VQE - note

Son Nguyen

Basis Sets

- A basis set is a set of functions combined linearly to model molecular orbitals. Basis functions can be considered as representing the atomic orbitals of the atoms and are introduced in quantum chemical calculations because the equations defining the molecular orbitals are otherwise very difficult to solve.

  Slater-Type Orbitals (STO's)

  - These are functions used as atomic orbitals in the linear combination of atomic orbitals molecular orbital method.
  - STOs have the following radial part:

$$R(r) = Nr^{n-1}e^{-\zeta r} \tag{1}$$

  - Where:
    - n is a natural number that corresponds to the principal quantum number ($n = 1, 2, \ldots$).
    - N is a normalization constant.
    - r is the distance of the electron from the atomic nucleus.
    - ζ is a constant related to the effective nuclear charge, which is partly shielded by electrons. The effective nuclear charge can be estimated by Slater's rules.

LibreTexts

Basis Set Exchange

  Gaussian-type Orbitals (GTOs)

  - STOs are computationally difficult and it was later realized that these Slater-type orbitals could in turn be approximated as linear combination of Gaussian orbitals instead.

$$G(r) = N \cdot e^{-\alpha r^2} \tag{2}$$

  - where:
    - N is a normalization constant.
    - α controls the width of the Gaussian.
    - r is the distance between the electron and nucleus.

STO-3G basis set

- STO-nG basis sets are minimal basis sets. where n primitve Gaussian orbitals (GTOs) are fitted to a single Slater-type orbital (STO). n originally took the value of 2 - 6. A minimum basis set is where only sufficient orbitals are used to contain all the electrons in the neutral atom. The core and valence orbitals are represented by the same number of primitve Gaussian function ϕ_i

$$\phi STO \approx \sum_{i=1}^{3} c_i G_i(r) \tag{3}$$

- where:
  - $G_i(r)$ are the Gaussian functions centered at the atom, with exponents α_i controlling the spread of the Gaussian
  - c_i are the coefficients that weight each Gaussian function
  - r is the distance from the nucleus

Molecular orbital

- Using the linear combination of atomic orbitals (LCAO method) to construct the molecular orbitals

$$\Psi(r) = \sum_i c_i \phi_i(r) \tag{4}$$

- where:
  - $\phi_i(r)$ are the atomic orbitals represented by basis functions (in this case STO-3G).
  - c_i are coefficients obtained through HF method (still need to look into more)