I. Definition of basis

$$|\Psi^s\rangle = \sum_{ij} c_{ij}\, |{}^s\Phi_i^j\rangle = \sum_i \bar{c}_i\, |{}^s\Phi_i\rangle$$

$$|{}^s\Phi_i\rangle \equiv \left\{ {}^s\Phi_i^1, {}^s\Phi_i^2, \ldots, {}^s\Phi_i^{N_{CSF}} \right\}$$

$$\bar{c}_i \equiv \left\{ c_i^1, c_i^2, \ldots, c_i^{N_{CSF}} \right\}$$

$$|{}^s\Phi_i^j\rangle = \sum_k o_{i,k}^j\, |{}^s\phi_k(i,j)\rangle$$

$$|{}^s\phi_k(i,j)\rangle = (i\bar{i}) \ldots (j,k) \ldots (l\,(m \ldots$$

$$(i\bar{i}) = |i\bar{i}\rangle$$

$$(j,k) = \frac{|j\bar{k}\rangle - |\bar{j}k\rangle}{\sqrt{2}}$$

$$(l = |l\rangle$$

a.) Overlap matrix:

$$|{}^s\Phi_i\rangle = \sum_j c_i^j\, |{}^s\Phi_i^j\rangle$$

$$\Rightarrow \langle {}^s\Phi_i | {}^s\Phi_i\rangle = \sum_j \sum_k c_i^j c_i^k\, \langle {}^s\Phi_i^j | {}^s\Phi_i^k\rangle$$

$$\langle {}^s\Phi_i^j | {}^s\Phi_i^k\rangle = \sum_l \sum_m \left(o_{i,m}^j\right)^\dagger o_{i,m}^k\, \underbrace{\langle {}^s\phi_l(i,j) | {}^s\phi_m(i,k)\rangle}_{\Downarrow\; S_{l,m}(j,k)}$$

$$\langle {}^s\Phi_i^j | {}^s\Phi_i^k\rangle = O_i^j \cdot S_j^k \cdot O_i^k$$

$$\Rightarrow \langle {}^s\Phi_i | {}^s\Phi_i\rangle = \sum_j \sum_k c_i^j c_i^k\, O_i^j \cdot S_j^k \cdot O_i^k$$

$$O_i^j = \begin{array}{c|cccccc} N_{CSF} \backslash N_{BF} & 1 & 2 & \ldots & l & \ldots & N_{BF} \\ \hline 1 & & & & & & \\ 2 & & & & & & \\ \vdots & & & & & & \\ j & & & & & & \\ \vdots & & & & & & \\ N_{csf} & & & & & & \end{array}$$

$$S = \begin{array}{c|cccccc} N_{BF}^j \backslash N_{BF}^k & 1 & 2 & \ldots & m & \ldots & N_{BF}^k \\ \hline 1 & & & & & & \\ 2 & & & & & & \\ \vdots & & & & & & \\ l & & & & & & \\ \vdots & & & & & & \\ N_{BF}^j & & & & & & \end{array}$$

$$\Rightarrow \langle {}^s\Phi_i | {}^s\Phi_j\rangle = \left(C_{i,l}\right)^\dagger \cdot \left[O_i \cdot S_{ij} \cdot O_j \right] C_{j,l}$$

b.) Matrix Element

$$\langle {}^s\Phi_i | \hat{E}_{pq} | {}^s\Phi_j\rangle = \sum_k \sum_l c_i^k c_j^l\, \langle {}^s\Phi_i^k | \hat{E}_{pq} | {}^s\Phi_j^l\rangle$$

$$\langle {}^s\phi_i^k | \hat{E}_{pq} | {}^s\Phi_j^l\rangle = \sum_m \sum_n \left(O_{i,m}^k\right)^\dagger \underbrace{\langle {}^s\phi_m(i,k) | \hat{E}_{pq} | {}^s\phi_n(j,l)\rangle}_{A_{mn}^{ij}} \cdot O_{j,n}^k$$

$$\Rightarrow \langle {}^s\Phi_i^k | \hat{E}_{pq} | {}^s\Phi_j^l\rangle = O_i^k \cdot A_{pq}^{ij}\; O_j^k$$

$$A_{pq}^{ij} = \begin{array}{c|cccccc} N_{BF}^i \backslash N_{BF}^j & 1 & 2 & \ldots & n & \ldots & N_{BF}^j \\ \hline 1 & & & & & & \\ 2 & & & & & & \\ \vdots & & & & & & \\ m & & & & & & \\ \vdots & & & & & & \\ N_{BF}^i & & & & & & \end{array}$$

$$\Rightarrow \langle {}^s\Phi_i | \hat{E}_{pq} | {}^s\Phi_j\rangle = \left(C_{i,l}\right)^\dagger \cdot \left[O_i \cdot A_{pq} \cdot O_j \right] \cdot C_{j,l}$$

$$\Rightarrow \langle \Psi | \hat{E}_{pq} | \Psi\rangle = \sum_i \sum_j \langle {}^s\Phi_i | \hat{E}_{pq} | {}^s\Phi_j\rangle$$

$$= \sum_i \sum_j \left(C_{i,l}\right)^\dagger \cdot \left[O_i\; A_{pq}^{ij}\; O_j \right] \cdot C_{j,l}$$

c.) Sigma-Vector

$$\langle \Psi | \hat{H} | \Psi\rangle$$

$$\hat{H} = \sum_{pq} \hat{E}_{pq} \tilde{h}_{pq} + \frac{1}{2} \sum_{pq} \sum_{rs} \hat{E}_{pq} \hat{E}_{rs}\, g(pq,rs)$$

$$\Rightarrow \langle \Psi | \hat{H} | \Psi\rangle$$

$$= \sum_{pq} \tilde{h}_{pq} \langle \Psi | \hat{E}_{pq} | \Psi\rangle \quad \text{—— I}$$

$$+ \frac{1}{2} \sum_{pq} \sum_{rs} g(pq,rs) \langle \Psi | \hat{E}_{pq} \hat{E}_{rs} | \Psi\rangle \text{ — II}$$

i) Part I.

$$\sum_{pq} \tilde{h}_{pq} \langle \Psi | \hat{E}_{pq} | \Psi\rangle$$

$$= \sum_{pq} \tilde{h}_{pq} \sum_i \sum_j \left(\bar{C}_{i,l}\right)^\dagger \cdot \left[O_i \cdot A_{pq}^{ij} \cdot O_j \right] \cdot \bar{C}_{j,l}$$

ii) Part II

$$\sum_{pq} \sum_{rs} \langle \Psi | \hat{E}_{pq} \hat{E}_{rs} | \Psi\rangle$$

$$= \sum_K \left[\sum_{pq} \sum_{rs} \langle \Psi | \hat{E}_{pq} | K\rangle \langle K | \hat{E}_{rs} | \Psi\rangle\, g(pq,rs) \right]$$

$$= \sum_K \left[\left(\bar{C}_{i,l}\right)^\dagger \cdot \left(\sum_{pq} \sum_{rs} \underbrace{\left[\left[O_i \cdot A_{ij}^{pq} \cdot O_k \right]_{pq} \cdot \left[O_k \cdot A_{kj}^{rs} \cdot O_j \right]^{rs} \right]_{pq}^{rs}}_{\Downarrow\ \text{BLAS}\ \ T_{pq}^{rs}(i,j)} \cdot g_{pq}^{rs} \right) \cdot \bar{C}_{j,l} \right]$$

$$\langle \Psi | \hat{E}_{pq} \hat{E}_{rs} | \Psi\rangle = \sum_k \left(\bar{C}_{i,l}\right)^\dagger \cdot \left(T_{pq,rs}^k \cdot g(pq,rs) \right) \cdot \bar{C}_{j,l}$$