HARTREE-FOCK

QMMM study group

July 21, 2018

BACKGROUND

SLATER DETERMINANT

We want a wavefunction that...

- made up of single particle functions
- is antisymmetric

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$$\Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) & \cdots & \chi_N(x_1) \\ \chi_1(x_2) & \chi_2(x_2) & \cdots & \chi_N(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(x_N) & \chi_2(x_N) & \cdots & \chi_N(x_N) \end{vmatrix}$$

SLATER DETERMINANT

The wavefunction can be expressed as

$$\Psi = \sum_{k}^{\infty} D_k \Phi_k$$

Hartree-Fock uses a single slater determinant to model ground state

$$\Psi_0 = \Phi$$

all effort goes to finding the best set of orbitals

VARIATIONAL PRINCIPLE

Exact wavefunction:

$$H\Psi_o = E_o\Psi_o$$

$$E_o = \frac{\langle\Psi_o|\,\hat{H}\,|\Psi_o\rangle}{\langle\Psi_o|\Psi_o\rangle}$$

Trial wavefunction:

$$H\Psi_T = E_o\Psi_T$$

$$E_T = \frac{\langle\Psi_T|\,\hat{H}\,|\Psi_T\rangle}{\langle\Psi_T|\Psi_T\rangle}$$

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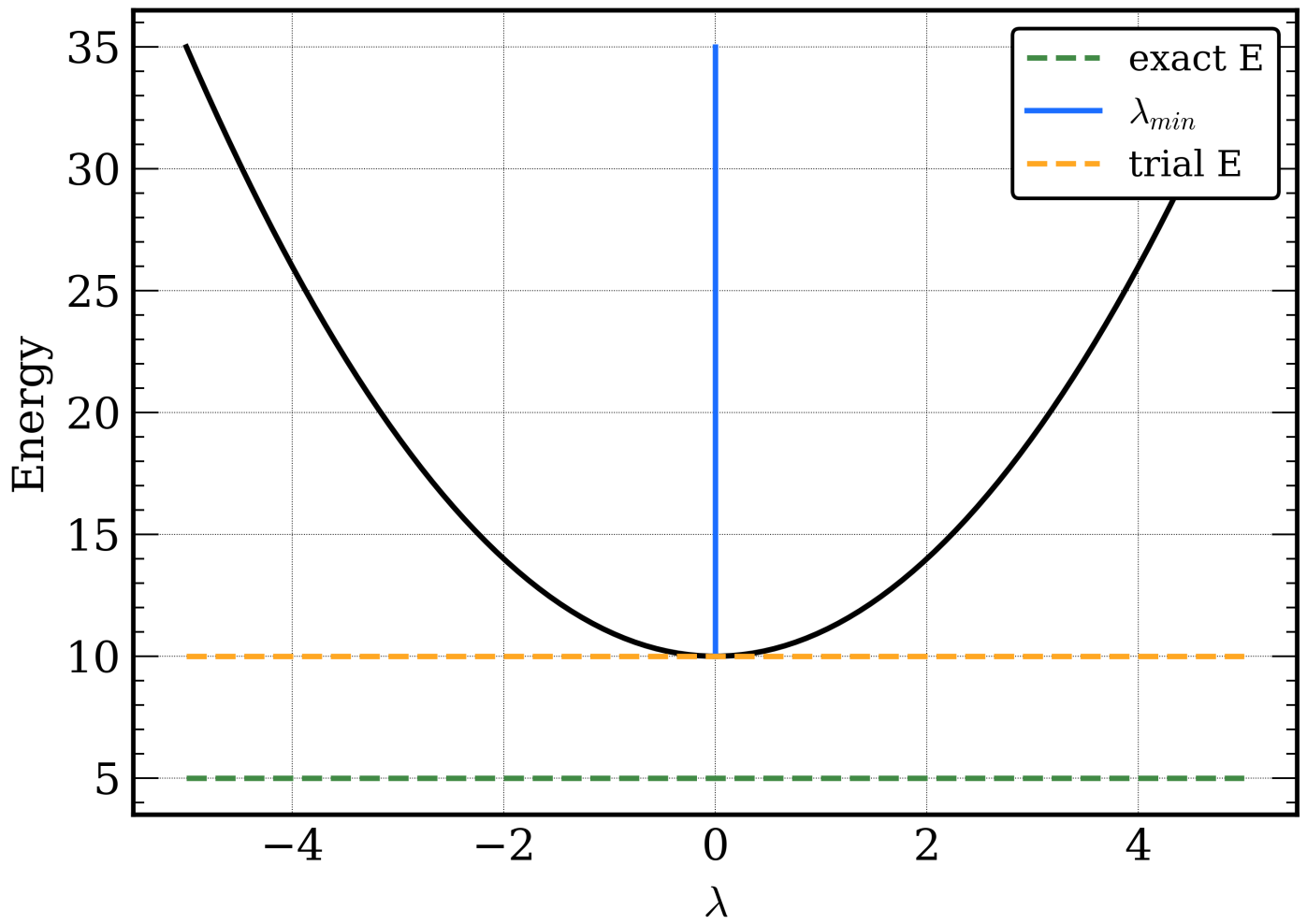
variational principle:

$$E_T \geq E_o$$


exact E
λ_{min}
trial E
Energy
35
30
25
20
15
10
5
−4
−2
0
2
4
λ

$$\hat{H} = \hat{T}_e + \hat{V}_{en} + \hat{V}_{ee} + \hat{V}_{nn}$$

first introduce born-oppenheimer approximation

$$\hat{H}_{el} = \hat{T}_e + \hat{V}_{en} + \hat{V}_{ee}$$

However, evaluation $\hat{V}_{ee}$ is still expensive

FOCK OPERATOR

$$F = H^{core} + G$$

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where

$$H^{core} = T + V$$

Kinetic

$$T_{\mu\nu} = (\mu \left| -\frac{\nabla}{2} \right| \nu) = \int dr \phi_\mu^*(r) \left(-\frac{\nabla}{2} \right) \phi_\nu(r)$$

Nuclear Attraction

$$V_{\mu\nu} = (\mu | r^{-1} | \nu) = \int dr \phi_\mu^*(r) r^{-1} \phi_\nu(r)$$

FOCK OPERATOR

$$F = H^{core} + G$$

$$G_{\mu\nu} = \sum_{\sigma}^{num\ ao} P_{\lambda\sigma}[2(\mu\nu|\lambda\sigma) - (\mu\lambda|\nu\sigma))]$$

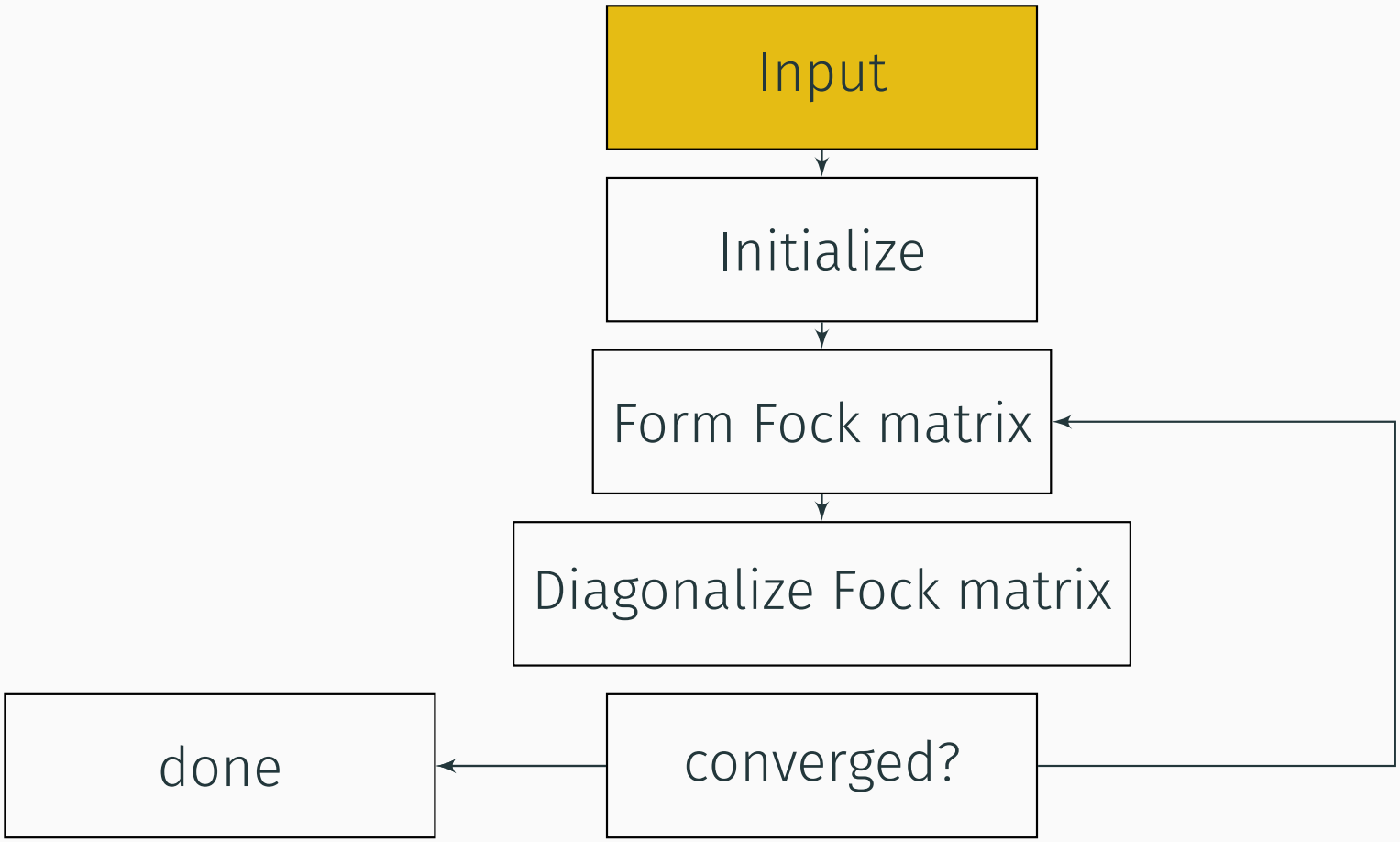
Two electron integrals

$$(\mu\nu|\lambda\sigma) = \int dr_1 dr_2 \phi_\mu^*(r_1)\phi_\nu(r_1) r_{12}^{-1} \phi_\lambda(r_2)\phi_\sigma(r_2)$$

$$(\mu\lambda|\nu\sigma) = \int dr_1 dr_2 \phi_\mu^*(r_1)\phi_\lambda(r_1) r_{12}^{-1} \phi_\nu(r_2)\phi_\sigma(r_2)$$

ALGORITHM

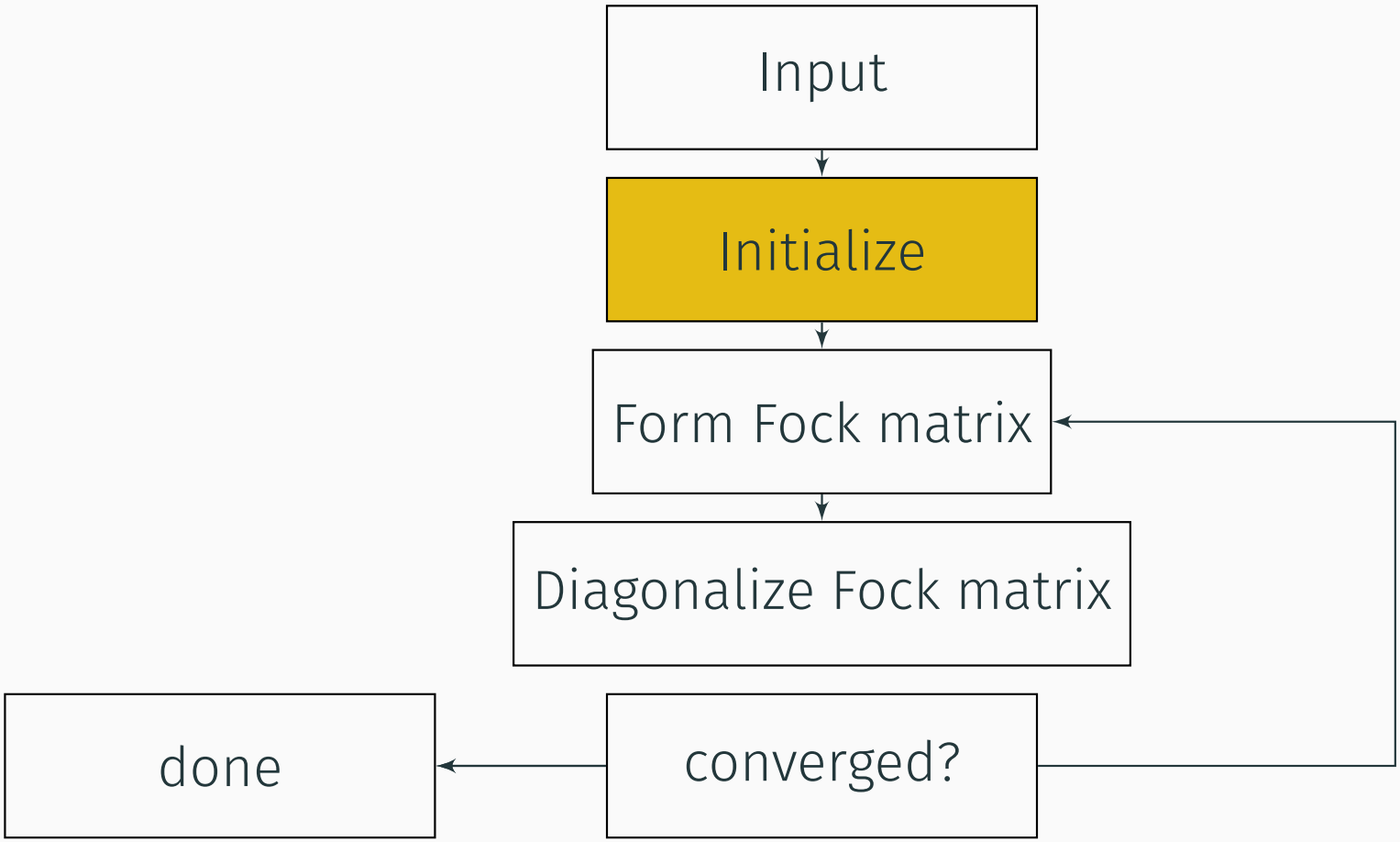
INPUT


Input
Initialize
Form Fock matrix
Diagonalize Fock matrix
converged?
done

INPUT

- atomic positions
- basis

INITIALIZE


Input
Initialize
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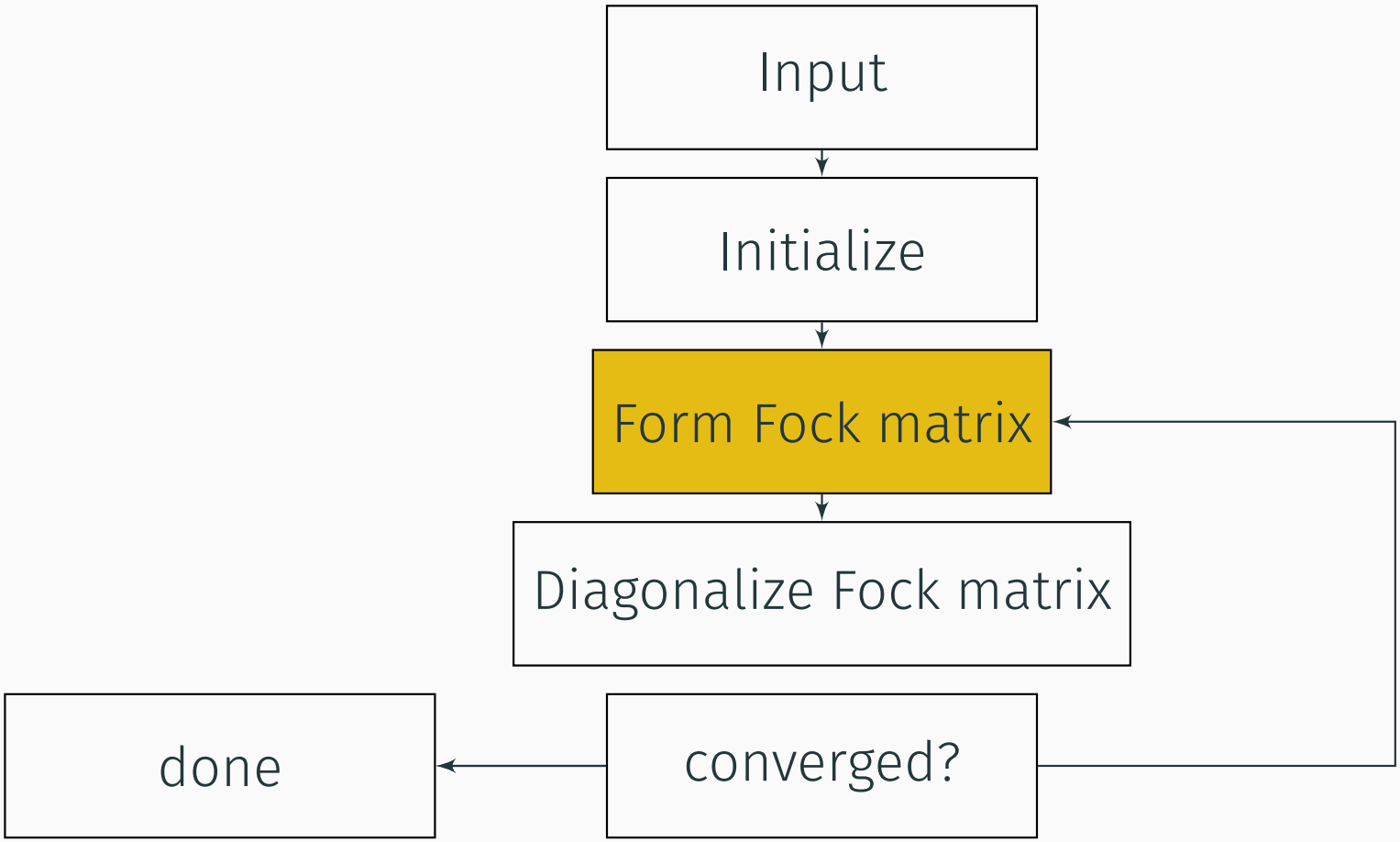
converged?
done

INITIALIZE

- use pyscf/psi4 to calculate 1-2 electron integrals
- initialize density matrix (here, as all zeros)

FORM FOCK MATRIX

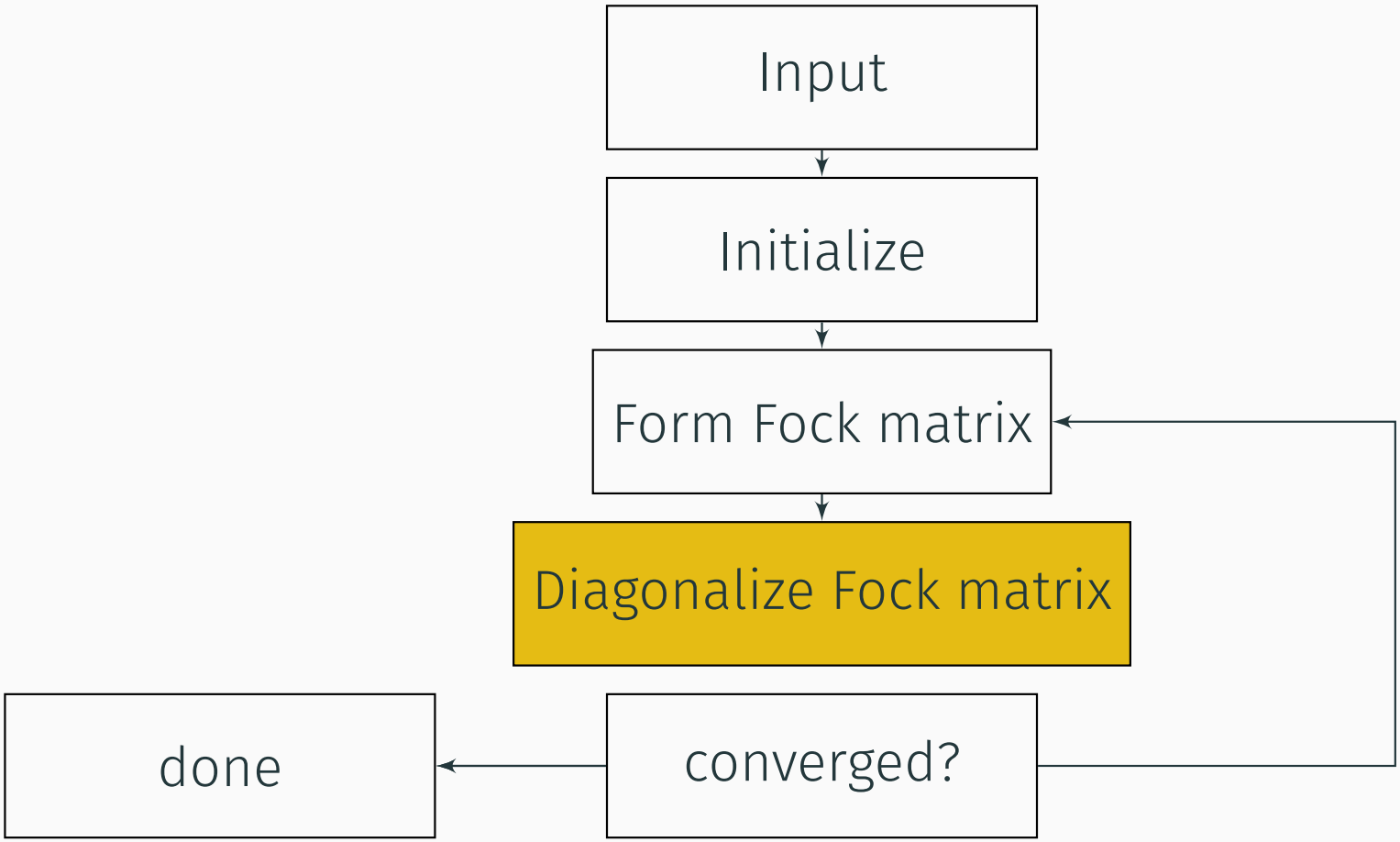


FORM FOCK MATRIX

- use previous iteration's density to calculate the new G matrix
- form the new Fock matrix
- calculate energy:

$$E^k = V_{NN} + \sum_{\mu\nu}^{K} D_{\mu\nu}(H_{\mu\nu} + F_{\mu}\nu)$$

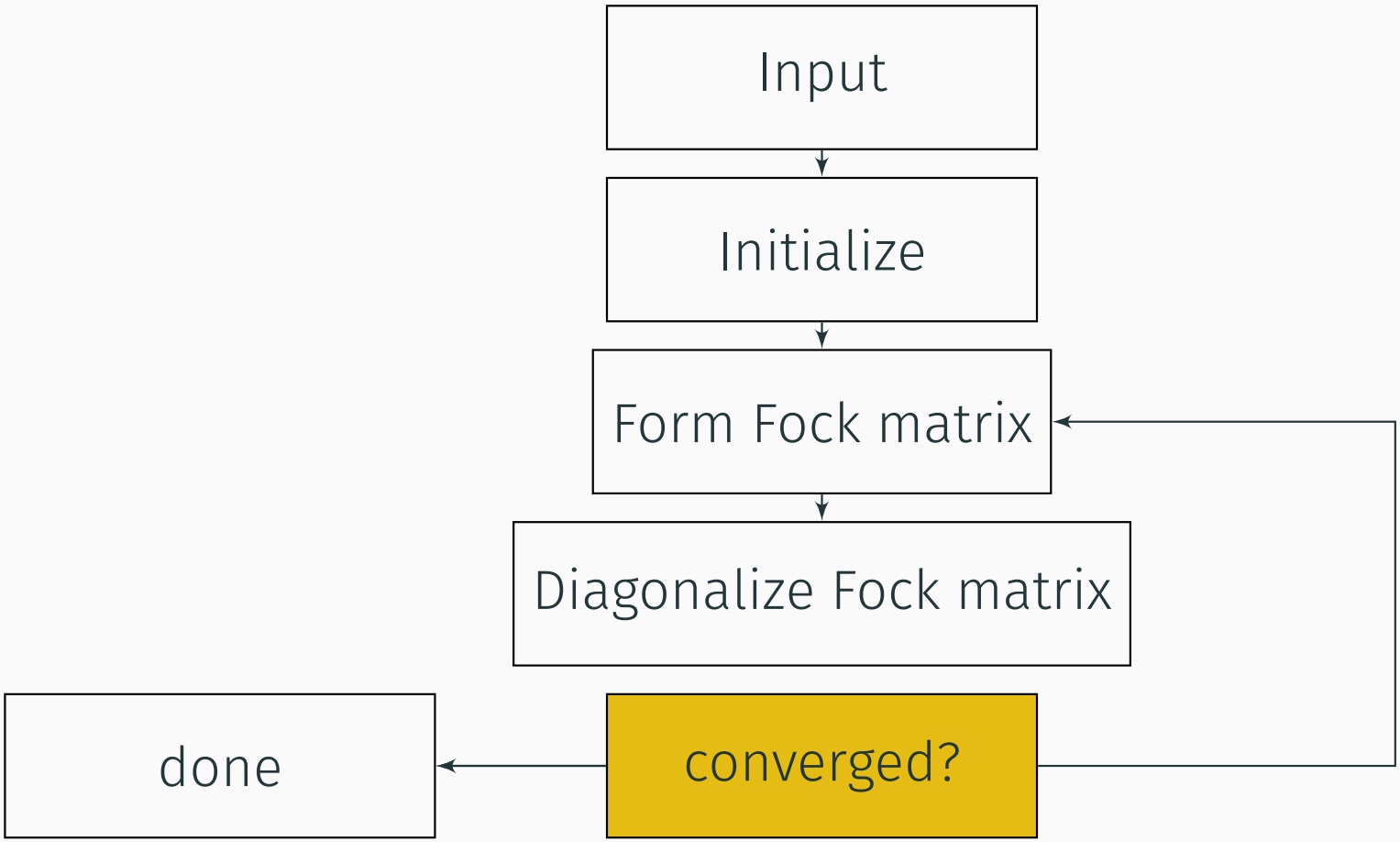
DIAGONALIZE FOCK MATRIX



DIAGONALIZE FOCK MATRIX

- diagonalize Fock matrix
- calculate density resulting from new MOs

DIAGONALIZE FOCK MATRIX



DIAGONALIZE FOCK MATRIX

- check if energy and density difference from previous and current iteration is less than a specified threshold