2) \rangle \quad (63)$$

$$= \iint \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \quad (64)$$

The exchange operator  $\hat{\mathcal{K}}$  is a bit unique. It is a direct consequence of the antisymmetry principle for which there is no classical analogue. Exchange integrals take on a form similar to that of Coulomb integrals except now the orbital indices  $i$  and  $j$  are permuted in the ket.

$$\langle \chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2) | \hat{\mathcal{K}} | \chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2) \rangle = \langle \chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2) | \frac{1}{r_{12}} | \chi_j(\mathbf{x}_1) \chi_i(\mathbf{x}_2) \rangle \quad (65)$$

$$= \iint \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_j(\mathbf{x}_1) \chi_i(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \quad (66)$$

## Integral Notation

Integral notation can be cumbersome, but it's important to stay consistent when derivations get messy. Thus far, for explicit integrals and bra-kets, we have been using **physicists' notation**. However, there is also the widely adopted **chemists' notation**. I know right? What strange folk would confuse us like that?

### Integral Notation:

Physicists' Notation:

$$\langle pq|rs\rangle = \langle \chi_p \chi_q | \chi_r \chi_s \rangle = \iint \chi_p^*(\mathbf{x}_1) \chi_q^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_r(\mathbf{x}_1) \chi_s(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \quad (67)$$

$$\langle pq|rs\rangle = \langle pq|rs\rangle - \langle pq|sr\rangle \quad (68)$$

$$= \iint \chi_p^*(\mathbf{x}_1) \chi_q^*(\mathbf{x}_2) \frac{1}{r_{12}} (1 - \hat{\mathcal{P}}_{12}) \chi_r(\mathbf{x}_1) \chi_s(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \quad (69)$$

$$= \iint \chi_p^*(\mathbf{x}_1) \chi_q^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_r(\mathbf{x}_1) \chi_s(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \quad (70)$$

$$- \iint \chi_p^*(\mathbf{x}_1) \chi_q^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_s(\mathbf{x}_1) \chi_r(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \quad (71)$$

$$\langle pq|rs\rangle = \langle qp|sr\rangle \quad (72)$$

$$\langle pq|rs\rangle = \langle rs|pq\rangle^* \quad (73)$$

$$\langle pq|rr\rangle = 0 \quad (74)$$

Chemists' Notation:

$$[pq|rs] = [\chi_p \chi_q | \chi_r \chi_s] = \iint \chi_p^*(\mathbf{x}_1) \chi_q(\mathbf{x}_1) \frac{1}{r_{12}} \chi_r^*(\mathbf{x}_2) \chi_s(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \quad (75)$$

This notation signifies that we're dealing with spin-orbitals. Using parenthesis, we have chemists' notation for spatial orbitals:

$$(pq|rs) = (\psi_p \psi_q | \psi_r \psi_s) = \iint \psi_p^*(\mathbf{r}_1) \psi_q(\mathbf{r}_1) \frac{1}{r_{12}} \psi_r^*(\mathbf{r}_2) \psi_s(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (76)$$

$$(pq|rs) = (rs|pq) \quad (77)$$

For the antisymmetrized two-electron integrals, the physicists' notation maps onto the chemists' notation in the following way:

$$\langle pq|rs\rangle = \langle pq|rs\rangle - \langle pq|sr\rangle \quad (78)$$

$$= [pr|qs] - [qs|pr] \quad (79)$$

Shared Features:

$$\langle i|\hat{h}|j\rangle = [i|\hat{h}|j] = \int \chi_i^*(\mathbf{x}_1)\hat{h}\chi_j(\mathbf{x}_1) d\mathbf{x}_1 \quad (80)$$

The one-electron integrals in chemists' and physicists' notation are identical. Here's a shortcut to understanding the notation conventions:

$$\langle pq|rs\rangle = \langle 12|12\rangle = \iint \chi_p^*(1)\chi_q^*(2)\frac{1}{r_{12}}\chi_r(1)\chi_s(2) d\mathbf{x}_1 d\mathbf{x}_2 \quad (81)$$

$$[pq|rs] = [11|22] = \iint \chi_p^*(1)\chi_q(1)\frac{1}{r_{12}}\chi_r^*(2)\chi_s(2) d\mathbf{x}_1 d\mathbf{x}_2 \quad (82)$$

If the orbitals are real, we are left with eightfold permutation symmetry:

$$\begin{aligned} \langle pq|rs\rangle &= \langle qp|sr\rangle = \langle rs|pq\rangle = \langle sr|qp\rangle \\ &= \langle rq|ps\rangle = \langle sp|qr\rangle = \langle ps|rq\rangle = \langle qr|sp\rangle \end{aligned} \quad (83)$$

$$\begin{aligned} [pq|rs] &= [rs|pq] = [qp|sr] = [sr|qp] \\ &= [qp|rs] = [sr|pq] = [pq|sr] = [rs|qp] \end{aligned} \quad (84)$$

In chemists' notation, you'll sometimes see the Coulomb integral written as  $[ii|jj]$  and the exchange integral written as  $[ij|ji]$ .

## Spin Integration

Spin plays an important role in integral evaluation. The Hamiltonian we use is considered to be "spin free" because none of its terms operates on spin. We are then able to separate spin and spatial coordinates in the integral expansions. Take the Coulomb integral for instance:

$$\mathcal{J} = [ii|jj] = \iint \psi_i^*(\mathbf{r}_1)\psi_i(\mathbf{r}_1)\frac{1}{r_{12}}\psi_j^*(\mathbf{r}_2)\psi_j(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (85)$$

$$\times \iint \sigma_i^*(\omega_1)\sigma_i(\omega_1)\sigma_j^*(\omega_2)\sigma_j(\omega_2) d\omega_1 d\omega_2 \quad (86)$$

In this case, we maintain that:

$$\langle \sigma_i | \sigma_j \rangle = \delta_{ij} \quad (87)$$

For orbitals with the same spin, the spin integrals equate to unity. This yields only the spatial integral.

$$\mathcal{J} = [ii|jj] = \iint \psi_i^*(\mathbf{r}_1)\psi_i(\mathbf{r}_1) \frac{1}{r_{12}} \psi_j^*(\mathbf{r}_2)\psi_j(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (88)$$

$$\times \iint \cancel{\alpha_i^*(\omega_1)\alpha_i(\omega_1)} \cancel{\alpha_j^*(\omega_2)\alpha_j(\omega_2)} d\omega_1 d\omega_2 \quad (89)$$

$$= \iint \psi_i^*(\mathbf{r}_1)\psi_i(\mathbf{r}_1) \frac{1}{r_{12}} \psi_j^*(\mathbf{r}_2)\psi_j(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (90)$$

$$= (ii|jj) \quad (91)$$

For the exchange integral, the spin parts may or may not integrate out. The only  $\mathcal{K}$  terms that survive are those with orbitals with the same spin. Here are two examples:

$$\mathcal{K} = [ij|ji] = \iint \psi_i^*(\mathbf{r}_1)\psi_j(\mathbf{r}_1) \frac{1}{r_{12}} \psi_j^*(\mathbf{r}_2)\psi_i(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (92)$$

$$\times \iint \cancel{\alpha^*(\omega_1)\alpha(\omega_1)} \cancel{\alpha^*(\omega_2)\alpha(\omega_2)} d\omega_1 d\omega_2 \quad (93)$$

$$= \iint \psi_i^*(\mathbf{r}_1)\psi_i(\mathbf{r}_1) \frac{1}{r_{12}} \psi_j^*(\mathbf{r}_2)\psi_j(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (94)$$

$$\mathcal{K} = [i\bar{j}|\bar{j}i] = \iint \psi_i^*(\mathbf{r}_1)\psi_j(\mathbf{r}_1) \frac{1}{r_{12}} \psi_j^*(\mathbf{r}_2)\psi_i(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (95)$$

$$\times \iint \cancel{\alpha^*(\omega_1)\beta(\omega_1)} \cancel{\beta^*(\omega_2)\alpha(\omega_2)} d\omega_1 d\omega_2 \quad (96)$$

$$= 0 \quad (97)$$

Note that we have chosen the overbar notation for orbitals with an electron in the down-spin configuration  $\beta(\omega)$ . Those without overbars are orbitals with an electron in the up-spin configuration  $\alpha(\omega)$ .



**Basic Spin Algebra:** *Intrinsic angular momentum, or spin, is an quantum mechanical degree of freedom. The inclusion of spin is mandatory for determining expectation values that map onto physical observables. Here we give a very brief overview spin algebra as it pertains to integral evaluation within the HF approximation.*

Consider the z-axis spin projection operator:

$$\hat{S}_z = \frac{\hbar}{2} \sigma_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (98)$$

Where  $\sigma_z$  is the Pauli matrix for the  $z$ -component. The eigenvectors of this operator representation make up the standard orthonormal spin basis:

$$|\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad |\beta\rangle = \begin{pmatrix} 0 \\ -1 \end{pmatrix} \quad (99)$$

Here are examples of spin integration between two spin functions:

$$\langle\alpha|\alpha\rangle = \begin{pmatrix} 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \int \alpha^*(\omega)\alpha(\omega) d\omega = 1 \quad (100)$$

$$\langle\beta|\beta\rangle = \begin{pmatrix} 0 & -1 \end{pmatrix} \begin{pmatrix} 0 \\ -1 \end{pmatrix} = \int \beta^*(\omega)\beta(\omega) d\omega = 1 \quad (101)$$

$$\langle\alpha|\beta\rangle = \begin{pmatrix} 1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ -1 \end{pmatrix} = \int \alpha^*(\omega)\beta(\omega) d\omega = 0 \quad (102)$$

$$\langle\beta|\alpha\rangle = \begin{pmatrix} 0 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \int \beta^*(\omega)\alpha(\omega) d\omega = 0 \quad (103)$$

## Integral Evaluation

For many-electron systems, we will need to determine the elements of the  $h$ ,  $\mathcal{J}$ , and  $\mathcal{K}$  matrices. This, of course, will require solving a few integrals to scores upon scores of integrals. There exists a defined set of rules quantum chemists use to evaluate one- and two-electron integrals. They are called the **Slater-Condon rules**.

**The Slater-Condon Rules:**One-electron operators

$$\hat{\mathcal{O}}_1 = \sum_i^N \hat{h}_i \quad (104)$$

Case 1: No Difference

$$\langle \Psi | \hat{\mathcal{O}}_1 | \Psi \rangle = \langle \cdots p \cdots | \hat{\mathcal{O}}_1 | \cdots p \cdots \rangle = \sum_p^N \langle p | \hat{h} | p \rangle \quad (105)$$

Case 2: One Difference

$$\langle \Psi | \hat{\mathcal{O}}_1 | \Phi \rangle = \langle \cdots pq \cdots | \hat{\mathcal{O}}_1 | \cdots rq \cdots \rangle = \langle p | \hat{h} | r \rangle \quad (106)$$

Case 3: Two Differences or More

$$\langle \Psi | \hat{\mathcal{O}}_1 | \Xi \rangle = \langle \cdots pq \cdots | \hat{\mathcal{O}}_1 | \cdots rs \cdots \rangle = 0 \quad (107)$$

Two-electron operators

$$\hat{\mathcal{O}}_2 = \sum_{i>j}^N \frac{1}{r_{ij}} \quad (108)$$

Case 1: No Difference

$$\langle \Psi | \hat{\mathcal{O}}_2 | \Psi \rangle = \langle \cdots pq \cdots | \hat{\mathcal{O}}_2 | \cdots pq \cdots \rangle = \frac{1}{2} \sum_{pq}^N \langle pq | pq \rangle \quad (109)$$

Case 2: One Difference

$$\langle \Psi | \hat{\mathcal{O}}_2 | \Phi \rangle = \langle \cdots pq \cdots | \hat{\mathcal{O}}_2 | \cdots rq \cdots \rangle = \sum_q^N \langle pq | rq \rangle \quad (110)$$

Case 3: Two Differences

$$\langle \Psi | \hat{\mathcal{O}}_2 | \Xi \rangle = \langle \cdots pq \cdots | \hat{\mathcal{O}}_2 | \cdots rs \cdots \rangle = \langle pq | rs \rangle \quad (111)$$

Case 4: Three Differences or More

$$\langle \Psi | \hat{\mathcal{O}}_2 | \Omega \rangle = \langle \cdots pqr \cdots | \hat{\mathcal{O}}_2 | \cdots stu \cdots \rangle = 0 \quad (112)$$

## Fock Operator

The core Hamiltonian and the two-electron operators can be consolidated into an effective one-electron operator known as the **Fock Operator**.

$$\hat{\mathcal{F}} = \hat{h} + \sum_j^{N_{occ}} [\hat{\mathcal{J}}_j - \hat{\mathcal{K}}_j] \quad (113)$$

The sum for  $\hat{\mathcal{J}}_j$  and  $\hat{\mathcal{K}}_j$  runs over all occupied orbitals or, in essence, all electrons. Now the question is: how do we use  $\hat{\mathcal{F}}$  to systematically solve for the MO expansion coefficients and their corresponding energies?

## Constrained Optimization

Our goal within the HF approximation is to find a set of orbitals (MO coefficients) that minimize the energy of the system. To do this we must employ the **Lagrange method of undetermined multipliers**—a technique from calculus of variations (*vide infra*).

**The Lagrange Multipliers:** *The extrema of a function under certain constraints may be found by setting up a Lagrangian.* We can begin by deriving a general expression for this constrained optimization problem.

$$\mathcal{L} = (\text{some function}) - \lambda (\text{thing minus constraint}) \quad (114)$$

In HF, the constraint we maintain is the orthonormality of the MOs:  $\langle \chi_i | \chi_j \rangle = \delta_{ij}$ .

$$\mathcal{L} [\{\chi_i\}] = E_{HF} [\{\chi_i\}] - \lambda_{ji} \sum_{ij}^{N_{elec}} (\langle \chi_i | \chi_j \rangle - \delta_{ij}) \quad (115)$$

The undetermined multipliers are represented by  $\lambda_{ji}$ .  $E_{HF}$  is a function of the set of spin-orbitals  $\{\chi_i\}$ . Note that the Lagrangian  $\mathcal{L}$  is a functional, a function of a function. A condition we enforce is that  $\mathcal{L}$  must remain stationary with respect to infinitesimal changes in the orbitals.

$$\chi_i \rightarrow \chi_i + \delta\chi_i \quad \mathcal{L} \rightarrow \mathcal{L} + \delta\mathcal{L} \quad \delta\mathcal{L} = 0 \quad (116)$$

Taking the first variation of  $\mathcal{L}$  and finding that  $\delta\mathcal{L}$  is 0 verifies that we are at a stationary point. With tools from complex and functional analysis, solving for the variation in  $\mathcal{L}$  is simple.

Without going into much detail, the rules for Wirtinger derivatives show that we can vary the bra and ket independently:

$$\delta\langle\chi_i|\chi_j\rangle = \langle\delta\chi_i|\chi_j\rangle + \langle\chi_i|\delta\chi_j\rangle \quad (117)$$

and with ERI permutation symmetries:

$$\langle\chi_i\delta\chi_j|\chi_i\chi_j\rangle = \langle\delta\chi_j\chi_i|\chi_j\chi_i\rangle \quad (118)$$

Note that in basic formulations such as this, we work with real orbitals. So, the properties of regular partial derivatives w.r.t. real variables apply. Now let us find the functional derivative  $\delta\mathcal{L}$ :

$$\delta\mathcal{L} = \delta E_{HF}[\{\chi_i\}] - \lambda_{ji} \sum_{ij}^{N_{elec}} \delta(\langle\chi_i|\chi_j\rangle - \delta_{ij}) \quad (119)$$

$$= \delta E_{HF}[\{\chi_i\}] - \lambda_{ji} \sum_{ij}^{N_{elec}} (\langle\delta\chi_i|\chi_j\rangle + \langle\chi_i|\delta\chi_j\rangle) \quad (120)$$

Recall that the expectation value for the total energy (sans  $V_{NN}$ ) is:

$$E_{HF} = \sum_i^{N_{elec}} \langle i | \hat{h} | i \rangle + \sum_{i>j}^{N_{elec}} \left[ \langle ij | \hat{\mathcal{J}}_j | ij \rangle - \langle ij | \hat{\mathcal{K}}_j | ij \rangle \right] \quad (121)$$

Hint: indicating a sum over  $i > j$  in front of the two electron terms corrects for double counting, otherwise a  $1/2$  is needed instead. Let's start with the latter option.

$$\begin{aligned} &= \sum_i^{N_{elec}} \left[ \langle\delta\chi_i|\hat{h}|\chi_i\rangle + \langle\chi_i|\hat{h}|\delta\chi_i\rangle \right] + \frac{1}{2} \sum_{ij}^{N_{elec}} \left[ \langle\delta\chi_i\chi_j|\chi_i\chi_j\rangle \right. \\ &+ \langle\chi_i\delta\chi_j|\chi_i\chi_j\rangle + \langle\chi_i\chi_j|\delta\chi_i\chi_j\rangle + \langle\chi_i\chi_j|\chi_i\delta\chi_j\rangle \left. \right] \\ &- \frac{1}{2} \sum_{ij}^{N_{elec}} \left[ \langle\delta\chi_i\chi_j|\chi_j\chi_i\rangle + \langle\chi_i\delta\chi_j|\chi_j\chi_i\rangle + \langle\chi_i\chi_j|\delta\chi_j\chi_i\rangle \right. \\ &+ \left. \langle\chi_i\chi_j|\chi_j\delta\chi_i\rangle \right] - \lambda_{ji} \sum_{ij}^{N_{elec}} (\langle\delta\chi_i|\chi_j\rangle + \langle\chi_i|\delta\chi_j\rangle) \end{aligned} \quad (122)$$

Let's expand that last term.

$$\sum_{ij}^{N_{elec}} \lambda_{ji} \langle\delta\chi_i|\chi_j\rangle + \sum_{ij}^{N_{elec}} \lambda_{ji} \langle\chi_i|\delta\chi_j\rangle \quad (123)$$

Following the rules for complex conjugation, we can rewrite the second term from above:

$$\sum_{ij}^{N_{elec}} \lambda_{ji} \langle \delta \chi_i | \chi_j \rangle + \sum_{ij}^{N_{elec}} \lambda_{ij}^* \langle \delta \chi_j | \chi_i \rangle^* = \sum_{ij}^{N_{elec}} \lambda_{ji} \langle \delta \chi_i | \chi_j \rangle + c.c. \quad (124)$$

Eigenvalues of Hermitian operators are real, so it's reasonable to say that the Lagrangian multipliers are also real:

$$\lambda_{ji} = \lambda_{ij}^* \quad (125)$$

The abbreviation *c.c.* stands for complex conjugate. We can do the same complex conjugation procedure for all integral terms of  $E_{HF}$ . Indistinguishability allows us to swap the dummy indices for the electron coordinates (not written out explicitly above). This is done in both the bras and kets for one- and two-electron integrals. On top of that, notice each term has a complex conjugate which will be bundled together in the *c.c.* term. The remaining integrals with either a  $\delta \chi_i$  or a  $\delta \chi_j$  in the bra will be equivalent:

$$\frac{1}{2} \sum_{ij}^{N_{elec}} \left[ \langle \delta \chi_i \chi_j | \chi_i \chi_j \rangle + \langle \delta \chi_j \chi_i | \chi_j \chi_i \rangle \right] = \frac{1}{2} \sum_{ij}^{N_{elec}} \left[ \langle \delta \chi_i \chi_j | \chi_i \chi_j \rangle + \langle \delta \chi_i \chi_j | \chi_j \chi_i \rangle \right] \quad (126)$$

The  $\mathcal{J}$  integrals reduce to:

$$\frac{1}{2} \sum_{ij}^{N_{elec}} 2 \left[ \langle \delta \chi_i \chi_j | \chi_i \chi_j \rangle \right] \quad (127)$$

The addition of two equivalent integrals will cancel out the factor of  $1/2$  in front of the ERI sums. The  $\mathcal{K}$  integrals can be simplified in the same manner. The first variation now becomes:

$$\begin{aligned} \delta \mathcal{L} = & \sum_i^{N_{elec}} \langle \delta \chi_i | \hat{h} | \chi_i \rangle + \sum_{ij}^{N_{elec}} \left[ \langle \delta \chi_i \chi_j | \chi_i \chi_j \rangle - \langle \delta \chi_i \chi_j | \chi_j \chi_i \rangle \right] \\ & - \lambda_{ji} \sum_{ij}^{N_{elec}} \langle \delta \chi_i | \chi_j \rangle + c.c. \end{aligned} \quad (128)$$

Let's factor out the bra:

$$\delta \mathcal{L} = \sum_i^{N_{elec}} \langle \delta \chi_i | \left[ \hat{h} | \chi_i \rangle + \sum_j^{N_{elec}} \left[ \langle \chi_j | \chi_i \chi_j \rangle - \langle \chi_j | \chi_j \chi_i \rangle \right] - \lambda_{ji} \sum_j^{N_{elec}} | \chi_j \rangle \right] + c.c. \quad (129)$$

The variation  $\delta\chi_i$  is arbitrary—representing infinitesimal slices in the space contained by the boundary conditions. For  $\delta\mathcal{L}$  to be 0, the argument within the largest bracket above must also be zero.

$$\hat{h}|\chi_i\rangle + \sum_j^{N_{elec}} \left[ \langle\chi_j|\chi_i\chi_j\rangle - \langle\chi_j|\chi_j\chi_i\rangle \right] - \lambda_{ji} \sum_j^{N_{elec}} |\chi_j\rangle = 0 \quad (130)$$

Notice the emergence of the Fock operator.

$$\hat{h}|\chi_i\rangle + \sum_j^{N_{elec}} \left[ \hat{\mathcal{J}}_j |\chi_i\rangle - \hat{\mathcal{K}}_j |\chi_i\rangle \right] - \lambda_{ji} \sum_j^{N_{elec}} |\chi_j\rangle = 0 \quad (131)$$

$$\hat{\mathcal{F}}_i |\chi_i\rangle - \lambda_{ji} \sum_j^{N_{elec}} |\chi_j\rangle = 0 \quad \longrightarrow \quad \hat{\mathcal{F}}_i |\chi_i\rangle = \lambda_{ji} \sum_j^{N_{elec}} |\chi_j\rangle \quad (132)$$

Here we have the **non-canonical Hartree-Fock equations**.

## Unitary Transformations

Notice that the expression we found does not represent an eigensystem since the action of  $\hat{\mathcal{F}}$  on  $\chi_i$  does not return  $\chi_i$ . However, we can find a **unitary transformation** of the spin-orbitals that diagonalizes the Lagrange multiplier matrix  $\lambda_{ji}$ . Unitary transformations are said to be norm-preserving in that the magnitude (“length”) or inner product ( $\langle\psi|\psi\rangle$ ) between two vector spaces is left unchanged.

**Unitary Transformations:** *The diagonalization of a Hermitian matrix involves finding a unitary matrix. A change of basis occurs under the auspices of a unitary transformation. This results in a new set of orthonormal eigenvectors along with corresponding eigenvalues of the newly generated diagonal matrix.*

Unitary matrices are Hermitian and obey the following relationships:

$$UU^\dagger = U^\dagger U = \mathbf{1} \quad \longrightarrow \quad \sum_r U_{rp}^* U_{rq} = \delta_{pq} \quad (133)$$

$$\det(UU^\dagger) = \det(U^\dagger U) = \det(\mathbf{1}) = 1 \quad (134)$$

$$\det(U^\dagger) \cdot \det(U) = \det(U) \cdot \det(U^\dagger) = 1 \quad (135)$$

Here are unitary matrices that satisfy the conditions above:

$$U = \begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix} \quad U^\dagger = \begin{pmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{pmatrix} \quad (136)$$

Using Euler's formula it is clear that:

$$\det(U) = 1 \quad (137)$$

An alternative expression also holds for  $\phi \in [0, 2\pi)$ . Note that it takes the form of a rotation operator.

$$U = e^{i\phi} \quad (138)$$

Let's look at a basic example of how we use unitary operators to gain insight into quantum systems. Consider an electronic wavefunction  $\Psi$ . Let us rotate the spin components about the  $z$ -axis. The unitary operator that generates such a rotation is:

$$U_z(\phi) = e^{-i\phi(\mathbf{n}_z \cdot \frac{\sigma_z}{\hbar})} \quad \text{or} \quad U_z(\phi) = e^{-i(\frac{\phi}{2})(\mathbf{n}_z \cdot \sigma_z)} \quad (139)$$

The unit vector in the  $z$ -direction is  $\mathbf{n}_z$  and  $\sigma_z$  is again  $z$  Pauli matrix. Using Euler's identity we can expand the operator:

$$U_z(\phi) = \cos\left(\frac{\phi}{2}\right) - i\sigma_z \sin\left(\frac{\phi}{2}\right) \quad (140)$$

If we do a full  $2\pi$  rotation about the  $z$ -axis, what is the action of  $U_z(\phi)$  on  $|\Psi\rangle$ ?

$$U_z(2\pi) |\Psi\rangle = (-1) |\Psi\rangle \quad (141)$$

We merely have a global phase change:

$$|\Psi'\rangle = -|\Psi\rangle \quad (142)$$

If we wish to revert back to the original  $\Psi$  from the transformed  $\Psi'$ , we must perform another  $2\pi$  rotation.

$$U_z(2\pi)U_z(2\pi) |\Psi\rangle = |\Psi\rangle \quad (143)$$

After two unitary transformations, we get back  $\Psi$ . This approach works if we restrict the types of unitary matrices to those with determinants equal to 1. This particular class of unitary matrices belongs to the special unitary group  $SU(2)$ . It just so happens that for fermions, the Pauli matrices are suitable basis representations for  $SU(2)$  symmetry. This defines the algebra we use to study the physics of electron spin.

## Roothaan-Hall Equations

Recall the non-canonical HF equations:

$$\hat{\mathcal{F}} |\chi_l\rangle = \lambda_{jl} \sum_j^{N_{elec}} |\chi_j\rangle$$

We are going to turn this into an eigensystem by performing a unitary transformation. We can create a set transformed orbitals like this (watch how you manage your dummy indices!):

$$\chi'_j = \chi'_l = \sum_l^{N_{elec}} \chi_l U_{lj} \quad (144)$$

As we discussed earlier, certain representations of  $U$  that satisfy Hermiticity requirements include Euler formulas. Since  $U$  can take angular arguments, its action on  $\{|\chi_i\rangle\}$  is commonly referred to as **orbital rotation**. To obtain expectation values for  $\hat{\mathcal{F}}$ , we introduce a projective dual space of complex elements, a bra, to the left and right sides of the non-canonical HF equation.

$$\langle \chi_k | \hat{\mathcal{F}} | \chi_l \rangle = \lambda_{jl} \sum_j^{N_{elec}} \langle \chi_k | \chi_j \rangle \quad (145)$$

If  $\chi_k$  and  $\chi_j$  are orthonormal, they become Kronecker delta  $\delta_{kj}$ .

$$\langle \chi_k | \hat{\mathcal{F}} | \chi_l \rangle = \sum_j^{N_{elec}} \lambda_{jl} \delta_{kj} \quad (146)$$

Choose  $j = k$ .

$$\langle \chi_k | \hat{\mathcal{F}} | \chi_l \rangle = \sum_k^{N_{elec}} \lambda_{kl} \quad (147)$$

Perform a unitary transformation on  $\chi_k$  and  $\chi_l$ .

$$\left\langle \sum_k^{N_{elec}} U_{ki} \chi_k \middle| \hat{\mathcal{F}} \middle| \sum_l^{N_{elec}} U_{lj} \chi_l \right\rangle = \sum_k^{N_{elec}} \sum_i^{N_{elec}} U_{ki}^* \lambda_{kl} U_{lj} \quad (148)$$



Substitute in the transformed orbitals. Operators taken out of their bra become a complex conjugate.

$$\langle \chi'_i | \hat{\mathcal{F}} | \chi'_j \rangle = (U^\dagger \lambda U)_{ij} \quad (149)$$

We obtain  $\lambda'_{ij}$  after unitary transformation.

$$\langle \chi'_i | \hat{\mathcal{F}} | \chi'_j \rangle = \lambda'_{ij} \quad (150)$$

At this point, you've probably caught on and realized that the Lagrangian multipliers  $\lambda_{ji}$  were actually the MO energies  $\epsilon$ . The matrix  $\epsilon$  is Hermitian, therefore it is always possible to find a unitary transformation that diagonalizes it.

$$\epsilon'_{ij} = (U^\dagger \epsilon U)_{ij} \quad (151)$$

Substitute  $\lambda'_{ij} \rightarrow \epsilon'_{ij}$

$$\langle \chi'_i | \hat{\mathcal{F}} | \chi'_j \rangle = \epsilon'_{ij} \quad (152)$$

$\epsilon'$  is diagonal.

$$\epsilon'_{ij} = \delta_{ij} \epsilon'_i \quad (153)$$

Rewrite the non-canonical HF equations using our transformed basis and diagonal MO energy matrix.

$$\hat{\mathcal{F}} | \chi'_i \rangle = \epsilon'_i \delta_{ij} | \chi'_j \rangle \quad (154)$$

Choose  $i = j$

$$\hat{\mathcal{F}} | \chi'_i \rangle = \epsilon'_i | \chi'_i \rangle \quad (155)$$

We now have the **canonical Hartree-Fock equations**—a seemingly true eigensystem using canonical spin-orbitals. Here’s an important detail: although we invoke some “picture change” with occupied orbital rotation, the Fock operator and the energies remain invariant to unitary transformation—they don’t change. We can drop the primes and abbreviate  $\{|\chi'_i\rangle\}$  as  $\{|i\rangle\}$ .

$$\hat{\mathcal{F}} |i\rangle = \epsilon_i |i\rangle \quad (156)$$

If we want to solve this eigensystem, we’ll need to form the Fock matrix. Since we usually don’t know the set of MOs  $\{|i\rangle\}$  *a priori*, we can more intuitively work in the AO basis  $\{|\nu\rangle\}$ . Let’s first project into a basis defined by known, normalized functions  $\{|\mu\rangle\}$  and expand things out:

$$\langle\mu|\hat{\mathcal{F}}|\sum_{\nu}^{N_{basis}} c_{\nu i} \nu\rangle = \epsilon_i \langle\mu|\sum_{\nu}^{N_{basis}} c_{\nu i} \nu\rangle \quad (157)$$

The expansion coefficients  $c_{\nu i}$  are what we want to solve for. Rearranging further:

$$\sum_{\nu}^{N_{basis}} c_{\nu i} \langle\mu|\hat{\mathcal{F}}|\nu\rangle = \sum_{\nu}^{N_{basis}} c_{\nu i} \underbrace{\langle\mu|\nu\rangle}_{S_{\mu\nu}} \epsilon_i \quad (158)$$

Summing over the number of basis functions describing each orbital, we obtain a matrix representation of what looks to be a generalized eigenvalue problem. The atomic orbital overlap matrix  $S_{\mu\nu}$  is used as a metric or a tool to give us a sense of distance in Hilbert space where the orbitals reside.

$$\sum_{\nu}^{N_{basis}} c_{\nu i} F_{\mu\nu} = \epsilon_i \sum_{\nu}^{N_{basis}} c_{\nu i} S_{\mu\nu} \quad (159)$$

We have defined the **Roothaan-Hall equations**. This expression can be further compacted:

$$\mathbf{FC} = \mathbf{SC}\epsilon \quad (160)$$

Since the AO functions are not necessarily orthogonal,  $S_{\mu\nu}$  is not  $\delta_{\mu\nu}$ . So, once again, we don’t have a proper eigensystem. This can be rectified with **Löwdin Symmetric Orthogonalization (LSO)**.

**Löwdin Symmetric Orthogonalization:** *A new basis of orthogonal vectors may be constructed via linear transformation of a non-orthogonal basis vectors. This method reorients the vectors by the same angles to ensure the inner products between them go to zero (e.g. picture two vectors,  $\vec{x}$  and  $\vec{y}$ , symmetrically pivoted away from each other so that the angle between them is  $90^\circ$ ).*

The chosen transformation matrix  $\mathbf{X}$  is Hermitian and is built from the unitary transformation that diagonalizes the inverse square root of the AO overlap matrix  $\mathbf{S}^{-1/2}$ .

$$\mathbf{X} = \mathbf{U}\mathbf{s}^{-1/2}\mathbf{U}^\dagger \quad (161)$$

The matrix  $\mathbf{s}^{-1/2}$  is a diagonal matrix whose elements are inverse square roots of overlap integrals. Since  $\mathbf{S}$  is Hermitian,  $\mathbf{S}^{-1/2}$  is also Hermitian. Due to the properties of unitary matrices, the transformation matrix  $\mathbf{X}$  ends up being conveniently equally to  $\mathbf{S}^{-1/2}$ .

$$\mathbf{X} = \mathbf{S}^{-1/2} \quad (162)$$

We shall use this to define how the MO coefficient matrix is transformed into an orthogonal one:

$$\begin{aligned} \mathbf{C}' &= \mathbf{X}^{-1}\mathbf{C} \\ &= (\mathbf{S}^{-1/2})^{-1}\mathbf{C} \end{aligned} \quad (163)$$

or conversely:

$$\begin{aligned} \mathbf{C} &= \mathbf{X}\mathbf{C}' \\ &= \mathbf{S}^{-1/2}\mathbf{C}' \end{aligned} \quad (164)$$

Substitute our new expression of  $\mathbf{C}$  in the Roothaan-Hall equation:

$$\mathbf{F}\mathbf{S}^{-1/2}\mathbf{C}' = \mathbf{S}\mathbf{S}^{-1/2}\mathbf{C}'\epsilon \quad (165)$$

Hit it on the left with  $\mathbf{S}^{-1/2}$ :

$$\underbrace{\mathbf{S}^{-1/2}\mathbf{F}\mathbf{S}^{-1/2}}_{\mathbf{F}'}\mathbf{C}' = \underbrace{\mathbf{S}^{-1/2}\mathbf{S}\mathbf{S}^{-1/2}}_{\mathbf{1}}\mathbf{C}'\epsilon \quad (166)$$

We have a transformed Fock matrix  $\mathbf{F}'$  and a transformed coefficient matrix  $\mathbf{C}'$  that diagonalizes it to yield MO energies  $\epsilon$ . Transforming or “rotating”  $\mathbf{C}'$  back to  $\mathbf{C}$  gives us eigenvectors of  $\mathbf{F}$  and corresponding eigenvalues. In other words, we get orbitals and orbital energies. Finally, a real eigensystem.

$$\mathbf{F}'\mathbf{C}' = \mathbf{C}'\epsilon \quad (167)$$

## Hartree-Fock Energy

Think of the general chemistry picture of molecules. Say we have a closed-shell system of  $\alpha$  and  $\beta$  electrons that are restricted to sharing the same spatial parts of the orbitals they occupy. How do we use the HF equations to describe the electronic structure of a molecule in this framework? Let's start with the closed-shell Fock operator:

$$\hat{\mathcal{F}} = \hat{h} + \sum_i^{N_{occ}/2} [2\hat{\mathcal{J}}_i - \hat{\mathcal{K}}_i] \quad (168)$$

All  $\alpha$  and  $\beta$  one electron operators are implicit in  $\hat{h}$ . Since  $\alpha$  and  $\beta$  electrons are paired up, there are half as many occupied orbitals so sum over, so a factor of 2 appears in front of  $\mathcal{J}$  appears. The only  $\mathcal{K}$  terms that survive are those with the same spins (see section on spin integration). To get a better idea of what the total energy expression looks like, we expand the Fock matrix  $F_{\mu\nu}$ :

$$\langle \mu | \hat{\mathcal{F}} | \nu \rangle = \langle \mu | \hat{h} | \nu \rangle + \langle \mu | \sum_i^{N_{occ}/2} [2\hat{\mathcal{J}}_i - \hat{\mathcal{K}}_i] | \nu \rangle \quad (169)$$

Remember  $\mathcal{J}$  and  $\mathcal{K}$  are actually:

$$\hat{\mathcal{J}}_i(\mathbf{r}_1) | \nu(\mathbf{r}_1) \rangle = \langle i(\mathbf{r}_2) | \frac{1}{r_{12}} | i(\mathbf{r}_2) \rangle | \nu(\mathbf{r}_1) \rangle \quad (170)$$

$$\hat{\mathcal{K}}_i(\mathbf{r}_1) | \nu(\mathbf{r}_1) \rangle = \langle i(\mathbf{r}_2) | \frac{1}{r_{12}} | \nu(\mathbf{r}_2) \rangle | i(\mathbf{r}_1) \rangle \quad (171)$$

Projecting into  $\langle \mu |$  gives us spatial ERIs.

$$F_{\mu\nu} = h_{\mu\nu} + \sum_i^{N_{occ}/2} [2(\mu\nu|ii) - (\mu i|i\nu)] \quad (172)$$

Recall coefficients  $\{c_{\lambda i}\}$  and AOs  $\{|\lambda\rangle\}$  build the functions in the basis set  $\{|i\rangle\}$ . As seen before, they can be extracted out of the integrals (refer to section on Pople notation).

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\lambda\sigma}^{N_{basis}} \left[ \sum_i^{N_{occ}/2} c_{\sigma i}^* c_{\lambda i} \right] \left[ 2(\mu\nu|\lambda\sigma) - (\mu\sigma|\lambda\nu) \right] \quad (173)$$

We define the total density in the AO basis  $P_{\lambda\sigma}$  as:

$$P_{\lambda\sigma} = 2 \sum_i^{N_{occ}/2} c_{\sigma i}^* c_{\lambda i} \quad (174)$$

Our index  $i$  runs over half of the occupied orbitals. So, to account for the rest of the matrix elements of  $P_{\lambda\sigma}$ , we double the sum. Substitute:

$$F_{\mu\nu} = h_{\mu\nu} + \frac{1}{2} \sum_{\lambda\sigma}^{N_{basis}} P_{\lambda\sigma} \left[ 2(\mu\nu|\lambda\sigma) - (\mu\sigma|\lambda\nu) \right] \quad (175)$$

Distribute the factor of 1/2:

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\lambda\sigma}^{N_{basis}} P_{\lambda\sigma} \left[ (\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\sigma|\lambda\nu) \right] \quad (176)$$

Sometimes, you'll see the ERIs coupled to the density matrix within another into a two-electron operator,  $G_{\mu\nu}$ .

$$F_{\mu\nu} = h_{\mu\nu} + G_{\mu\nu} \quad (177)$$

We have obtained a simpler expression for  $F_{\mu\nu}$ . The electronic energy  $E_{elec}$  is determined with the following:

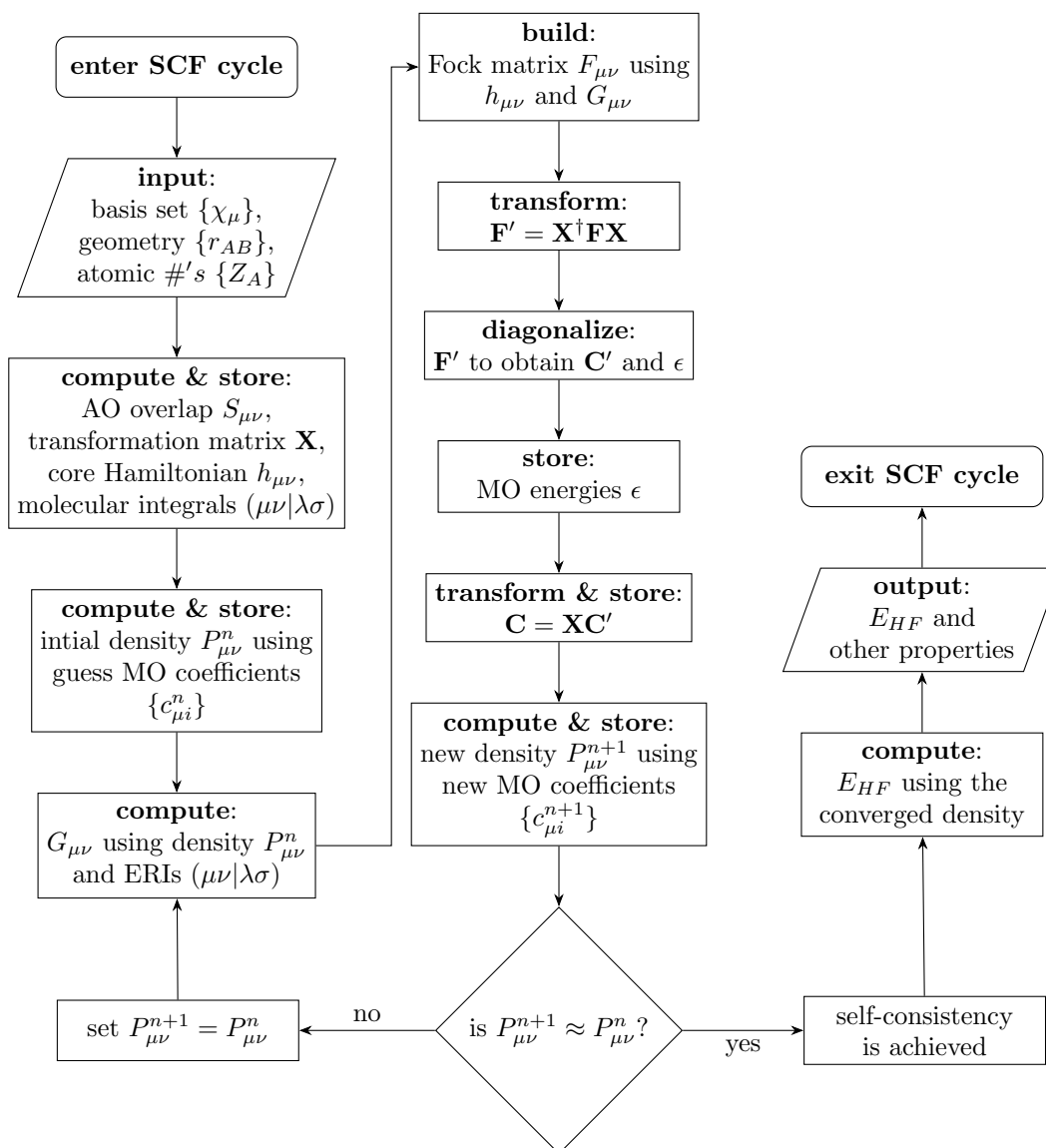
$$E_{elec} = \frac{1}{2} \sum_{\mu\nu}^{N_{basis}} P_{\mu\nu} \left[ h_{\mu\nu} + \sum_{\lambda\sigma}^{N_{basis}} P_{\lambda\sigma} \left[ (\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\sigma|\lambda\nu) \right] \right] \quad (178)$$

Adding the nuclear-nuclear repulsion energy  $V_{NN}$  and simplifying further yields the total HF energy:

$$E_{HF} = \frac{1}{2} \sum_{\mu\nu}^{N_{basis}} P_{\mu\nu} \left[ h_{\mu\nu} + G_{\mu\nu} \right] + V_{NN} \quad (179)$$

The benefit of using these forms of  $F_{\mu\nu}$  and  $E_{HF}$  is that they can be computed using basic matrix algebra. As such, they are quite intuitive to implement on a computer.

## Self-Consistent Field Procedure



The so-called **self-consistent field** (SCF) procedure presents a workflow to iteratively solve the many-electron problem. We begin by selecting a molecular geometry and a basis set of AOs. We then solve the integro-differential equations needed to construct the integrals, AO overlap, and the core Hamiltonian. With a set of guess MO coefficients, we create a guess density used to build the Fock matrix. We transform the Fock matrix, diagonalize it, and back-rotate the transformed orbitals. A new density is computed and compared to the old density. If they are sufficiently similar (by some arbitrary threshold), we proceed to calculate the total HF energy and other miscellaneous properties. If not, we set the newest density equal to the old density and loop back to the fock build step. The cycle repeats until the density converges. At which point we say that the system has reached self-consistency.

Needless to say, performing an SCF calculation can require a large amount of computational resources. The main numerical bottleneck is the computation and storage of the four-center molecular integrals, which scales  $\mathcal{O}(N^4)$ . In this instance,  $N$  is the number of AO basis functions. Increasing  $N$  will drastically increase the polynomial time complexity. This is where discretizing Hilbert space (i.e. truncating the basis) helps reduce the computational cost and keep things tractable, but at the expense of some degree of accuracy. As discussed earlier, some symmetry can be exploited. However, memory resource allocation will always be a rate-limiting step. Diagonalizing of the Fock matrix scales  $\mathcal{O}(N^3)$  times some multiplicative factor for every SCF cycle. The integrals only need to be computed once, so the secondary bottleneck is attributed to the Fock build step. Much progress has been made with respect to code optimization and hardware development that aim to accelerate the performance of HF programs.

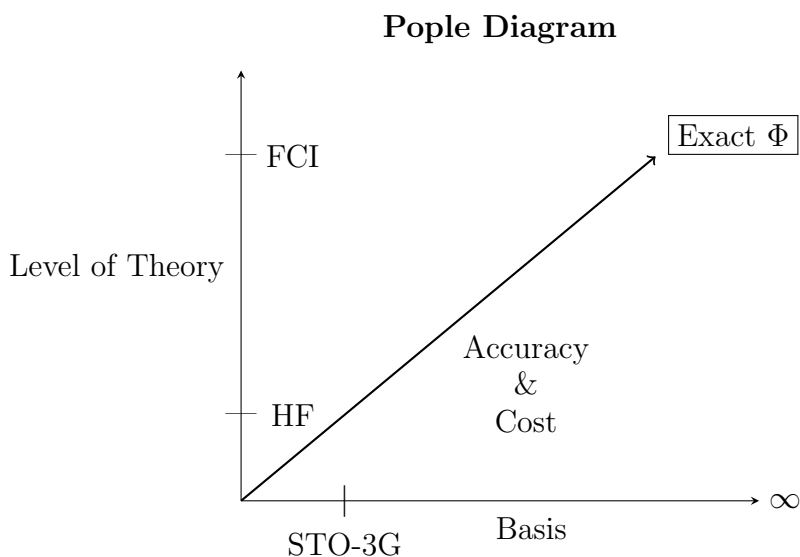
## Correlation

The term “correlation energy” is attributed to Löwdin who defined it as:

$$E_{corr} = \varepsilon_0 - E_{HF} \quad (180)$$

The missing correlation energy  $E_{corr}$  is the difference between the exact, non-relativistic energy  $\varepsilon_0$  and the HF energy  $E_{HF}$ . Post-Hartree-Fock methods emerged to go beyond the HF approximation. For example, there is Møller-Plesset perturbation theory (MP), configuration interaction (CI), and coupled cluster (CC)—all of which are higher echelons of theory that seek to add electron correlation. HF, on its own, has Fermi correlation. This type of correlation comes from the antisymmetry of fermions and, consequently, the action of the exchange operator on electrons with parallel spin. Experience with different levels of theory can help us build intuition for selecting the appropriate methods for chemical investigation.

Here we have a simple **Pople diagram**—a representation of the choices we have to make in order to balance chemical accuracy and computational cost.



## Afterthoughts

Other classes of HF methods can be obtained by varying the constraints on spin. In this document, we outlined **restricted Hartree-Fock** (RHF). In RHF,  $\alpha$  and  $\beta$  electrons share the same spatial functions and every orbital is doubly occupied—enforcing a closed-shell system. We will very briefly go over other versions of HF.

In **unrestricted Hartree-Fock** (UHF),  $\alpha$  and  $\beta$  electrons reside in separate orbitals. This permits our system to be open-shell. UHF solutions may suffer from spin contamination. This is a virtual artifact of a single determinant approximation. Because  $\alpha$  and  $\beta$  orbitals don't have to perfectly overlap like in RHF, the total spin-squared expectation value  $\langle \hat{S}^2 \rangle$  in UHF will be greater than or equal to the exact value for a specific spin state. Although an eigenstate of the  $\hat{S}_z$  operator, a spin contaminated wavefunction will not be an eigenstate of  $\hat{S}^2$  and, since  $\hat{S}^2$  commutes with the non-relativistic electronic Hamiltonian, calculated properties and bond dissociation energies will not be accurate. We say that a spin contaminated state possesses multi-determinantal character in that it will require a linear combination of degenerate or near-degenerate SDs to obtain the proper spin quantum numbers. Spin projection techniques can be used to rectify this problem. Obtaining UHF solutions requires solving two HF equations, one for  $\alpha$  orbitals and one for  $\beta$  orbitals. These are known as the **Pople–Nesbet equations**:

$$\mathbf{F}^\alpha \mathbf{C}^\alpha = \mathbf{S} \mathbf{C}^\alpha \epsilon^\alpha \quad (181)$$

$$\mathbf{F}^\beta \mathbf{C}^\beta = \mathbf{S} \mathbf{C}^\beta \epsilon^\beta \quad (182)$$



Lastly, in **general Hartree-Fock** (GHF), we lose both  $\hat{S}^2$  and  $\hat{S}_z$  symmetry. GHF puts no restrictions on the orbitals other than orthonormality. Because of this, we are allowed to project our spin-orbitals into the complex plane and use complex coefficients. So, the spin-orbitals may be written as a linear combination of  $\alpha$  and  $\beta$  spin components:

$$\chi_i(\mathbf{x}) = \psi_i^\alpha(\mathbf{r})\alpha(\omega) + \psi_i^\beta(\mathbf{r})\beta(\omega) \quad (183)$$

where

$$\psi_i^\alpha(\mathbf{r}) = \sum_{\mu}^N c_{\mu i}^\alpha \phi_{\mu}(\mathbf{r}) \quad \text{and} \quad \psi_i^\beta(\mathbf{r}) = \sum_{\mu}^N c_{\mu i}^\beta \phi_{\mu}(\mathbf{r}) \quad (184)$$

When either  $\{c_{\mu i}^\alpha\}$  or  $\{c_{\mu i}^\beta\}$  is zero for all  $\mu$  of orbital  $i$ , we would get the UHF case. Similarly, if  $\{c_{\mu i}^\alpha\}$  and  $\{c_{\mu i}^\beta\}$  happen to be the same, we fall into the RHF case. Hence, due to certain constraints, RHF and UHF are special cases of GHF.

By relieving our system of constraints, the increase in degrees of freedom can lead us to a lower variational solution. Albeit, at the cost of breaking symmetry.

HF methods have undergone extensive study and development. The reader is invited to investigate how HF methods compare with DFT or correlated wavefunction methods.

## Selected Exercises

1. In RHF, the density matrix is defined as  $P_{\mu\nu} = 2 \sum_i^{N_{elec}/2} c_{\mu i}^* c_{\nu i}$ . Note that the density matrix is self-adjoint,  $\mathbf{P} = \mathbf{P}^\dagger$ . The AO overlap matrix is defined as  $S_{\mu\nu} = \langle \mu | \nu \rangle$ . The trace of  $\mathbf{PS}$  is equal to the contraction of these two matrices. Show that  $\text{tr}(\mathbf{PS}) = N_{elec}$ .

2. Given that  $\mathbf{C}$  is a matrix of MO coefficients and that the  $\mathbf{S}$  is the AO overlap matrix, show that  $\mathbf{C}^\dagger \mathbf{S} \mathbf{C} = \mathbf{1}$ . How is this related to the MO overlap?

3. Show that  $\mathcal{J}$  and  $\mathcal{K}$  are invariant to unitary transformation.

Begin with the sum of  $\mathcal{J}$  over all occupied orbitals:

$$\sum_i^{N_{occ}} \mathcal{J}_i = \sum_i^{N_{occ}} \int \chi_i^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_i(\mathbf{x}_2) d\mathbf{x}_2$$

Transformed orbitals would be defined as:

$$\chi'_i = \sum_j^{N_{occ}} \chi_j U_{ji}$$

4. Diagonalize the transformed Fock matrix  $\mathbf{F}'$  to obtain eigenvector matrix  $\mathbf{C}'$  and eigenvalue matrix  $\mathbf{E}$ . Use  $\mathbf{C}'$  to rotate back to  $\mathbf{C}$ .

$$\mathbf{F}' = \begin{bmatrix} 0.098604 & -0.739481 \\ -0.739481 & 0.098604 \end{bmatrix}$$

5. In RHF, the total SCF energy is sometimes written as:

$$E_{HF} = \frac{1}{2} \left[ \text{tr} \left[ P_{\mu\nu} (h_{\mu\nu} + F_{\mu\nu}) \right] \right] + V_{NN}$$

Given  $\mathbf{P}$ ,  $\mathbf{H}$ , and  $\mathbf{F}$  below, compute  $E_{HF}$ . Let  $V_{NN} = 0.881962$  Hartrees.

$$\mathbf{F} = \begin{bmatrix} -0.457044 & -0.665389 \\ -0.665389 & -0.457044 \end{bmatrix} \quad \mathbf{H} = \begin{bmatrix} -1.220844 & -1.129914 \\ -1.129914 & -1.220844 \end{bmatrix}$$

$$\mathbf{P} = \begin{bmatrix} 0.570971 & 0.570971 \\ 0.570971 & 0.570971 \end{bmatrix}$$