Python to perform a basic DFT calculation on a simple molecule of Water and analyse its electronic structure.

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Introduction

The notebook contains a Density Functional Theory (DFT) analysis of a water molecule using the PySCF library. Here's a summary of the contents and findings, including an explanation of DFT, its importance, and the relevant code and libraries used.

What is DFT and Why is it Important?

Density Functional Theory (DFT) is a quantum mechanical method used to investigate the electronic structure of many-body systems, particularly atoms, molecules, and condensed matter. DFT provides a practical and relatively accurate way to study the electronic properties of materials by solving the Schrödinger equation approximately. It is widely used in physics, chemistry, and materials science due to its balance between accuracy and computational cost.

Importance of DFT:

- **Material Science:** Helps in designing new materials with specific properties.
- **Chemistry:** Aids in understanding chemical reactions and the properties of molecules.
- **Physics:** Provides insights into the electronic properties and behaviours of solids.

B3LYP Functional:

B3LYP is a popular hybrid exchange-correlation functional used within DFT. It combines:

1. **Becke's Three-Parameter Exchange Functional (B3):** A hybrid approach that mixes a portion of exact exchange from Hartree-Fock theory with exchange from other methods.
2. **Lee-Yang-Parr (LYP) Correlation Functional:** A correlation functional that accounts for electron correlation effects, providing an accurate description of the energy contributions due to electron-electron interactions.

The combination of these components in B3LYP provides a good balance between accuracy and computational efficiency, making it a popular choice for studying molecular systems.

The DFT energy obtained using the B3LYP functional includes several contributions:

1. **Kinetic Energy of Electrons:** The energy associated with the motion of electrons.
2. **Nuclear Attraction Energy:** The potential energy due to the attraction between the electrons and the nuclei.
3. **Electron-Electron Repulsion Energy:** The Coulomb repulsion energy between electrons.

4. **Exchange-Correlation Energy:** An essential term in DFT, which includes:
   - **Exchange Energy:** Arising from the Pauli exclusion principle and electron antisymmetry.
   - **Correlation Energy:** Accounts for electron-electron interactions not captured by a mean-field approach.

The B3LYP function is particularly effective for calculating the electronic properties of molecules, such as bond energies, molecular geometries, and electronic spectra. The DFT energy using B3LYP is often used as an approximation of the ground state energy of a molecular system, providing valuable insights into chemical reactivity, stability, and electronic structure.

Hartree-Fock (HF) Method

The **Hartree-Fock** method is a fundamental quantum mechanical approach used to approximate the electronic structure of atoms and molecules. It is based on the mean-field theory, which simplifies the complex many-electron problem into a system of single-electron equations. The key ideas behind the

Hartree-Fock method include:

- **Wavefunction Approximation:** The many-electron wavefunction of a system is approximated by a single Slater determinant, which is a mathematical construct representing the antisymmetrization of the product of single-electron wavefunctions (orbitals). This antisymmetrization ensures that the Pauli exclusion principle is satisfied, meaning that no two electrons can occupy the same quantum state.

- **Self-Consistent Field (SCF) Procedure:** The method iteratively solves for the optimal set of single-electron orbitals by minimising the total energy of the system. The procedure involves:
  - Starting with an initial guess for the electron orbitals.
  - Calculating the effective potential each electron experiences, which includes the nuclear attraction and the mean field created by all other electrons.
  - Solving the resulting equations to obtain a new set of orbitals.
  - Repeating the process until the orbitals converge to a stable solution.
- **Exchange Interaction:** The Hartree-Fock method explicitly accounts for the exchange interaction, a quantum mechanical effect that arises due to the indistinguishability of electrons and the requirement for the wavefunction to be antisymmetric with respect to the exchange of any two electrons.

Hartree-Fock Energy:

The Hartree-Fock energy is the total electronic energy of the system calculated using the Hartree-Fock method. It consists of several components:

- **Kinetic Energy:** The sum of the kinetic energies of all the electrons.

- **Nuclear Attraction Energy:** The energy due to the attraction between the electrons and the nuclei.
- **Electron-Electron Repulsion Energy:** The energy arising from the repulsion between electrons.
- **Exchange Energy:** A correction term due to the exchange interaction, which is a result of the antisymmetrization of the wavefunction.

The Hartree-Fock energy provides a useful approximation of the true ground state energy of the electronic system, but it does not account for electron correlation effects, which are interactions between electrons not captured by the mean-field approximation. More sophisticated methods, such as post-Hartree-Fock and Density Functional Theory (DFT), include these correlation effects for more accurate results.

Application and Code

Libraries Used:

- **PySCF (Python Strongly Constrained and Appropriately Normed):** A Python library for quantum chemistry, providing tools for DFT and other electronic structure methods.
- **Functions:**
    - `gto`: Defines the molecular geometry and basis set.
    - `scf`: Performs self-consistent field calculations (e.g., Hartree-Fock).
    - `dft`: Provides DFT functionalities including various functionals.

Code Summary:

1. **Define the Water Molecule:**
    - Cartesian coordinates are specified for the oxygen and hydrogen atoms.
    - A minimal basis set (STO-3G) is used.
2. **Set Molecular Properties:**
    - Charge: 0 (neutral molecule)
    - Spin: 0 (singlet state)
3. **Build the Molecule:**
    - Finalises the molecular structure setup.
4. **Perform Calculations:**
    - **Hartree-Fock (RHF) Calculation:** Computes the Hartree-Fock energy.
    - **DFT Calculation with B3LYP Functional:** Uses the B3LYP functional, a common choice in DFT, to compute the DFT energy.
5. **Analyse Results:**
    - Extracts molecular orbital (MO) energies, Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) energies, and calculates the HOMO-LUMO gap.

Findings and Implications

The DFT calculations revealed:

- **Hartree-Fock Energy: "-74.96306312972763 Hartree"**
- **DFT Energy (B3LYP): "-75.31258739989367 Hartree"**
- **HOMO Energy:** The energy level of the highest occupied molecular orbital. Calculated energy for water molecule is **"-0.1442125609860971 Hartree"**
- **LUMO Energy:** The energy level of the lowest unoccupied molecular orbital. Calculated energy for water molecule is **"0.355325315709403"**
- **HOMO-LUMO Gap:** The energy difference between the HOMO and LUMO, which indicates the electronic excitation energy. Calculated energy for water molecule is **"0.4995378766955001"**

Implications: The HOMO-LUMO gap is crucial for understanding the electronic properties of molecules. A smaller gap suggests higher reactivity and potential as a semiconductor. For water, the relatively large gap reflects its stability and low reactivity under normal conditions.

References

- **Chatgpt**
- **PySFC Documentations**