Periodic HF: SCF cycle and EDIIS + DIIS

- Hartree-Fock equations:

$$\sum_{\gamma}\left(\langle\alpha|\hat{T}+\hat{U}|\gamma\rangle+\sum_{\beta\delta}\langle\alpha\beta|\hat{V}|\gamma\delta\rangle\rho_{\beta\delta}\right)c_{\gamma}^{n}=\epsilon_{n}c_{\alpha}^{n}$$

- Fock matrix $F(\rho)$ depends on single-particle density matrix. Dimension of supercell sp Hilbert space (say M). Block-diagonal due to point-group symmetry.

- Input I need: different components to construct Fock matrix, *i.e.* matrix elements.

SCF cycle

- Initial guess of 1DM:

$$\rho_{\alpha\gamma} = \delta_{\alpha\gamma} \sum_{\mu=1}^{\frac{N}{2}} \delta_{\alpha\mu}$$

- Construct $F(\rho)$
- Diagonalization leads to M eigenvalues ϵ_n and eigenvectors c^n.
- New 1DM out of $\frac{N}{2}$ lowest energy eigenvectors:

$$\rho_{\alpha\gamma} = \sum_{n=1}^{\frac{N}{2}} (c_\alpha^n)^* c_\gamma^n$$

- Repeat until convergence is reached.

SCF convergence acceleration techniques: DIIS

- SCF unstable, often oscillates back and forward, solution $\rightarrow$ relaxation:

$$\rho^{k+1} = \sum_{i=1}^{k} b_i \, \rho^i$$

- DIIS: algorithm to choose the b_i's, least square of some error vector:

$$\{b_i\} = \inf \left\{ \left| \sum_{i=1}^{k} b_i \, [F(\rho_i), \rho_i] \right|^2 \quad \text{u.c.t.} \quad \sum_{i=1}^{k} b_i = 1 \right\}$$

- Simple linear system of equations. Works very well when close to optimum.

SCF convergence acceleration techniques: EDIIS

- With bad initial guess, DIIS fails to converge.
- Alternative optimization problem for the coëfficients b_i: EDIIS

$$\{b_i\} = \inf \left\{ E^{HF} \left(\sum_{i=1}^{k} b_i \rho_i \right) \text{ u.c.t. } \sum_{i=1}^{k} b_i = 1 \text{ and } 0 \leq b_i \leq 1 \right\}$$

- Convex quadratic programming problem. Works well when far away from solution.
- Standard option: combine EDIIS with DIIS for optimal results.