

## OMP2

1. Build  $h_p^q$  and  $\bar{g}_{pq}^{rs}$  in the Hartree-Fock spin-orbital basis.
2. Build an empty array of amplitudes,  $t_{ab}^{ij} = 0$ .
3. Build the Fock matrix.

$$f_p^q = h_p^q + \bar{g}_{pi}^{qi} \quad (1)$$

4. Build the off-diagonal Fock matrix and the orbital energies.

$$\epsilon_p = f_p^p \quad f_p'^q = (1 - \delta_p^q) f_p^q \quad (2)$$

5. Update the amplitudes.

$$t_{ab}^{ij} = (\mathcal{E}_{ab}^{ij})^{-1} \left( \bar{g}_{ab}^{ij} + P_{(a/b)} f_a'^c t_{cb}^{ij} - P^{(i/j)} f_k'^i t_{ab}^{kj} \right) \quad (3)$$

6. Build the one- and two-particle density matrices.

$$\gamma_q^p = \tilde{\gamma}_q^p + \circ\gamma_q^p \quad \gamma_{rs}^{pq} = \tilde{\gamma}_{rs}^{pq} + P_{(r/s)}^{(p/q)} \tilde{\gamma}_r^p \circ\gamma_s^q + P_{(r/s)} \circ\gamma_r^p \circ\gamma_s^q \quad \circ\gamma_q^p = \begin{cases} \delta_j^i & \text{for } p = i, q = j \\ 0 & \text{otherwise} \end{cases} \quad (4)$$

$$\tilde{\gamma}_b^a = \frac{1}{2} t_{ij}^{ac*} t_{bc}^{ij} \quad \tilde{\gamma}_j^i = -\frac{1}{2} t_{jk}^{ab*} t_{ab}^{ik} \quad \tilde{\gamma}_{cd}^{ab} = \frac{1}{2} t_{ij}^{ab*} t_{cd}^{ij} \quad \tilde{\gamma}_{kl}^{ij} = \frac{1}{2} t_{kl}^{ab*} t_{ab}^{ij} \quad (5)$$

$$\tilde{\gamma}_{ib}^{aj} = -\tilde{\gamma}_{bi}^{aj} = -\tilde{\gamma}_{ib}^{ja} = \tilde{\gamma}_{bi}^{ja} = t_{ik}^{ac*} t_{cb}^{kj} \quad \tilde{\gamma}_{ij}^{ab} = t_{ij}^{ab*} \quad \tilde{\gamma}_{ab}^{ij} = t_{ab}^{ij} \quad (6)$$

7. Compute the Newton-Raphson step.

$$x_a^i = \frac{(\mathbf{F} - \mathbf{F}^\dagger)_a^i}{\epsilon_i - \epsilon_a} \quad (\mathbf{F})_p^q \equiv h_p^r \gamma_r^q + \frac{1}{2} \bar{g}_{pr}^{st} \gamma_{st}^{qr} \quad (7)$$

8. Build the Newton-Raphson orbital rotation matrix.

$$\mathbf{U} = \exp(\mathbf{X} - \mathbf{X}^\dagger) \quad \mathbf{X}_{\text{vo}} = [x_a^i] \quad (8)$$

9. Rotate the spin-orbital coefficients.

$$\mathbf{C} \leftarrow \mathbf{C} \mathbf{U} \quad (9)$$

10. Transform the one- and two-electron integrals to the spin-orbital basis using the new coefficient matrix.

$$h_p^q = \sum_{\mu\nu} C_{\mu p}^* h_{\mu\nu} C_{\nu q} \quad \bar{g}_{pq}^{rs} = \sum_{\mu\nu\rho\sigma} C_{\mu p}^* C_{\nu q}^* \langle \mu\nu || \rho\sigma \rangle C_{\rho r} C_{\sigma s} \quad (10)$$

11. Evaluate the energy.

$$E = h_p^q \gamma_q^p + \frac{1}{4} \bar{g}_{pq}^{rs} \gamma_{rs}^{pq} \quad (11)$$

12. If the energy is converged, quit. Otherwise, return to step 3.