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Problem:
Write the algorithm to solve Roothan-Hall matrix equation!

Answer:
The algorithm to solve this Roothan-Hall matrix equation is called self-consistent field (SCF) method.

1. **Preprocessing**
   The input of this equation is one-electron and two electron integral, in detail such as:
   - nuclear repulsion energy (E_{nuc})
   - overlap integrals ($\boldsymbol{S}_{\mu\nu}$)
   - one-electron kinectic energy integrals ($\boldsymbol{T}_{\mu\nu}$)
   - one-electron nuclear repulsion integrals ($\boldsymbol{V}_{\mu\nu}$) → with $\boldsymbol{T}_{\mu\nu}$ form the core Hamiltonian matrix ($\boldsymbol{H}_{\mu\nu}^{core} = \boldsymbol{T}_{\mu\nu} + \boldsymbol{V}_{\mu\nu}$)
   - two-electron repulsion integrals
   $(\mu\nu \mid \lambda\sigma)$

2. **Orthogonalization of the basis set: the $\boldsymbol{S}^{-1/2}$ matrix**
   a. Diagonalize the overlap matrix, $\boldsymbol{S}$,
   $$\boldsymbol{S}\boldsymbol{L}_{\boldsymbol{S}} = \boldsymbol{L}_{\boldsymbol{S}}\boldsymbol{\Lambda}_{\boldsymbol{S}}$$
   where $\boldsymbol{L}_{\boldsymbol{S}}$ is the matrix of eigenvectors and $\boldsymbol{\Lambda}_{\boldsymbol{S}}$ is a diagonal matrix (eigenvalues)

   b. Build the symmetric orthogonalization matrix, $\boldsymbol{S}^{-1/2}$, defined as
   $$\boldsymbol{S}^{-1/2} = \boldsymbol{L}_{\boldsymbol{S}}\boldsymbol{\Lambda}_{\boldsymbol{S}}^{-1/2}\tilde{\boldsymbol{L}}_{\boldsymbol{S}}$$
   $\tilde{\boldsymbol{L}}_{\boldsymbol{S}}$ is transpose of the matrix

3. **The initial (guess) of density matrix**
   a. Form an initial Fock matrix $\boldsymbol{F}'_0$, in the orthonormal basis using the core Hamiltonian
   $$\boldsymbol{F}'_0 = \tilde{\boldsymbol{S}}^{-1/2}\boldsymbol{H}^{core}\boldsymbol{S}^{-1/2}$$

   b. Diagonalize $\boldsymbol{F}'_0$, such that
   $$\boldsymbol{F}'_0\boldsymbol{C}'_0 = \boldsymbol{C}'_0\varepsilon_0$$

   c. Transform the resulting eigenvectors into the original (non-orthonormal) basis,
   $$\boldsymbol{C}_{\boldsymbol{0}} = \tilde{\boldsymbol{S}}^{-1/2}\boldsymbol{C}'_0$$

   d. Construct the initial-guess density matrix from $\boldsymbol{C}_{\boldsymbol{0}}$
   $$D^0_{\mu\nu} = \Sigma^{occ}_m (\boldsymbol{C}_{\boldsymbol{0}})^m_\mu (\boldsymbol{C}_{\boldsymbol{0}})^m_\nu$$
   where m is indexes column of $\boldsymbol{C}_{\boldsymbol{0}}$ and the summation includes onlu occupied (spatial) molecular orbitals.

   e. Compute the electronic and total (Born-Oppenheimer) energies
   $$E^0_{elec} = \Sigma^{AO}_{\mu\nu} D^0_{\mu\nu}(\boldsymbol{H}^{\boldsymbol{core}}_{\boldsymbol{\mu\nu}} + \boldsymbol{F}_{\boldsymbol{\mu\nu}}) \quad \& \quad E^0_{total} = E^0_{elec} + E_{nuc}$$
   where 0 denotes the initial SCF energy.

4. **The SCF iteration**

after the initial guess we can iterate the same procedure, after check the convergence if the energy and density metrix result.

a. For a new matrix, $\boldsymbol{F}$, that includes the two-electron integral contributions,

$$\boldsymbol{F}_{\mu\nu} = \boldsymbol{H}_{\mu\nu} + \Sigma_{\mu\nu}^{AO} D_{\mu\nu}[2(\mu\nu|\lambda\sigma) - (\mu\lambda|\nu\sigma)]$$

where the double summation runs over all the basis functions.

b. Transform the new Fock matrix to the orthonormal basis

$$\boldsymbol{F}' = \boldsymbol{S}^{-1/2}\,\boldsymbol{F}\,\boldsymbol{S}^{-1/2}$$

c. Diagonalize the transformed Fock matrix

$$\boldsymbol{F}'\boldsymbol{C}' = \boldsymbol{C}'\varepsilon$$

d. Transform the resulting eigenvectors into the original basis

$$\boldsymbol{C} = \boldsymbol{S}^{-1/2}\boldsymbol{C}'$$

e. Construct the new density matrix C

$$D_{\mu\nu}^{i} = \Sigma_{m}^{occ} (\boldsymbol{C})_{\mu}^{m} (\boldsymbol{C})_{\nu}^{m}$$

where *i* denotes the current iteration

f. Compute the new electronic and total energies

$$E_{elec}^{i} = \Sigma_{\mu\nu}^{AO} D_{\mu\nu}^{i} (\boldsymbol{H}_{\mu\nu}^{core} + \boldsymbol{F}_{\mu\nu}) \quad \& \quad E_{total}^{i} = E_{elec}^{i} + E_{nuc}$$

g. Test convergence of the density matrix and the electronic energy

$$rms_D = [\Sigma_{\mu\nu}^{AO} (D_{\mu\nu}^{i} - D_{\mu\nu}^{i-1})^2]^{1/2} < \delta_1 \quad \& \quad \Delta E = E_{elec}^{i} - E_{elec}^{i-1} < \delta_2$$

if the root-mean-square (rms_D) difference in the densities and/or the change in the electronic energy does not fall below the chosen thresholds, then return to the start this SCF iteration.

5. **Diagram of SCF**

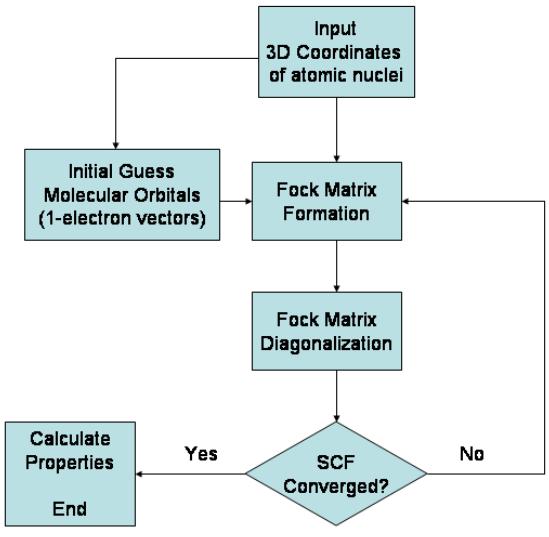

Image source: wikipedia

Ref: lecture notes Dr. Yukio Yamaguchi