Introduction to the Hartree-Fock Method and Basis Sets

Dibyajyoti Chakravarti
Department of Physical and Chemical Sciences,
University of L'Aquila, Italy
15/10/2024

Some reference books to follow

- 1. **Molecular Quantum Mechanics** by Peter W. Atkins
- 2. **Quantum Chemistry** by Ira N. Levine

Agenda

- 1. Introduction to Quantum Chemistry
- 2. Hartree-Fock Approximation
- 3. Mathematical Foundation
- 4. Self-Consistent Field (SCF) Procedure
- 5. Basis Sets in Hartree-Fock
- 6. Limitations and Extensions
- 7. Applications in Chemistry and Physics
- 8. Conclusion

What is Quantum Chemistry?

$$H(t)\,|\,\psi(t)\rangle = i\hbar \frac{d}{dt}\,|\,\psi(t)\rangle$$

- Application of quantum mechanics to chemical systems.

- Behavior of atoms, molecules, and their interactions by considering the quantum nature of particles (electrons, protons, neutrons)

- Explain molecular structures, predict reaction outcomes, understand spectroscopic properties, and design new materials or drugs at the molecular level.

Schrödinger Equation and the Molecular Hamiltonian

In quantum chemistry, for multi-electron systems (such as atoms and molecules), the Schrödinger equation becomes more complex due to the interactions between multiple electrons and the nucleus.

- Our aim is to solve the nonrelativistic time-independent Schrödinger equation of a molecular system (in S.I. units):

$$\hat{\tilde{H}}_{\mathrm{mol}}\tilde{\Psi}_k = \tilde{U}_k\tilde{\Psi}_k, \qquad k = 0, 1, 2, \ldots$$

- In the absence of external (electric and magnetic) fields, the molecular Hamiltonian reads:

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

- The kinetic energy operators are (in S.I. units):

$$\hat{\tilde{T}}_n = -\sum_{A=1}^{N} \frac{\hbar^2}{2\tilde{m}_A}\tilde{\Delta}_A, \qquad \hat{\tilde{T}}_e = -\sum_{\mu=1}^{n} \frac{\hbar^2}{2\tilde{m}_e}\tilde{\Delta}_\mu, \qquad \tilde{\Delta} = \left(\frac{\partial^2}{\partial\tilde{x}^2} + \frac{\partial^2}{\partial\tilde{y}^2} + \frac{\partial^2}{\partial\tilde{z}^2}\right)$$

Schrödinger Equation and the Molecular Hamiltonian

- The potential energy operators are (in S.I. units):

$$\hat{\tilde{V}}_{nn} = \sum_{B=2}^{N}\sum_{A=1}^{B-1} \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 |\tilde{\mathbf{r}}_A - \tilde{\mathbf{r}}_B|} = \sum_{B=2}^{N}\sum_{A=1}^{B-1} \frac{Z_A Z_B e^2}{4\pi\varepsilon_0\, \tilde{r}_{AB}}$$

$$\hat{\tilde{V}}_{ne} = -\sum_{A=1}^{N}\sum_{\nu=1}^{n} \frac{Z_A e^2}{4\pi\varepsilon_0 |\tilde{\mathbf{r}}_A - \tilde{\mathbf{r}}_\nu|} = -\sum_{A=1}^{N}\sum_{\nu=1}^{n} \frac{Z_A e^2}{4\pi\varepsilon_0\, \tilde{r}_{A\nu}}$$

$$\hat{\tilde{V}}_{ee} = \sum_{\nu=2}^{n}\sum_{\mu=1}^{\nu-1} \frac{e^2}{4\pi\varepsilon_0 |\tilde{\mathbf{r}}_\mu - \tilde{\mathbf{r}}_\nu|} = \sum_{\nu=2}^{n}\sum_{\mu=1}^{\nu-1} \frac{e^2}{4\pi\varepsilon_0 \tilde{r}_{\mu\nu}}$$

- We introduce atomic units, which simplify the equations drastically. Consider the dimensionless variable $r = \tilde{r}/a_0$, where a_0 is the Bohr radius, $a_0 = 52.917\,721\,0544(82)$ pm.

- The Coulomb repulsion between two electrons at a distance $\tilde{r}$ can then be written as:

$$\hat{\tilde{V}} = \frac{e^2}{4\pi\varepsilon_0\, \tilde{r}} = \frac{e^2}{4\pi\varepsilon_0\, r\, a_0}$$

Atomic units (a.u.)

- Also $\hat{V}$ is dimensionless!

- We abbreviate $e^2/4\pi\varepsilon_0\, a_0$ as $E_{\rm h}$: Hartree, the unit of energy.
  $E_{\rm h} = 4.359\,744\,722\,2060(48) \times 10^{-18}$ J.

  Easy to remember: $\quad 0.04\, E_{\rm h} \cong 1\text{ eV} \cong 100\text{ kJ/mol} \cong 10{,}000\text{ cm}^{-1}$

- Hence, $\hat{V} = \hat{\tilde{V}}/E_{\rm h}$, or $\hat{\tilde{V}} = \hat{V} \times E_{\rm h}$.

- **What about kinetic energy?** The general kinetic energy operator is: $\hat{\tilde{T}} = -\hbar^2/(2\tilde{m})\tilde{\Delta}$.
  In terms of the dimensionless mass $m = \tilde{m}/m_e$ and dimensionless Laplacian
  $\Delta = a_0^2\tilde{\Delta}$, we obtain

$$\hat{\tilde{T}} = -\frac{1}{2m}\left(\frac{\hbar^2}{m_e a_0^2}\right)\Delta$$

- Indeed, we find that $E_{\rm h} = \hbar^2/m_e a_0^2$ and hence, $\hat{T} = -\frac{1}{2m}\Delta$.

The molecular Hamiltonian in a.u.

$$\hat{H}_{\mathrm{mol}} = \hat{T}_n + \hat{T}_e + \hat{V}_{nn} + \hat{V}_{ne} + \hat{V}_{ee}, \quad \text{with}$$

$$\hat{T}_n = -\sum_A \frac{1}{2m_A}\Delta_A, \quad \hat{T}_e = -\sum_\mu \frac{1}{2}\Delta_\mu,$$

$$\hat{V}_{nn} = \sum_{A<B} \frac{Z_A Z_B}{r_{AB}}, \quad \hat{V}_{ne} = -\sum_{A,\nu} \frac{Z_A}{r_{A\nu}}, \quad \hat{V}_{ee} = \sum_{\mu<\nu} \frac{1}{r_{\mu\nu}}$$

Without going into detailed derivations, we will present the final electronic Schrodinger equation which is obtained after imposing the Born-Oppenheimer approximation (electronic and nuclear coordinates are treated independently).

The electronic Schrodinger equation

- The electronic SE reads:

$$\hat{H}\Phi_\kappa = E_\kappa \Phi_\kappa, \qquad \text{with } \hat{H} = T_e + \hat{V}_{nn} + \hat{V}_{ne} + \hat{V}_{ee}$$

- In the following, we are only concerned with the electronic Hamiltonian $\hat{H}$.

- However, the exact solution of the electronic SE is hopeless.

- Therefore, we shall apply the variation method,

$$E[\Phi] = \langle \Phi | \hat{H} | \Phi \rangle / \langle \Phi | \Phi \rangle \geq E_0, \qquad \delta_\Phi E[\Phi] = 0 \leftrightarrow \Phi = \text{exact}$$

- If the energy functional (i.e., the expectation value) is stationary with respect to all possible variations δ_Φ in the function Φ, then Φ is the exact solution.

Origin of the Hartree-Fock (HF) Method

- The Hartree-Fock method, developed by Douglas Hartree and Vladimir Fock around 1927-1930, represents a pivotal step in quantum chemistry.

- By incorporating the Pauli Exclusion Principle and using self-consistent fields and Slater determinants, it provided a workable approximation for multi-electron systems.

- Over time, refinements like the Roothaan-Hall equations and increased computational power made it a vital tool for studying molecular systems.

- Despite its limitations, particularly regarding electron correlation, it remains a fundamental technique in computational chemistry.

Basic Assumptions of Hartree-Fock method

- **Born-Oppenheimer approximation:** Assumes nuclei are fixed, focusing on the electronic wavefunction.

- **Independent particles:** Each electron moves in a mean field created by the others. Does not fully account for the instantaneous repulsion between electrons (known as, electron correlation).

- **Orbital approximation:** The total wavefunction is approximated by single-electron orbitals (i.e. the exact solution of the one-electron Schrodinger equation).

- **Single Slater determinant:** A determinantal form of the electronic wavefunction is used to ensure antisymmetry of fermions and obeying the Pauli Exclusion Principle. Only considers the ground-state wavefunction with a single Slater determinant.

The Wavefunction in Hartree-Fock

- Slater Determinant (SD):

Fundamental construct in quantum chemistry that ensures the correct antisymmetric behavior of the wavefunction for systems of fermions, such as electrons.

The Pauli Exclusion Principle states that no two fermions can occupy the same quantum state simultaneously.

$$\Psi(\mathbf{r_1}, \mathbf{r_2}, \ldots, \mathbf{r_i}, \mathbf{r_j}, \ldots) = -\Psi(\mathbf{r_1}, \mathbf{r_2}, \ldots, \mathbf{r_j}, \mathbf{r_i}, \ldots)$$

- $\mathbf{r_1}, \mathbf{r_2}, \ldots, \mathbf{r_N}$ are the spatial coordinates of the N electrons.
- $\phi_1(\mathbf{r}), \phi_2(\mathbf{r}), \ldots, \phi_N(\mathbf{r})$ are the spin-orbitals occupied by the electrons.
- The factor $\frac{1}{\sqrt{N!}}$ normalizes the wavefunction.

$$\Psi(\mathbf{r_1}, \mathbf{r_2}, \ldots, \mathbf{r_N}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r_1}) & \phi_2(\mathbf{r_1}) & \cdots & \phi_N(\mathbf{r_1}) \\ \phi_1(\mathbf{r_2}) & \phi_2(\mathbf{r_2}) & \cdots & \phi_N(\mathbf{r_2}) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathbf{r_N}) & \phi_2(\mathbf{r_N}) & \cdots & \phi_N(\mathbf{r_N}) \end{vmatrix}$$

Simple Example: Two-Electron System

Consider a two-electron system where the electrons occupy spin-orbitals $\phi_1(\mathbf{r})$ and $\phi_2(\mathbf{r})$. The Slater determinant for this system is:

$$\Psi(\mathbf{r_1}, \mathbf{r_2}) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(\mathbf{r_1}) & \phi_2(\mathbf{r_1}) \\ \phi_1(\mathbf{r_2}) & \phi_2(\mathbf{r_2}) \end{vmatrix}$$

Expanding the determinant:

$$\Psi(\mathbf{r_1}, \mathbf{r_2}) = \frac{1}{\sqrt{2}} \left(\phi_1(\mathbf{r_1})\phi_2(\mathbf{r_2}) - \phi_2(\mathbf{r_1})\phi_1(\mathbf{r_2}) \right)$$

This expression is antisymmetric under the exchange of electrons 1 and 2 (swapping $\mathbf{r_1}$ and $\mathbf{r_2}$) because it changes sign. If $\phi_1 = \phi_2$, the wavefunction becomes zero, reflecting the Pauli Exclusion Principle.

Why a Single Slater Determinant is used in HF?

- The many-electron Schrödinger equation is highly complex due to the **electron-electron interactions**, making it nearly impossible to solve exactly for systems with more than one electrons.

- By using a **single-determinant** wavefunction, the Hartree-Fock method simplifies the problem by treating the total wavefunction as a product of **one-electron orbitals** (spin-orbitals) that can be optimized individually.

- Allows for easier mathematical manipulation and the development of efficient computational algorithms.

- Many-electron problem is reduced to a set of **one-electron equations**, which are much easier to solve.

- Good Approximation for the Ground State for many systems, especially smaller atoms and molecules.

- **Foundation for Advanced Methods**: The single-determinant wavefunction serves as a starting point for more accurate theories.

Mathematical Foundations of Hartree-Fock method

The Many-Electron Schrödinger Equation

$$\hat{H}\Psi(\mathbf{r_1}, \mathbf{r_2}, \ldots, \mathbf{r_N}) = E\Psi(\mathbf{r_1}, \mathbf{r_2}, \ldots, \mathbf{r_N})$$

The Hamiltonian for a system of N electrons in the field of M nuclei is given by:

$$\hat{H} = -\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{|\mathbf{r_i} - \mathbf{R_A}|} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{|\mathbf{r_i} - \mathbf{r_j}|}$$

where:

- The first term represents the **kinetic energy** of the electrons,

- The second term represents the **Coulomb attraction** between electrons and nuclei (with nuclear charge Z_A at position $\mathbf{R_A}$),

- The third term represents the **Coulomb repulsion** between pairs of electrons.

Mathematical Foundations of Hartree-Fock method

Slater Determinant

$$\Psi_{\mathrm{HF}}(\mathbf{r_1}, \mathbf{r_2}, \ldots, \mathbf{r_N}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r_1}) & \phi_2(\mathbf{r_1}) & \cdots & \phi_N(\mathbf{r_1}) \\ \phi_1(\mathbf{r_2}) & \phi_2(\mathbf{r_2}) & \cdots & \phi_N(\mathbf{r_2}) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathbf{r_N}) & \phi_2(\mathbf{r_N}) & \cdots & \phi_N(\mathbf{r_N}) \end{vmatrix}$$

Here, $\phi_i(\mathbf{r})$ are the **spin-orbitals** (one-electron wavefunctions), which are to be determined.

The Variational Principle

For any approximate wavefunction Ψ_{approx}, the expectation value of the Hamiltonian provides an upper bound to the true ground-state energy E_0:

$$E[\Psi_{\mathrm{approx}}] = \frac{\langle \Psi_{\mathrm{approx}} | \hat{H} | \Psi_{\mathrm{approx}} \rangle}{\langle \Psi_{\mathrm{approx}} | \Psi_{\mathrm{approx}} \rangle} \geq E_0$$

In Hartree-Fock theory, the wavefunction Ψ is approximated by a **single Slater determinant** Ψ_{HF}, and the goal is to minimize the energy with respect to the orbitals that form the determinant.

Hartree-Fock Approximation

The Hartree-Fock method involves minimizing the expectation value of the energy E with respect to the wavefunction $|\Psi\rangle$, i.e.,

$$E = \langle \Psi | \hat{H} | \Psi \rangle$$

subject to the orthonormality of the orbitals:

$$\langle \phi_i | \phi_j \rangle = \delta_{ij}$$

Slater-Condon Rules

The **Slater-Condon rules** provide a systematic way to calculate matrix elements of one- and two-electron operators between Slater determinants.

- For a one-electron operator $\hat{H}_1$, the matrix element between two Slater determinants Φ and Φ' that differ only in a single orbital (but are otherwise identical) is:

$$\langle\Phi|\hat{H}_1|\Phi\rangle = \sum_i \langle\phi_i|\hat{h}_1|\phi_i\rangle$$

  where $\hat{h}_1$ is the one-electron operator and the sum is over all occupied orbitals ϕ_i.

- If two Slater determinants differ by a single electron (in a single orbital), the off-diagonal matrix element is simply the matrix element of the one-electron operator between those two orbitals:

$$\langle\Phi'|\hat{H}_1|\Phi\rangle = \langle\phi_i|\hat{h}_1|\phi_j\rangle$$

- If the two determinants differ by more than one orbital, the matrix element vanishes.

Slater-Condon Rules

The matrix elements of a two-electron operator $\hat{H}_2$ between two Slater determinants depend on the Coulomb and exchange integrals. For example, the diagonal matrix element of a two-electron repulsion operator is:

$$\langle \Phi | \hat{H}_2 | \Phi \rangle = \sum_{i,j} \left(\langle \phi_i \phi_j | \hat{h}_2 | \phi_i \phi_j \rangle - \langle \phi_i \phi_j | \hat{h}_2 | \phi_j \phi_i \rangle \right)$$

where $\hat{h}_2$ represents the two-electron repulsion operator.

Hartree-Fock Energy Expression

The **Hartree-Fock energy** E_{HF} is expressed in terms of the spin-orbitals $\phi_i(\mathbf{r})$ and consists of several contributions:

$$E_{\text{HF}} = \sum_{i=1}^{N} \langle \phi_i | \hat{h} | \phi_i \rangle + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left[\langle \phi_i \phi_j | \frac{1}{|\mathbf{r_i} - \mathbf{r_j}|} | \phi_i \phi_j \rangle - \langle \phi_i \phi_j | \frac{1}{|\mathbf{r_i} - \mathbf{r_j}|} | \phi_j \phi_i \rangle \right]$$

where:

- $\hat{h}$ is the **one-electron Hamiltonian**, which includes the kinetic energy and the electron-nuclear attraction,

- The first term represents the sum of the **one-electron energies** for each orbital,

- The second term represents the **electron-electron repulsion** (Coulomb interaction),

- The third term is the **exchange interaction**, which arises due to the antisymmetry of the wavefunction.

Fock Operator

The Fock operator is defined as:

$$\hat{f} = \hat{h} + \sum_{j=1}^{N} \left(\hat{J}_j - \hat{K}_j \right)$$

where:

- $\hat{h}$ is the one-electron Hamiltonian,

- $\hat{J}_j$ is the **Coulomb operator**, which represents the classical electron-electron repulsion,

- $\hat{K}_j$ is the **exchange operator**, which represents the quantum mechanical exchange interaction due to the antisymmetric nature of the wavefunction.

Introduction to one-electron and two-electron integrals

One-Electron Hamiltonian Integrals

- One-electron integrals h_{pq} describe the **kinetic energy** of electrons and their attraction to the nuclei.

  The **one-electron Hamiltonian** for an electron is given by:

  $$\hat{h}(i) = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M} \frac{Z_A}{|\mathbf{r_i} - \mathbf{R_A}|}$$

  where:

  - ∇_i^2 is the Laplacian operator representing the kinetic energy of the i-th electron,

  - Z_A is the charge of nucleus A,

  - $\mathbf{r_i}$ is the position vector of the i-th electron,

  - $\mathbf{R_A}$ is the position of nucleus A,

  - The sum is over all nuclei A.

One-electron Hamiltonian integrals

The **one-electron integrals** are expressed in terms of spin-orbitals ϕ_i, which represent the one-electron wavefunctions (including spin). These integrals are written as:

$$h_{pq} = \int \phi_p^*(\mathbf{r})\hat{h}\phi_q(\mathbf{r})\,d\mathbf{r}$$

where:

- $\hat{h}$ is the one-electron Hamiltonian,

- ϕ_p and ϕ_q are the spin-orbitals,

- The integral is performed over the spatial and spin coordinates of the electron.

One-electron Hamiltonian integrals

This integral has two contributions:

- **Kinetic energy term**: The first part represents the kinetic energy of the electron.

$$T_{pq} = \int \phi_p^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 \right) \phi_q(\mathbf{r})\, d\mathbf{r}$$

- **Nuclear attraction term**: The second part represents the attraction between the electron and the nuclei.

$$V_{pq}^{\text{nuc}} = -\sum_{A=1}^{M} Z_A \int \phi_p^*(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{R_A}|} \phi_q(\mathbf{r})\, d\mathbf{r}$$

Thus, the full one-electron integral is:

$$h_{pq} = T_{pq} + V_{pq}^{\text{nuc}}$$

Two-electron Hamiltonian integrals

Two-electron integrals $(pq|rs)$ describe the **Coulomb repulsion** between pairs of electrons, with the Coulomb integral J_{pq} and exchange integral K_{pq} representing the classical and quantum mechanical contributions, respectively.

Two-electron Hamiltonian integrals

The **two-electron Hamiltonian** for electrons i and j is given by:

$$\hat{V}_{ij} = \frac{1}{|\mathbf{r_i} - \mathbf{r_j}|}$$

This operator represents the repulsive Coulomb potential between two electrons located at $\mathbf{r_i}$ and $\mathbf{r_j}$

.

The corresponding **two-electron integrals** are written as:

$$(pq|rs) = \iint \frac{\phi_p^*(\mathbf{r_1})\phi_q(\mathbf{r_1})\phi_r^*(\mathbf{r_2})\phi_s(\mathbf{r_2})}{|\mathbf{r_1} - \mathbf{r_2}|} d\mathbf{r_1} d\mathbf{r_2}$$

where:

- ϕ_p, ϕ_q are spin-orbitals associated with electron 1,

- ϕ_r, ϕ_s are spin-orbitals associated with electron 2,

- $\mathbf{r_1}$ and $\mathbf{r_2}$ are the spatial coordinates of the two electrons.

Two-electron Hamiltonian integrals

This integral quantifies the repulsive interaction between the charge distributions described by the spin-orbitals $\phi_p(\mathbf{r_1})$ and $\phi_q(\mathbf{r_1})$ for electron 1, and $\phi_r(\mathbf{r_2})$ and $\phi_s(\mathbf{r_2})$ for electron 2.

There are two key contributions to the two-electron integrals in the Hartree-Fock method:

- **Coulomb Integral** J_{pq}: Represents the classical electrostatic repulsion between the charge distributions associated with two electrons. It quantifies the repulsion between electrons p and q

  .

$$J_{pq} = (pq|pq)$$

- **Exchange Integral** K_{pq}: Arises from the quantum mechanical requirement that the wavefunction be antisymmetric with respect to the exchange of two electrons. The exchange integral is a non-classical term that has no classical counterpart.

$$K_{pq} = (pq|qp)$$

Hartree-Fock Equations

In atomic units (which simplify the equations by setting fundamental constants like $\hbar = 1$ and the electron charge to 1), the **Fock operator** $\hat{f}(i)$ is the central operator that governs the motion of each electron in the system. For an electron i, the **Hartree-Fock equations** take the form of a set of one-electron eigenvalue equations:

$$\hat{f}(i)\phi_i(\mathbf{r_i}) = \epsilon_i \phi_i(\mathbf{r_i})$$

where:

- $\hat{f}(i)$ is the **Fock operator** acting on the i-th electron,

- $\phi_i(\mathbf{r_i})$ is the **spin-orbital** of the i-th electron (a one-electron wavefunction that includes both spatial and spin coordinates),

- ϵ_i is the corresponding **orbital energy** of the i-th electron.

Hartree-Fock Equations

The integro-differential nature of the Hartree-Fock equations arises from the inclusion of the **Coulomb** and **exchange operators**. These operators are **integral operators** because they involve integrals over the spatial coordinates of other electrons. In the Hartree-Fock equation for electron i, the Fock operator $\hat{f}(i)$ depends on integrals over the coordinates of all other electrons. This means that the equation for each electron depends on the orbitals of all the other electrons, leading to a coupled system of equations.

The **Hartree-Fock equation** for each electron can be written as:

$$\left[-\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M} \frac{Z_A}{|\mathbf{r_i} - \mathbf{R_A}|} + \sum_{j=1}^{N} \left(\hat{J}_j(i) - \hat{K}_j(i) \right) \right] \phi_i(\mathbf{r_i}) = \epsilon_i \phi_i(\mathbf{r_i})$$

This is an **integro-differential equation** because it contains both **differential terms** (kinetic energy, nuclear attraction) and **integral terms** (Coulomb and exchange interactions).

The Self-consistent Field (SCF) procedure

The Hartree-Fock equations must be solved **iteratively** because the Fock operator depends on the spin-orbitals, which are also the unknowns in the equation. The procedure is as follows:

1. Start with an **initial guess** for the spin-orbitals $\{\phi_i\}$.

2. Construct the **Fock operator** $\hat{f}$ using the current guess for the orbitals.

3. Solve the **Fock equation** to obtain new orbitals.

4. Update the Fock operator with the new orbitals.

5. Repeat the process until the orbitals and Fock operator **converge** to a self-consistent solution.

This iterative method is called the **Self-Consistent Field (SCF) procedure**, and the final solution provides the Hartree-Fock energy and wavefunction.

Basis Sets in Hartree-Fock

In quantum chemistry, **basis sets** are a crucial mathematical tool used to describe the wavefunctions of electrons in atoms and molecules.

A wavefunction, which is a solution to the Schrödinger equation, represents the quantum state of a system.

Basis sets allow these wavefunctions to be approximated more efficiently in practical calculations.

Basis sets enable the quantum chemistry calculations by providing a set of predefined functions that can be linearly combined to approximate the actual wavefunction of the system.

1. **Gaussian-type orbitals (GTOs)**: Functions based on the Gaussian distribution, favored in computational chemistry due to their computational efficiency.

2. **Slater-type orbitals (STOs)**: More closely resemble the actual shape of atomic orbitals, but are less common due to being computationally more demanding.
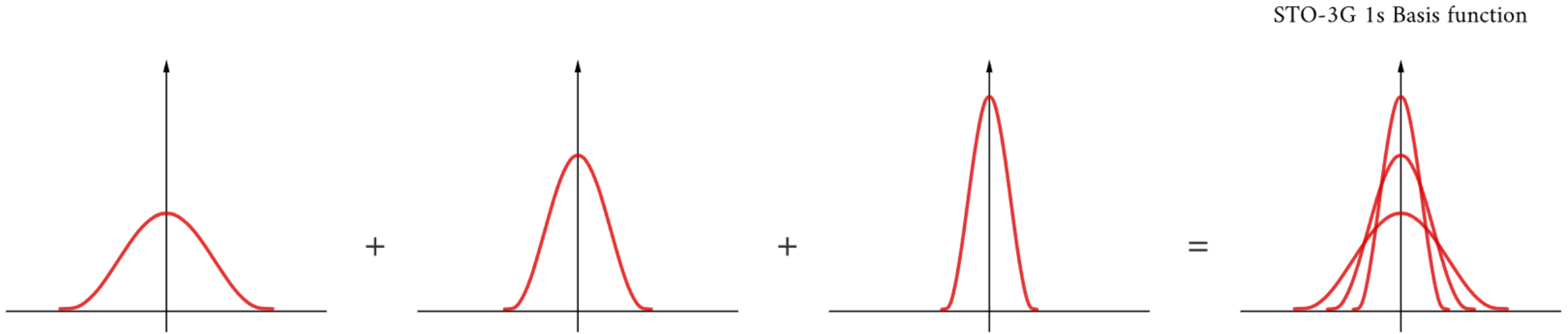
Gaussian Basis Sets

$$\Phi(r) = e^{-\alpha r}$$
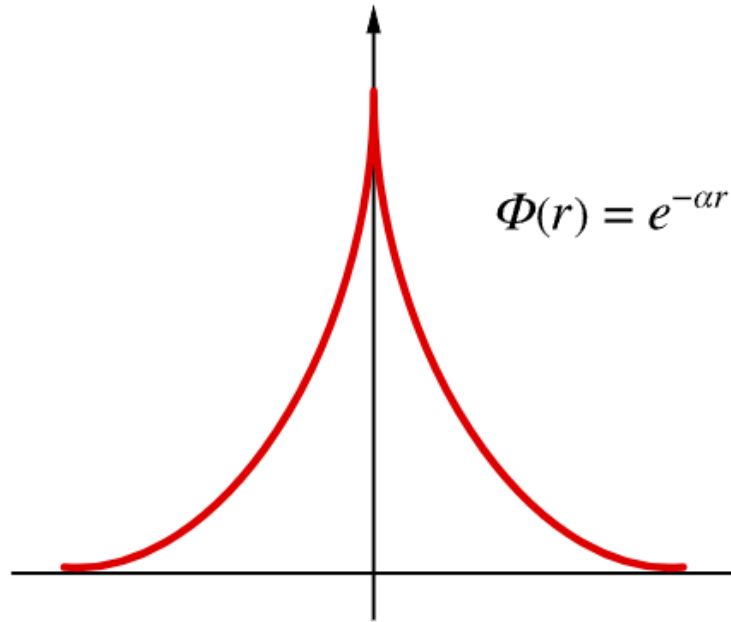
Slater - type 1s orbital

$$\Phi(r) = e^{-\alpha r^2}$$
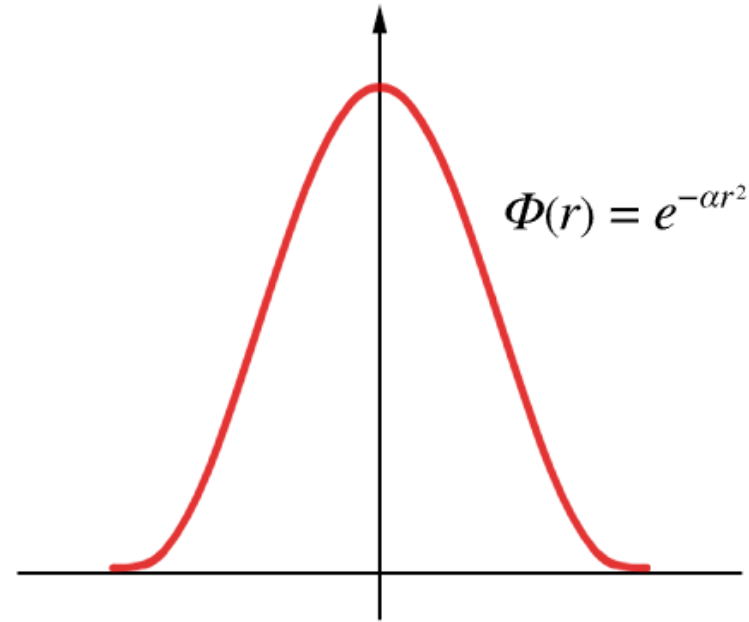
Gaussian - type 1s orbital

Unfortunately Gaussian functions do not match the shape of an atomic orbital very well. In particular, they are flat rather than steep near the atomic nucleus at r=0, and they fall off more rapidly at large values of r

Gaussian Basis Sets

STO-3G 1s Basis function

Each STO is replaced with a number of Gaussian functions with different values for the exponential parameter. These Gaussian functions form a *primitive Gaussian basis set*.

The linear combination of **primitive Gaussian functions** is called a **contracted Gaussian function**. Although more functions and more integrals now are part of the calculation, the integrals involving Gaussian functions are quicker to compute than those involving exponentials, so there is a net gain in the efficiency of the calculation.

Minimal Basis Sets

Minimal basis sets like STO-3G are used for small, preliminary calculations where computational efficiency is prioritized over accuracy.
While they provide a simplified description of the wavefunction, they are valuable for understanding basic molecular behavior without the computational cost of more advanced basis sets.

In a minimal basis set, each atomic orbital (such as 1s, 2s, 2p, etc.) is described by a single basis function.

- A hydrogen atom (with only a 1s orbital) is described by one basis function.

- A carbon atom (with 1s, 2s, and 2p orbitals) is described by five basis functions.

Minimal basis sets provide only a rough approximation of the molecular wavefunction. They are not flexible enough to capture subtle effects like polarization (where electron clouds shift during bonding) or electron correlation (interaction between electrons).

Pople Basis Sets (e.g. 6-31G)

Sir John Anthony Pople

(31 October 1925 – 15 March 2004)

Shared the Nobel Prize in Chemistry in 1998 for his development of computational methods in quantum chemistry

These basis sets go beyond the basic approximation provided by minimal sets by introducing additional functions that allow for better modeling of the electron distribution, especially in more chemically interesting situations like bonding, reactions, and molecular excitations.

6-31G Basis

The **6-31G** basis set is an example of a **split-valence basis set**, a widely used type of basis set that represents core and valence electrons differently. It provides more flexibility and accuracy by "splitting" the description of valence electrons into multiple components. The name 6-31G has a specific meaning that reflects how the basis set is constructed:

- **6**: The core electrons (closer to the nucleus) are described by a single basis function made up of a linear combination of **6 Gaussian functions**. This provides a rigid and stable representation of the core orbitals.

- **31**: The valence electrons (those involved in bonding and chemical reactions) are described by two sets of basis functions. The first is a combination of **3 Gaussian functions**, while the second is a single Gaussian function. This "split-valence" approach allows for more flexibility in modeling the behavior of the valence electrons compared to minimal basis sets.

Why is 6-31G More Accurate?

1. **Split-Valence Flexibility**: By splitting the valence electrons into two sets, the 6-31G basis set provides a more detailed representation of how these electrons behave, especially in chemical bonding situations. The valence orbitals are not forced into a rigid shape, so they can adapt better to the molecular environment, which leads to more accurate calculations.

2. **Improved Treatment of Electron Density**: The additional functions in the split-valence approach allow the basis set to better describe how electron density is distributed around atoms. This is crucial for calculating properties like molecular geometries, energies, and charge distributions.

3. **Greater Flexibility for Molecular Bonding**: In chemical reactions, electrons redistribute as bonds are formed or broken. A more complex basis set like 6-31G can account for these changes more accurately than a minimal basis set, which would give only a rough approximation.

Extensions of 6-31G for Further Accuracy

1. *Polarization Functions (6-31G)***:

   - In 6-31G*, extra functions (denoted by the asterisk, or *) are added to describe the **polarization** of electron clouds. Polarization occurs when electron clouds shift or distort in response to bonding interactions.

   - For example, adding d-type polarization functions for atoms like carbon or oxygen (denoted as 6-31G(d)) helps capture the electron density distortions that occur during chemical reactions, improving the accuracy of bond lengths, angles, and energies.

2. **Diffuse Functions (6-31+G):**

   - Diffuse functions, indicated by the "+" sign in 6-31+G, add basis functions with broader spatial distribution to better describe weakly bound electrons, such as those in anions or molecules with long-range interactions.

   - These functions are especially useful for systems with negative charges, excited states, or when modeling weak intermolecular forces like van der Waals interactions.

Choosing the Right Basis Set

Factors Influencing the Balance between **computational cost** and **accuracy:**

- **Accuracy of Results:**
 For **high-precision** molecular energies, geometry optimization, reaction paths, or electronic spectra - **large basis sets**.
For **quick, exploratory calculations** where ultra-high accuracy is not needed – **smaller basis** sets.

- **Computational Cost:**
Larger basis sets result in more matrix elements to calculate and store, which increases the memory requirements and the number of computational operations.
The scaling of computational cost with respect to the number of basis functions is often non-linear.

- **Size of the Molecular System**

Limitations of Hartree-Fock energy

Single Determinant Wavefunction

- The Hartree-Fock model works well qualitatively only for the ground state of molecules near their equilibrium geometry.

- The HF determinant is actually the lowest energy Slater determinant that can be formed in a given basis set. For a N-electron system, the lowest N spinorbitals are occupied in it.

- If there are M spinorbitals in a basis, there are $^{M}C_{N}$ number of Slater determinants possible, where the remaining spin-orbitals in a given basis set are occupied .

- Away from the equilibrium, these other Slater determinants come close in energy to the HF determinant and hence the single configuration picture collapses.

- As a result, there is a collapse in the variational SCF procedure and we get divergent outcomes.

Limitations of Hartree-Fock energy

Mean-Field Approximation

- Hartree-Fock is a **mean-field theory**, meaning each electron only "feels" the averaged influence of all other electrons. This simplification fails to account for the instantaneous repulsion between electrons in close proximity (known as dynamical correlation), which is significant in many chemical systems

- This limitation leads to an overestimation of the system's energy because it does not capture the dynamic adjustments that electrons make in response to each other's positions.

- Post-Hartree-Fock methods are needed to correct the energy. For example Configuration Interaction (CI), Møller–Plesset perturbation theory (MP2), or Coupled Cluster (CC) are often used to account for electron correlation.

Extension of Hartree-Fock

Unrestricted Hartree-Fock (UHF)

In systems with unpaired electrons (open-shell systems), the Restricted Hartree-Fock (RHF) method often performs poorly because it enforces equal spatial orbitals for both spin-up and spin-down electrons.

- **Open-shell systems** are molecular or atomic systems where some orbitals are partially filled, meaning there are unpaired electrons. These systems are common in:

  - Radicals (species with unpaired electrons)

  - Transition metal complexes

  - Certain molecules in excited states

To address this, **Unrestricted Hartree-Fock (UHF)** allows electrons with different spins to occupy different spatial orbitals:

- **α-electrons** (spin-up) and **β-electrons** (spin-down) are described by separate sets of molecular orbitals.

- This makes UHF more flexible for describing the spatial distribution of unpaired electrons in open-shell systems.

Unrestricted Hartree-Fock (UHF)

- One drawback of UHF is the issue of **spin contamination**. In UHF, the wavefunction is no longer a pure spin eigenfunction, which can lead to a mixing of different spin states (for example, mixing of singlet and triplet states).

- **Spin contamination** means that the computed UHF wavefunction may not represent a system with the correct total spin. For example, a doublet system (with spin = 1/2) might have contributions from states with higher spin multiplicities (e.g., triplets).

Unrestricted Hartree-Fock (UHF)

UHF is particularly useful in:

- **Radical Chemistry**: Describing systems with unpaired electrons, such as free radicals, transition metal complexes, and organic molecules in non-singlet states.

- **Excited States**: In molecules where electrons are promoted to higher energy levels, leaving unpaired electrons in molecular orbitals.

- **Magnetic Materials**: Studying magnetic properties in molecules or materials with multiple unpaired electrons.

- **Chemical Reactions**: Investigating reaction intermediates and transition states, especially in reactions involving unpaired electrons, such as those in organic radical reactions or combustion chemistry.
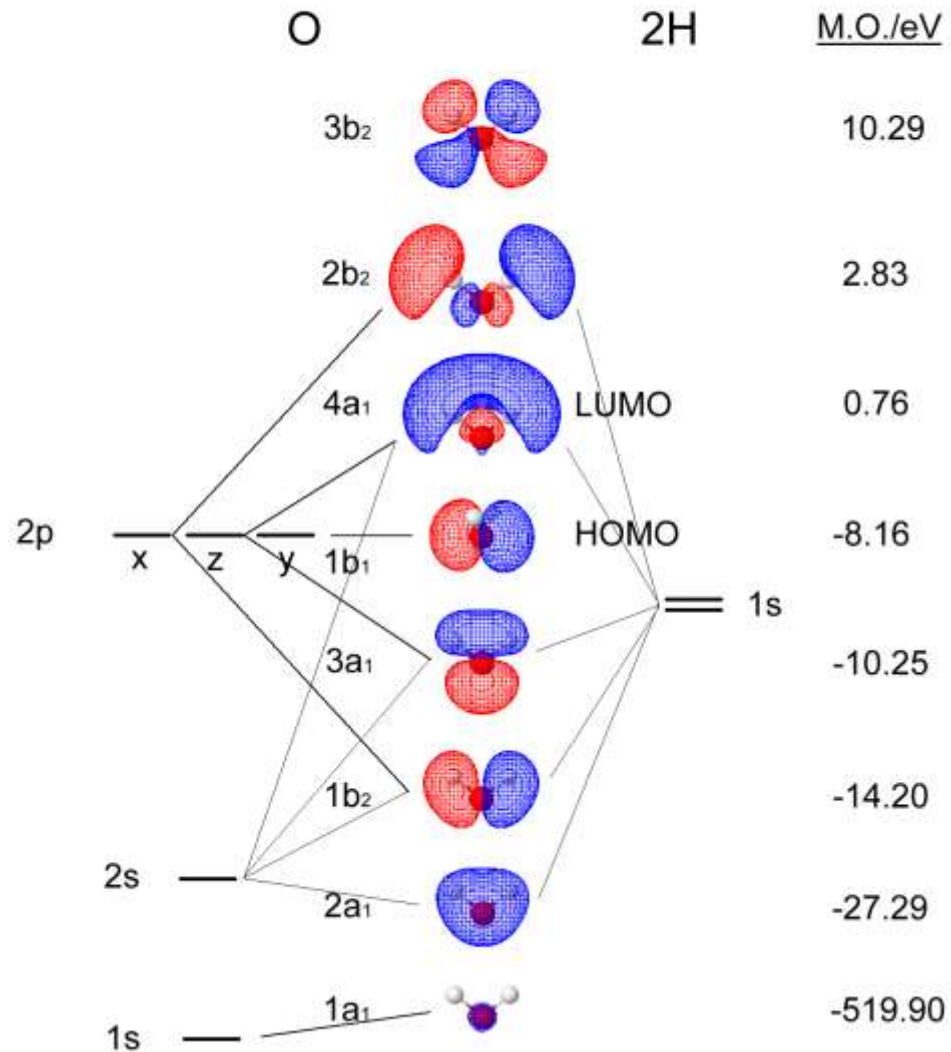
Applications of Hartree-Fock in Chemistry

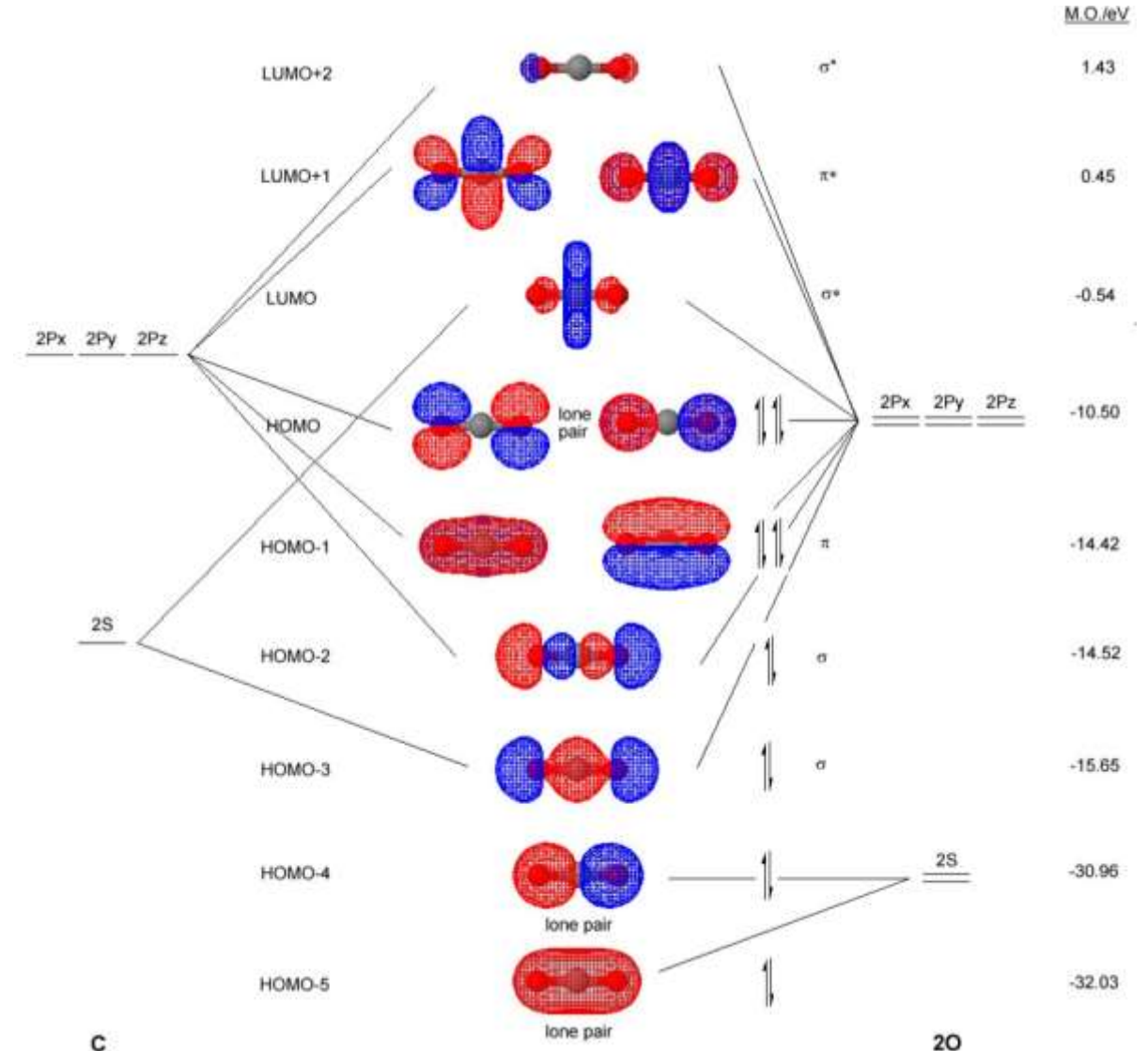**Using Hartree-Fock to predict and visualize molecular orbitals**

- After the SCF procedure converges, the Hartree-Fock method provides the energies (ϵ_i) of the molecular orbitals (MOs) and their shapes (the wavefunctions ϕ_i).

- The orbitals with the lowest energies are occupied by the system's electrons, according to the Pauli exclusion principle and Hund's rule.

Visualization of Hartree Fock molecular orbitals

Molecular Orbitals for Water

	O	2H	M.O./eV
3b₂			10.29
2b₂			2.83
4a₁		LUMO	0.76
1b₁	2p (x z y)	HOMO	-8.16
3a₁		1s	-10.25
1b₂			-14.20
2a₁	2s		-27.29
1a₁	1s		-519.90

Molecular Orbitals for Carbon Dioxide

		2Px 2Py 2Pz			M.O./eV
LUMO+2	σ*				1.43
LUMO+1	π*				0.45
LUMO	σ*				-0.54
HOMO	lone pair	2Px 2Py 2Pz			-10.50
HOMO-1	π				-14.42
HOMO-2	σ		2S		-14.52
HOMO-3	σ				-15.65
HOMO-4	σ	2S			-30.96
HOMO-5	lone pair				-32.03

c — 2O

Applications of Hartree-Fock in Chemistry

Predicting Molecular Properties

Geometry Optimization: Hartree-Fock calculations can be used to minimize the total energy of the molecule as a function of the positions of the nuclei. By adjusting the positions of the atoms and recalculating the electronic energy, the method identifies the optimal bond lengths that correspond to the lowest energy configuration.

Similar to bond lengths, the bond angles are optimized by minimizing the electronic energy with respect to the geometric arrangement of atoms.

In water, HF predicts a bond angle around 104.5° due to the repulsion between lone pairs and bond pairs, which causes the H–O–H bond to bend

Other properties that can be calculated: (a) Bond Dissociation Energy (b) Ionization energy (c) Vibrational frequencies (d) Dipole moments and Polarizabilities

Applications of Hartree-Fock in Physics

Hartree-Fock for Periodic Systems

$$\psi_k(r) = e^{ik \cdot r} u_k(r)$$

where $u_k(r)$ is a periodic function with the same periodicity as the crystal lattice, and k is the wavevector corresponding to the crystal momentum.

$$\left(-\frac{1}{2}\nabla^2 + V_{\text{ion}} + V_{\text{H}} + V_{\text{XC}} \right) \psi_i(r) = \varepsilon_i \psi_i(r)$$

Here:

- V_{ion} is the potential due to the ionic cores (periodic because of the crystal structure).

- V_{H} is the Hartree potential describing the mean-field electron-electron Coulomb interaction.

- V_{XC} is the exchange-correlation potential arising from the antisymmetry of the wavefunction (the Fock operator).

Hartree-Fock for solid state physics

- **Band Structure Calculations**: HF can be used to compute the electronic band structure of materials, where the exchange interaction can lead to more accurate descriptions of the energy bands, especially for wide-bandgap insulators or semiconductors.

- **Magnetic Properties**: The exchange term in Hartree-Fock plays a crucial role in determining magnetic properties like ferromagnetism or antiferromagnetism, which are often driven by exchange interactions between electron spins in solids.

- **Hartree-Fock+Methods**: HF is often combined with other techniques like HF+MP2 (for correlation), HF+GW (for quasiparticle corrections), or even as part of hybrid functionals in DFT (which blend HF exchange with DFT correlation).

Time-Dependent Hartree-Fock (TD-HF)

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

TDHF uses the **time-dependent Hartree-Fock equations**, which are derived from the TDSE under the assumption of a Slater determinant:

$$i\hbar\frac{\partial}{\partial t}\phi_i(t) = \hat{F}(t)\phi_i(t)$$

where $\phi_i(t)$ are the time-dependent single-particle orbitals, and $\hat{F}(t)$ is the **time-dependent Fock operator**, which includes the kinetic energy, potential energy, and time-varying mean field due to interactions between particles.

The **Fock operator** changes with time because the electron or nucleon densities, which generate the mean-field potential, evolve as the system evolves.

Main features of TD-HF

- **Time evolution of the orbitals**: Each orbital evolves according to the TDHF equations, which are numerically integrated over time to simulate the system's evolution.

- **Non-linear equations**: Like static Hartree-Fock, the TDHF equations are non-linear due to the dependence of the Fock operator on the orbitals themselves.

- **Effective one-body approximation**: Although the full many-body wavefunction is complex, TDHF reduces the problem to solving for a set of single-particle orbitals, where each particle moves in the mean field of all others.

- **Time-varying external fields**: TDHF is particularly useful for studying the response of a system to external perturbations, like electromagnetic fields, where the Hamiltonian is explicitly time-dependent.

Some Applications of TD-HF

- **Nuclear Physics**: TDHF is widely used to study nuclear reactions, such as collisions and fusion dynamics. It provides insight into the collective motion of nucleons and time-dependent phenomena in nuclei.

- **Quantum Chemistry**: In chemistry, TDHF can describe the time evolution of electronic systems in response to perturbations, like laser excitation, and is used in molecular dynamics simulations, optical response, and electronic excitations.

- **Condensed Matter Physics**: TDHF can model dynamic processes in solid-state systems, such as electron dynamics in response to ultrafast laser pulses or external fields.

Summarizing the key points on HF theory

Strengths of Hartree-Fock

- Simplicity and Conceptual Clarity
- First Step in Correlation Methods
- Computational Feasibility: Scales as $O(N^4)$
- Exchange Interactions
- Basis for Molecular Orbitals
- Application to Varied Systems

Weaknesses of Hartree-Fock

- Lack of Electron Correlation
- Overestimation of Energies
- Single Slater determinant wavefunction
- Poor Treatment of Excited States
- Inaccurate Potential Energy Surfaces

Hartree-Fock and Quantum Computing

Just like Hartree-Fock is a starting point in electronic structure theory, it is also the initial guess for finding the ground-state energy of a molecule in quantum chemistry simulations done by quantum algorithms.

In Variational Quantum Eigensolver (VQE), the HF method can be used to initialize variational circuits that explore more accurate wavefunctions, beyond the limitations of the classical approximations.

In Quantum Phase Estimation (QPE), the Hartree-Fock method provides a useful **starting point** for preparing the initial wavefunction.

The **Hartree-Fock reference state** can be used in algorithms to reduce the effects of quantum noise. By working from a known approximation, quantum error mitigation strategies can help refine and recover accurate results in energy estimations.

Quantum chemistry – a promising application for quantum computing

Predicting molecular structures, reaction mechanisms, and material properties—are all fundamentally governed by quantum mechanics.

As the size of a system grows, the number of possible configurations (or quantum states) increases exponentially, making classical simulations extremely resource-intensive.

Quantum computers, on the other hand, operate based on quantum principles (such as superposition and entanglement), which allow them to represent and process many possible configurations simultaneously. This could significantly reduce the computational complexity, enabling quantum computers to efficiently solve problems that are out of reach for classical systems.

Quantum chemistry – a promising application for quantum computing

Since molecules are quantum systems themselves, a quantum computer is naturally suited to simulate them. Quantum algorithms, like the **Variational Quantum Eigensolver (VQE)** and **Quantum Phase Estimation (QPE)**, are specifically designed to tackle problems such as finding ground-state energies and excited states of molecules.

Quantum computers could model how molecules interact at a subatomic level in a much more precise way, helping to discover new compounds and pharmaceuticals.

Thank you for your attention