Schrödinger Equation Solver

in Cartesian Gaussian Basis Sets

Reference: Modern Quantum Chemistry by Szabo & Ostlund

1. Read basis set information from file in NWChem format downloaded from EMSL Basis Set Library.
2. Read molecule information from XYZ file. (Elements and Coordinate)
3. Combine results of 1 and 2 to form contracted cartesian Gaussian basis functions.

$$CGF(\alpha_p; c_p; R_A; [lx, ly, lz]) = \sum_p c_p PGF(\alpha_p; R_A; [lx, ly, lz])$$

$$PGF(\alpha_p; R_A; [lx, ly, lz]) = N_{\alpha_p,[lx,ly,lz]} x^{lx} y^{ly} z^{lz} e^{-\alpha_p (r-R_A)^2}$$

For s-Gaussian, [lx, ly, lz] = [0,0,0]   [Eq. 3.203]

$$N_{\alpha_p,[lx,ly,lz]} = (2\alpha_p/\pi)^{3/4}$$

4. Evaluate Integrals on contracted cartesian gaussians
   - Overlap Integral **S** = (p|q) [Eq. A.9]
   - Kinetic Energy Integral **T** = (p|T|q) [Eq. A.11]
   - Nuclear-Electron Attraction Integral **V** = (p|V|q) [Eq. A.33]
   - Core Hamiltonian Integral **H** = (p|H|q) = (p|(T+V)|q) = **T** + **V**
   - Two-electron Integral (pq|rs) [Eq. A.41]
5. Solve the one-electron problem **HC** = e**SC**
   - Derivation

   1) $\mathbf{S}^{1/2} = \mathbf{U}\mathbf{s}^{1/2}\mathbf{U}^T$, where $\mathbf{S} = \mathbf{U}\mathbf{s}\mathbf{U}^T$, **U** = eigenvector matrix, **s** = eigenvalue matrix.

   2) $\mathbf{S} = \mathbf{S}^{1/2}\,\mathbf{S}^{1/2}$

   3) $\mathbf{HC} = e\mathbf{S}^{1/2}\mathbf{S}^{1/2}\mathbf{C}$

   4) $\mathbf{C}' = \mathbf{S}^{1/2}\mathbf{C}$, $\mathbf{C} = \mathbf{S}^{-1/2}\mathbf{C}'$

5) $\mathbf{HS^{-1/2}C'} = e\mathbf{S^{1/2}C'}$

6) $(\mathbf{S^{-1/2}HS^{-1/2}})\mathbf{C'} = (\mathbf{S^{-1/2}}e\mathbf{S^{1/2}})\mathbf{C'}$

7) $\mathbf{H'C' = eC'}$

- In forward steps

1) Diagonalize **S**, build $\mathbf{S^{-1/2}} = \mathbf{Us^{-1/2}U^T}$

2) Build $\mathbf{H'} = \mathbf{S^{-1/2}HS^{-1/2}}$

3) Diagonalize **H'** to obtain e and **C'**, the lowest eigenvalue e_0 is the electronic energy.

4) $\mathbf{C} = \mathbf{S^{-1/2}C'}$, **C** is the orbital coefficient matrix.

6. Evaluate the HF energy for n electron restricted closed-shell systems.

1) Number of doubly occupied orbitals $N_{docc} = N_{elec} / 2$

2) Build density matrix $D_{pq} = 2\sum_i C_{pi} \times C_{qi}$ $(i = 1 \ldots N_{docc})$

3) Build the restricted Fock matrix

$$F_{pq} = H_{pq} + \sum_{rs}^{N_{bas}} \left[D_{rs} \times (pq|rs) - \frac{1}{2} D_{rs} \times (pr|qs) \right]$$

4) Evaluate Hartree-Fock energy

$$E_{RHF} = \frac{1}{2} \sum_{pq}^{N_{bas}} D_{pq} \times \left(H_{pq} + F_{pq} \right)$$