CB2070 Ex 6

① Introduce a set of non-orthogonal basis functions

$\{\chi_\alpha\}$ (AOs)

Show that the Fock matrix can be written in the form

$$F_{\alpha\beta} = \langle \chi_\alpha | \hat{f} | \chi_\beta \rangle = h_{\alpha\beta} + \sum_{\gamma\delta} D_{\gamma\delta} \left[\langle \chi_\alpha \chi_\gamma | \hat{g} | \chi_\beta \chi_\delta \rangle - \langle \chi_\alpha \chi_\gamma | \hat{g} | \chi_\delta \chi_\beta \rangle \right]$$

We have the linear combination of atomic orbitals (LCAO)

spatial MO $\phi_a = \sum_\alpha C_{\alpha a} \chi_\alpha$

α-spin spinorbital: $\psi_{\bar{a}} = \phi_a \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \sum_\alpha C_{\alpha a} \chi_\alpha \begin{pmatrix} 1 \\ 0 \end{pmatrix}$

We can look at the spins separately (or one exclusively when closed-shell system)

In the new basis we write the Fock matrix element (with $\hat{f} = \hat{h} + \sum_j^N (\hat{J}_j - \hat{K}_j)$)

$$F_{\alpha\beta} = \langle \chi_\alpha | \hat{h} | \chi_\beta \rangle + \sum_j^N \left(\langle \chi_\alpha | \hat{J}_j | \chi_\beta \rangle - \langle \chi_\alpha | \hat{K}_j | \chi_\beta \rangle \right)$$

we exchange the spinorbitals $\{\psi_j\}$ in the two-elec operators with the LCAO

$$\psi_j = \sum_\delta C_{\delta j} \chi_\delta \; , \quad \psi_j^* = \sum_\gamma C_{\gamma j}^* \chi_\gamma^*$$

$$\Rightarrow \sum_j \langle \chi_\alpha | \hat{J}_j | \chi_\beta \rangle = \sum_j \sum_{\gamma,\delta} C_{\gamma j}^* C_{\delta j} \langle \chi_\alpha \chi_\gamma | \hat{g} | \chi_\beta \chi_\delta \rangle$$

$$\Rightarrow \sum_j \langle \chi_\alpha | \hat{K}_j | \chi_\beta \rangle = \sum_j \sum_{\gamma,\delta} C_{\gamma j}^* C_{\delta j} \langle \chi_\alpha \chi_\gamma | \hat{g} | \chi_\delta \chi_\beta \rangle$$

$$\Rightarrow F_{\alpha\beta} = h_{\alpha\beta} + \sum_{\gamma,\delta} \underbrace{\sum_j C_{\gamma j}^* C_{\delta j}}_{D_{\gamma\delta}} \left[\langle \chi_\alpha \chi_\gamma | \hat{g} | \chi_\beta \chi_\delta \rangle - \langle \chi_\alpha \chi_\gamma | \hat{g} | \chi_\delta \chi_\beta \rangle \right]$$

$$= h_{\alpha\beta} + \sum_{\gamma,\delta} D_{\gamma\delta} \left[\langle \chi_\alpha \chi_\gamma | \hat{g} | \chi_\beta \chi_\delta \rangle - \langle \chi_\alpha \chi_\gamma | \hat{g} | \chi_\beta \chi_\delta \rangle \right]$$

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② Show the relation

$$n(\bar{r}) = \sum_{\gamma\delta} D_{\gamma\delta} \chi_\gamma^*(\bar{r}) \chi_\delta(\bar{r})$$

We have that

$$n(\bar{r}) = \sum_i \langle \psi_i | \psi_i \rangle = \sum_i \sum_{\gamma\delta} C_{\gamma i}^* C_{\delta i} \langle \chi_\gamma | \chi_\delta \rangle = \sum_{\gamma\delta} D_{\gamma\delta} \langle \chi_\gamma | \chi_\delta \rangle$$

where $D_{\gamma\delta} = \sum_i C_{\gamma i}^* C_{\delta i}$

③ For the HF equation

$$\mathbb{F}\mathbb{C} = \mathbb{S}\mathbb{C}\varepsilon$$

we introduce a non-unitary change of the AO basis

$$\chi_\alpha' = \sum_\beta X_{\beta\alpha} \chi_\beta \quad , \quad \mathbb{X} = \mathbb{S}^{-1/2}$$

Show the orthonormality $\langle \chi_\alpha' | \chi_\beta' \rangle = \delta_{\alpha\beta}$

We have that

$$F_{\alpha\beta} = \langle \chi_\alpha | \hat{f} | \chi_\beta \rangle$$

$$S_{\alpha\beta} = \langle \chi_\alpha | \chi_\beta \rangle \, ,$$

$$X_{\alpha\beta} = S_{\alpha\beta}^{-1/2} \Rightarrow S_{\alpha\beta} = X_{\alpha\beta}^{-2} =$$

a) We write the inner product

$$\langle \chi_\alpha' | \chi_\beta' \rangle = \sum_{\gamma\delta} X_{\gamma\alpha}^* X_{\delta\beta} \langle \chi_\gamma | \chi_\delta \rangle = \sum_{\gamma\delta} X_{\gamma\alpha}^* S_{\gamma\delta} X_{\delta\beta}$$

⇒ written in matrix form

$$\mathbb{X}^\dagger \mathbb{S} \mathbb{X} = (\mathbb{S}^{-1/2})^\dagger \mathbb{S} \mathbb{S}^{-1/2}$$

p 143 in Szabo

The overlap matrix is Hermitian and thus $\mathbb{S}^{-1/2}$ is also Hermitian

$$(\mathbb{S}^{-1/2})^\dagger = \mathbb{S}^{-1/2}$$

$$\Rightarrow \mathbb{S}^{-1/2} \mathbb{S} \mathbb{S}^{-1/2} = \mathbb{S}^{-1/2} \mathbb{S}^{1/2} = \mathbb{S}^0 = \mathbb{I}$$

which shows that $\{\chi_\alpha'\}$ forms an orthonormal basis cont'd

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b) Show that S is Hermitian

The AOs are assumed to be normalized which makes the diagonal elements are unity

Hermitian: $S^\dagger = S$, $S_{\alpha\beta} = S^*_{\beta\alpha}$

Since the elements of S are simply the inner product of basis functions, we have

$$S_{\alpha\beta} = \langle \chi_\alpha | \chi_\beta \rangle = \langle \chi_\beta | \chi_\alpha \rangle^* = S^*_{\beta\alpha}$$

Positive-definite: symmetric with positive-only eigenvalues and:

$$x^* S x > 0 \quad \text{for any non-zero vector } x$$

Since the diagonal is always positive and the matrix is Hermitian, the overlap is positive-definite

Alternatively: the eigenvalue problem

$S c^i = s_i c^i$, where is a column in the unitary matrix U that diagonalizes S

$$\Rightarrow \sum_\beta S_{\alpha\beta} c^i_\beta = s_i c^i_\alpha$$

$$= \sum_\beta \int \psi^*_\alpha \psi_\beta \, d\bar{r} \, c^i_\alpha$$

Multiply by c^*_α and sum over α

$$\sum_{\alpha\beta} c^{i*}_\alpha \int \psi^*_\alpha \psi_\beta \, d\bar{r} \, c^i_\beta = \sum_\alpha s_i c^{i*}_\alpha c^i_\alpha$$

Sum over i also

$$\sum_i \sum_{\alpha\beta} c^{i*}_\alpha S_{\alpha\beta} c^i_\beta = \sum_i s_i \underbrace{\sum_\alpha c^{i*}_\alpha c^i_\alpha}_{=1 \text{ by normalization}}$$

$$\sum_i (c^i_\alpha)^* c^i_\beta = \delta_{\alpha\beta}$$

$$\Rightarrow \sum_{\alpha\beta} S_{\alpha\beta} \delta_{\alpha\beta} = s_i$$

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3c) Show that the HF equation in the new basis becomes

$$\mathbb{F}'\mathbb{C}' = \mathbb{C}'\varepsilon$$

We have shown that in the new basis, the overlap matrix is the identity matrix

$$S' = \mathbb{X}^{\dagger} S \mathbb{X} = \mathbb{1}$$

$\mathbb{X}$ is defined such that it possesses an inverse $\mathbb{X}^{-1}$ (book p. 143)

In matrix form, the new basis is

$$|\mathbb{X}'\rangle = |\mathbb{X}\rangle \mathbb{X}$$

By multiplying from the right with $\mathbb{X}^{-1}$ we get

$$|\mathbb{X}\rangle = |\mathbb{X}'\rangle \mathbb{X}^{-1}$$

Inserting this into the LCAO (in matrix form)

$$|\Psi\rangle = |\mathbb{X}\rangle \mathbb{C} = |\mathbb{X}'\rangle \mathbb{X}^{-1}\mathbb{C}$$

We get the new coefficient matrix

$$\mathbb{C}' = \mathbb{X}^{-1}\mathbb{C} \quad \text{and thus} \quad \mathbb{C} = \mathbb{X}\mathbb{C}'$$

Inserting into the HF equations

$$\mathbb{F}\mathbb{C} = \mathbb{S}\mathbb{C}\varepsilon$$

$$\mathbb{F}\mathbb{X}\mathbb{C}' = \mathbb{S}\mathbb{X}\mathbb{C}'\varepsilon$$

multiplying from the left by $\mathbb{X}^{\dagger}$

$$\underbrace{\mathbb{X}^{\dagger}\mathbb{F}\mathbb{X}}_{\mathbb{F}'}\mathbb{C}' = \underbrace{\mathbb{X}^{\dagger}\mathbb{S}\mathbb{X}}_{\mathbb{1}}\mathbb{C}'\varepsilon$$

which is the HF equation in the new basis

$$\mathbb{F}'\mathbb{C}' = \mathbb{C}'\varepsilon$$

This is an eigenvalue equation.