

1. Order the basis such that Φ is first. The matrix is block diagonal, with \mathbf{H}_{11} being its own block. By definition of \mathbf{H}_{PQ} , Brillouin's theorem guarantees all matrix elements of the form \mathbf{H}_{1Q} vanish, and exploiting hermiticity, the \mathbf{H}_{Q1} terms must vanish as well. This produces the block diagonal structure described.

2. Order the basis such that Φ is first. $\mathbf{H}_{11} = \langle \Phi | \hat{H}_e | \Phi \rangle = E_0$. But it was proved in problem 1 that \mathbf{H}_{11} is its own block. Thus, $\mathbf{H}_{11}e_1 = E_0e_1$. But our first basis vector, e_1 , is simply Φ by how we defined our basis.

$$\begin{aligned} 3. \mathbf{H}\mathbf{c}_K = E_K\mathbf{c}_K &\implies \mathbf{H}\mathbf{c}_K - E_0\mathbf{I}\mathbf{c}_K = E_K\mathbf{I}\mathbf{c}_K - E_0\mathbf{c}_K \implies \\ (\mathbf{H} - E_0\mathbf{I})\mathbf{c}_K &= (E_K - E_0)\mathbf{c}_K \implies \mathbf{H}\mathbf{c}_K = (E - E_0)\mathbf{c}_K \end{aligned}$$

Shifting your diagonals shifts your eigenvalues.

4a. The determinants differ in two positions, so the one-electron integral vanishes, and the two electron integral gives $\langle aj || ib \rangle$.

4b. The determinants differ in one position. We redefine the reference determinant Φ to be $(\Phi_0)_i^a$, making the integral $\langle \Phi | H | \Phi_a^b \rangle$. Slater's Rules give an expectation of $h_{ab} + \sum_{k \in \Phi} \langle ak || bk \rangle$, but we are summing over the orbitals of

our modified reference determinant. Noting that $f_{ab} = h_{ab} + \sum_{k \in \Phi_0} \langle ak || bk \rangle = h_{ab} + \sum_{k \in \Phi} \langle ak || bk \rangle - \langle ai || bi \rangle + \langle aa || ba \rangle$. We can therefore rewrite the expectation value in question as $h_{ab} - \langle ai || bi \rangle = h_{ab} + \langle ai || ib \rangle$ by the permutational symmetry of the two-electron integral.

4c. The determinants differ in two positions, but this can be manipulated to a difference in one position. First, the right determinant will have the orbitals in position i and j switched. Therefore, both determinants have orbital a in the i position, but in the j position, the right determinant will have orbital i while the left determinant has orbital j .

We redefine the reference determinant Φ to be $(\Phi_0)_i^a$. Therefore, $\mathcal{P}_{ij}((\Phi_0)_j^a) = \Phi_i^j$. Since a swap of two elements is its own inverse, we have that $(\Phi_0)_j^a = \mathcal{P}_{ij}(\Phi_i^j)$. Note that we refer to indices when subscripting permutations and to functions when subscripting or superscripting determinants. Therefore, $\langle (\Phi_0)_i^a | H | (\Phi_0)_j^a \rangle = \langle \Phi | H | \mathcal{P}_{ij}(\Phi_i^j) \rangle = -\langle \Phi | H | \Phi_i^j \rangle = -f_{ij} - \sum_{k \in \Phi} \langle ik || jk \rangle = -f_{ij} - (\sum_{k \in \Phi_0} \langle ik || jk \rangle - \langle ii || ji \rangle + \langle ia || ja \rangle) = -h_{ij} - \langle ia || ja \rangle$. We have made heavy use of the same tricks used in the previous section. Unfortunately, to make further progress, we must assume our integral is real. If so, then $-\langle ia || ja \rangle = -\langle ja || ia \rangle = \langle aj || ia \rangle$. Thus, our solution for this case is $-f_{ij} + \langle aj || ia \rangle$, which reduces to the expected solution in the case of real integrals.

4d. Redefine the reference wavefunction Φ to $(\Phi_0)_i^a$. The Slater-Condon rules give the expectation as $\sum_{k \in \Phi} f_{kk} + \frac{1}{2} \sum_{k \in \Phi} \sum_{l \in \Phi, l \neq k} \langle kl || kl \rangle$. We break this into pieces.

$$\sum_{k \in \Phi} f_{kk} = \sum_{k \in \Phi_0} f_{kk} - f_{ii} + f_{aa}. \quad \text{We also know that } \frac{1}{2} \sum_{k \in \Phi} \sum_{l \in \Phi, l \neq k} \langle kl || kl \rangle =$$

$$\frac{1}{2} \sum_{k \in \Phi_0} \sum_{l \in \Phi_0, l \neq k} \langle kl || kl \rangle - \frac{1}{2} \sum_{l \in \Phi_0, l \neq i} \langle il || il \rangle - \frac{1}{2} \sum_{k \in \Phi_0} \langle ki || ki \rangle + \frac{1}{2} \sum_{l \in \Phi_0, l \neq a} \langle al || al \rangle + \frac{1}{2} \sum_{k \in \Phi_0} \langle ka || ka \rangle + \langle ai || ai \rangle.$$

Adding these together, the expectation is $\sum_{k \in \Phi_0} f_{kk} - f_{ii} + f_{aa} + \frac{1}{2} \sum_{k \in \Phi_0} \sum_{l \in \Phi_0, l \neq k} \langle kl || kl \rangle -$

$$\frac{1}{2} \sum_{l \in \Phi_0, l \neq i} \langle il || il \rangle - \frac{1}{2} \sum_{k \in \Phi_0} \langle ki || ki \rangle + \frac{1}{2} \sum_{l \in \Phi_0, l \neq a} \langle al || al \rangle + \frac{1}{2} \sum_{k \in \Phi_0} \langle ka || ka \rangle + \langle ai || ai \rangle.$$

We recognize a familiar expression in there, so $E_0 - f_{ii} + f_{aa} - \frac{1}{2} \sum_{l \in \Phi_0, l \neq i} \langle il || il \rangle -$

$$\frac{1}{2} \sum_{k \in \Phi_0} \langle ki || ki \rangle + \frac{1}{2} \sum_{l \in \Phi_0, l \neq a} \langle al || al \rangle + \frac{1}{2} \sum_{k \in \Phi_0} \langle ka || ka \rangle + \langle ai || ai \rangle = E_0 - f_{ii} + f_{aa} -$$

$$\sum_{l \in \Phi_0} \langle il || il \rangle + \sum_{l \in \Phi_0} \langle al || al \rangle = E_0 - f_{ii} + f_{aa} + \langle ai || ai \rangle$$

This was as to be shown.

$$\begin{aligned} 5. \langle \Phi_i^a | \hat{H}_e - E_0 | \Phi_j^b \rangle &= \langle \Phi_i^a | \hat{H}_e | \Phi_j^b \rangle - \langle \Phi_i^a | E_0 | \Phi_j^b \rangle = E_0 \delta_{ij} \delta_{ab} + f_{ab} \delta_{ij} - f_{ij} \delta_{ab} + \\ &\langle aj || ib \rangle - E_0 \langle \Phi_i^a | \Phi_j^b \rangle = E_0 \delta_{ij} \delta_{ab} + f_{ab} \delta_{ab} \delta_{ij} - f_{ij} \delta_{ab} \delta_{ij} + \langle aj || ib \rangle - E_0 \delta_{ij} \delta_{ab} = \\ &(\epsilon_a - \epsilon_i) \delta_{ab} \delta_{ij} + \langle aj || ib \rangle \end{aligned}$$

Given a Hartree-Fock reference, the off-diagonal elements of the Fock Matrix vanish.