Chemische binding, MOL056, Uitwerkingen opgaven week 8

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Vraag 1: Hückel berekening voor etheen

1a.

$$H = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix}$$
$$S = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Seculiere vergelijking oplossen:

$$\begin{aligned}
\mathbf{Hc} &= \epsilon \mathbf{Sc} = \left(\alpha \mathbf{1} + \beta \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \right) \mathbf{c} \\
\begin{vmatrix} 0-\lambda & 1 \\ 1 & 0-\lambda \end{vmatrix} &= \lambda^2 - 1 = 0 \Rightarrow \\
\lambda &= \pm 1 \Rightarrow E = \alpha \pm \beta
\end{aligned}$$

$$\begin{aligned}
\lambda &= 1, \quad \mathbf{c_1} = \begin{bmatrix} 1 \\ 1 \end{bmatrix}, \quad E_1 = \alpha + \beta \;\; \text{(Grondtoestand)} \\
\lambda &= -1, \quad \mathbf{c_2} = \begin{bmatrix} 1 \\ -1 \end{bmatrix}, \quad E_2 = \alpha - \beta \\
\psi_1 &= \frac{1}{\sqrt{2}}(\phi_1 + \phi_2) \\
\psi_2 &= \frac{1}{\sqrt{2}}(\phi_1 - \phi_2)
\end{aligned}$$

1b.

$$E_{tot} = 2\alpha + 2\beta$$

De bijdrage van de π elektronen is 2β.

1c.

$$\begin{aligned}
\chi_S &= \frac{1}{\sqrt{2}}(\phi_1 + \phi_2) \\
< H_S > &= \langle \chi_S | \, \hat{h}_{eff} \, | \chi_S \rangle \\
&= \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \end{bmatrix} \begin{bmatrix} \alpha & \beta \\ \beta & \alpha \end{bmatrix} \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix} = \alpha + \beta = E^S \\
\psi_1 &= \chi_S
\end{aligned}$$

$$\begin{aligned}
\chi_A &= \frac{1}{\sqrt{2}}(\phi_1 - \phi_2) \\
< H_A > &= \langle \chi_A | \hat{h}_{eff} \chi_A \rangle = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & -1 \end{bmatrix} \begin{bmatrix} \alpha & \beta \\ \beta & \alpha \end{bmatrix} \begin{bmatrix} 1 \\ -1 \end{bmatrix} \frac{1}{\sqrt{2}} = \alpha - \beta = E^A \\
\psi_2 &= \chi_A
\end{aligned}$$

1d.

$$\Psi_0 = \frac{1}{\sqrt{2}} \left| \psi_1 \overline{\psi_1} \right|$$

1e.

$$\begin{aligned}
\sigma_{yz}\psi_1 &= \psi_1 \\
\sigma_{yz}\Psi_0 &= \sigma_{yz} \frac{1}{\sqrt{2}} \left| \psi_1 \overline{\psi_1} \right| = \frac{1}{\sqrt{2}} \left| \psi_1 \overline{\psi_1} \right| = \Psi_0
\end{aligned}$$

Dus Ψ_0 is even onder spiegeling in het yz-vlak.

1f.

$$\Psi_1 = \left| \psi_1 \psi_2 \right|$$

1g.

$$\begin{aligned}
\sigma_{yz}\psi_2 &= -\psi_2 \\
\sigma_{yz}\Psi_1 &= \sigma_{yz} \left| \psi_1 \psi_2 \right| = \left| \psi_1 (-\psi_2) \right| = - \left| \psi_1 \psi_2 \right| = -\Psi_1
\end{aligned}$$

Dus Ψ_1 is oneven onder spiegeling in het yz-vlak.

1h.

$$\begin{aligned}
\hat{i}\chi_S &= -\chi_S \\
\hat{i}\chi_A &= \chi_A \\
\hat{i}\Psi_1 &= -\Psi_1
\end{aligned}$$

Dus χ_S is oneven, χ_A is even en Ψ_1 is oneven onder inversie.

Vraag 2: Hückel berekening voor benzeen

2a. Als je C-atoom 1 en 4 op de y-as legt wordt je SALC-basis als volgt:

$\hat{\sigma}_{xz}$	$\hat{\sigma}_{yz}$	type	formule
S	S	I	$(1+\hat{\sigma}_{xz})(1+\hat{\sigma}_{yz})\ \phi$
S	A	II	$(1+\hat{\sigma}_{xz})(1-\hat{\sigma}_{yz})\ \phi$
A	S	III	$(1-\hat{\sigma}_{xz})(1+\hat{\sigma}_{yz})\ \phi$
A	A	IV	$(1-\hat{\sigma}_{xz})(1-\hat{\sigma}_{yz})\ \phi$

Type I:

$$\chi_1 = \frac{1}{\sqrt{2}}(\phi_1 + \phi_4)$$
$$\chi_2 = \frac{1}{2}(\phi_2 + \phi_3 + \phi_5 + \phi_6)$$

Type II:

$$\chi_3 = \frac{1}{2}(\phi_2 + \phi_3 - \phi_5 - \phi_6)$$

Type III:

$$\chi_4 = \frac{1}{\sqrt{2}}(\phi_1 - \phi_4)$$
$$\chi_5 = \frac{1}{2}(\phi_2 - \phi_3 - \phi_5 + \phi_6)$$

Type IV:

$$\chi_6 = \frac{1}{2}(\phi_2 - \phi_3 + \phi_5 - \phi_6)$$

2b. De matrix H blokt uit in 4 blokken, want de 4 types SALC hebben geen resonantie-overlap met elkaar (reken maar na als je wil). We gaan dus per type de H-matrix opstellen, waarbij SALCs van hetzelfde type wel resonantie-overlap met elkaar kunnen hebben.
Type I:

$$\begin{aligned}
H^I_{1,1} &= \langle\chi_1|\hat{h}|\chi_1\rangle = \frac{1}{2}\langle\phi_1+\phi_4|\hat{h}_{eff}|\phi_1+\phi_4\rangle = \frac{1}{2}(H_{1,1}+H_{4,4}+H_{1,4}+H_{4,1}) \\
&= \frac{1}{2}(\alpha+\alpha+0+0) = \alpha \\
H^I_{2,2} &= \langle\chi_2|\hat{h}|\chi_2\rangle = \frac{1}{4}\langle\phi_2+\phi_3+\phi_5+\phi_6|\hat{h}_{eff}|\phi_2+\phi_3+\phi_5+\phi_6\rangle \\
&= \alpha + \frac{1}{4}(H_{2,3}+H_{3,2}+H_{5,6}+H_{6,5}) = \alpha+\beta \\
H^I_{1,2} &= \langle\chi_1|\hat{h}|\chi_2\rangle = \frac{1}{2\sqrt{2}}\langle\phi_1+\phi_4|\hat{h}_{eff}|\phi_2+\phi_3+\phi_5+\phi_6\rangle \\
&= \frac{1}{2\sqrt{2}}(H_{1,2}+H_{1,6}+H_{4,3}+H_{4,5}) = \frac{1}{2\sqrt{2}}4\beta = \sqrt{2}\beta \\
H^I &= \begin{pmatrix} \alpha & \sqrt{2}\beta \\ \sqrt{2}\beta & \alpha+\beta \end{pmatrix} = \left(\alpha\mathbf{1} + \beta\begin{pmatrix} 0 & \sqrt{2} \\ \sqrt{2} & 1 \end{pmatrix}\right)
\end{aligned}$$

Om de eigenwaarden te vinden doen we het volgende:

$$\begin{aligned}
\begin{vmatrix} 0-\lambda & \sqrt{2} \\ \sqrt{2} & 1-\lambda \end{vmatrix} &= -\lambda+\lambda^2-2 = 0 \\
(\lambda-2)(\lambda+1) &= 0 \\
\lambda_1 &= 2, \quad E_1 = \alpha+2\beta \\
\lambda_2 &= -1, \quad E_2 = \alpha-\beta
\end{aligned}$$

Om de eigenvectoren te vinden doen we het volgende:
Voor $\lambda = 2$:

$$\begin{aligned}
\begin{bmatrix} -2 & \sqrt{2} \\ \sqrt{2} & -1 \end{bmatrix}\begin{bmatrix} c_1 \\ c_2 \end{bmatrix} &= \begin{bmatrix} 0 \\ 0 \end{bmatrix} \\
c_1 &= 1 \\
c_2 &= \sqrt{2} \\
c &= \frac{1}{\sqrt{3}}\begin{bmatrix} 1 \\ \sqrt{2} \end{bmatrix}
\end{aligned}$$

$$\Psi_1 = \frac{1}{\sqrt{3}}(\chi_1+\sqrt{2}\chi_2), \quad E_1 = \alpha+2\beta$$

Voor λ = -1 :

$$\begin{aligned}
\begin{bmatrix} 1 & \sqrt{2} \\ \sqrt{2} & 2 \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} &= \begin{bmatrix} 0 \\ 0 \end{bmatrix} \\
c_1 &= \sqrt{2} \\
c_2 &= -1 \\
c &= \frac{1}{\sqrt{3}} \begin{bmatrix} \sqrt{2} \\ -1 \end{bmatrix}
\end{aligned}$$

$$\Psi_2 = \frac{1}{\sqrt{3}}(\sqrt{2}\chi_1 - \chi_2), \quad E_2 = \alpha - \beta$$

Type II:

$$\begin{aligned}
H^{II}_{3,3} &= \langle \chi_3 | \hat{h} | \chi_3 \rangle = \frac{1}{4} \langle \phi_2 - \phi_3 + \phi_5 - \phi_6 | \hat{h} | \phi_2 + \phi_3 - \phi_5 - \phi_6 \rangle \\
&= \alpha + \frac{1}{4}(H_{2,3} + H_{3,2} + H_{5,6} + H_{6,5}) = \alpha + \beta \\
\Psi_3 &= \chi_3, \quad E_3 = \alpha + \beta
\end{aligned}$$

Type III:

$$\begin{aligned}
H^{III}_{4,4} &= \langle \chi_4 | \hat{h} | \chi_4 \rangle = \frac{1}{2} \langle \phi_1 - \phi_4 | \hat{h}_{eff} | \phi_1 - \phi_4 \rangle = \frac{1}{2}(H_{1,1} + H_{4,4} - H_{1,4} - H_{4,1}) \\
&= \frac{1}{2}(\alpha + \alpha - 0 - 0) = \alpha \\
H^{III}_{5,5} &= \langle \chi_5 | \hat{h} | \chi_5 \rangle = \frac{1}{4} \langle \phi_2 - \phi_3 - \phi_5 + \phi_6 | \hat{h}_{eff} | \phi_2 - \phi_3 - \phi_5 + \phi_6 \rangle \\
&= \alpha + \frac{1}{4}(-H_{2,3} - H_{3,2} - H_{5,6} - H_{6,5}) = \alpha - \beta \\
H^{III}_{5,6} &= \langle \chi_5 | \hat{h} | \chi_6 \rangle = \frac{1}{2\sqrt{2}} \langle \phi_1 - \phi_4 | \hat{h}_{eff} | \phi_2 - \phi_3 - \phi_5 + \phi_6 \rangle \\
&= \frac{1}{2\sqrt{2}}(H_{1,2} + H_{1,6} + H_{4,3} + H_{4,5}) = \frac{1}{2\sqrt{2}} 4\beta = \sqrt{2}\beta \\
H^{III} &= \begin{pmatrix} \alpha & \sqrt{2}\beta \\ \sqrt{2}\beta & \alpha - \beta \end{pmatrix} = \left(\alpha \mathbf{1} + \beta \begin{pmatrix} 0 & \sqrt{2} \\ \sqrt{2} & -1 \end{pmatrix} \right)
\end{aligned}$$

Voor de eigenwaarden:

$$\begin{aligned}
\begin{vmatrix} 0-\lambda & \sqrt{2} \\ \sqrt{2} & -1-\lambda \end{vmatrix} &= \lambda + \lambda^2 - 2 = 0 \\
(\lambda+2)(\lambda-1) &= 0 \\
\lambda_1 &= -2, \quad E_1 = \alpha - 2\beta \\
\lambda_2 &= 1, \quad E_2 = \alpha + \beta
\end{aligned}$$

Om de eigenvectoren te vinden doen we het volgende:
Voor λ = -2 :

$$\begin{aligned}
\begin{bmatrix} 2 & \sqrt{2} \\ \sqrt{2} & 1 \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} &= \begin{bmatrix} 0 \\ 0 \end{bmatrix} \\
c_1 &= 1 \\
c_2 &= -\sqrt{2} \\
c &= \frac{1}{\sqrt{3}} \begin{bmatrix} 1 \\ -\sqrt{2} \end{bmatrix}
\end{aligned}$$

$$\Psi_4 = \frac{1}{\sqrt{3}}(\chi_4 - \sqrt{2}\chi_5), \quad E_4 = \alpha - 2\beta$$

Voor $\lambda = 1$:

$$\begin{aligned}
\begin{bmatrix} -1 & \sqrt{2} \\ \sqrt{2} & -2 \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} &= \begin{bmatrix} 0 \\ 0 \end{bmatrix} \\
c_1 &= \sqrt{2} \\
c_2 &= 1 \\
c &= \frac{1}{\sqrt{3}} \begin{bmatrix} \sqrt{2} \\ 1 \end{bmatrix}
\end{aligned}$$

$$\Psi_5 = \frac{1}{\sqrt{3}}(\sqrt{2}\chi_4 + \chi_5), \quad E_5 = \alpha + \beta$$

Type IV:

$$\begin{aligned}
H_{6,6}^{IV} &= \langle \chi_6 | \hat{h} | \chi_6 \rangle = \frac{1}{4} \langle \phi_2 - \phi_3 + \phi_5 - \phi_6 | \hat{h} | \phi_2 - \phi_3 + \phi_5 - \phi_6 \rangle \\
&= \alpha + \frac{1}{4}(-H_{2,3} - H_{3,2} - H_{5,6} - H_{6,5}) = \alpha - \beta \\
\Psi_6 &= \chi_6, \quad E_6 = \alpha - \beta
\end{aligned}$$

2c.

	—		E_4	$\alpha - 2\beta$
—		—	E_2, E_6	$\alpha - \beta$
$\uparrow\downarrow$		$\uparrow\downarrow$	E_3, E_5	$\alpha + \beta$
	$\uparrow\downarrow$		E_1	$\alpha + 2\beta$

2d. De totale energie is dus $6\alpha + 8\beta$. De bindingsenergie is dan 8β. De delocalisatie energie is dan:

$$\begin{aligned} E_{del} &= E_{benzeen} - 3E_{etheen} \\ &= 6\alpha + 8\beta - 3(2\alpha + 2\beta) \\ &= 2\beta \end{aligned}$$

2e. Zie Opgave 2b:

$$\begin{aligned} \Psi_1 &= \frac{1}{\sqrt{6}}(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6) \\ \Psi_2 &= \frac{1}{\sqrt{3}}(\phi_1 + \phi_4 - \frac{1}{2}(\phi_2 + \phi_3 + \phi_5 + \phi_6)) \\ \Psi_3 &= \frac{1}{2}(\phi_2 + \phi_3 - \phi_5 - \phi_6) \\ \Psi_4 &= \frac{1}{\sqrt{6}}(\phi_1 - \phi_4 - \phi_2 - \phi_3 - \phi_5 + \phi_6) \\ \Psi_5 &= \frac{1}{\sqrt{3}}(\phi_1 - \phi_4) + \frac{1}{2}(\phi_2 - \phi_3 - \phi_5 + \phi_6)) \\ \Psi_6 &= \frac{1}{2}(\phi_2 - \phi_3 + \phi_5 - \phi_6) \end{aligned}$$

2f. Er werd geen gebruik gemaakt van $\hat{\sigma}_{xy}$, omdat hier alle functies dezelfde symmetrie hebben ($\hat{\sigma}_{xy}\phi_i = -\phi_i$ met i=1,...,6).

2g. Nee, want $\hat{i} = \hat{\sigma}_{xy}\hat{\sigma}_{xz}\hat{\sigma}_{yz}$

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Vraag 3: Localiseren van MOs voor water

3a.

$$\begin{aligned}\psi_1 + \psi_2 &= \frac{1}{\sqrt{2}}(\phi_{2p_y,O} + \phi_{2p_x,O} + \chi_S + \chi_A) \\ &= \frac{1}{\sqrt{2}}(\phi_{2p_y,O} + \phi_{2p_x,O} + \frac{1}{\sqrt{2}}(2\phi_{1s,A}))\end{aligned}$$

Zo ook

$$\begin{aligned}\psi_1 - \psi_2 &= \frac{1}{\sqrt{2}}(\phi_{2p_y,O} - \phi_{2p_x,O} + \chi_S - \chi_A) \\ &= \frac{1}{\sqrt{2}}(\phi_{2p_y,O} - \phi_{2p_x,O} + \frac{1}{\sqrt{2}}(2\phi_{1s,B}))\end{aligned}$$

3b. Denk even terug aan werkcollege 2/3, vraag 4, waarin de eigenschappen van determinanten werden uitgelicht. Daaruit volgt dat kolommen bij elkaar opgeteld kunnen worden en dat vermenigvuldiging van een kolom gelijk staat aan vermenigvuldiging van de hele determinant. Uit de vorige vraag blijkt dat $\psi_1 + \psi_2$ gelocaliseerd staat richting van het H_a atoom en $\psi_1 - \psi_2$ in de richting van H_b. De determinant wordt dan dus:

$$\Psi \propto \left| (\psi_1 + \psi_2) \quad \overline{(\psi_1 + \psi_2)} \quad (\psi_1 - \psi_2) \quad \overline{(\psi_1 - \psi_2)} \right|$$

NB: Als je dat netjes uitwerkt gaat het als volgt,

$$\begin{aligned}\left|\psi_1 \quad \overline{\psi_1} \quad \psi_2 \quad \overline{\psi_2}\right| &= \left|(\psi_1 + \psi_2) \quad \overline{\psi_1} \quad \psi_2 \quad \overline{\psi_2}\right| \\ &= \left|(\psi_1 + \psi_2) \quad \overline{\psi_1} \quad \psi_2 - 1/2(\psi_1 + \psi_2) \quad \overline{\psi_2}\right| \\ &= \left|(\psi_1 + \psi_2) \quad \overline{\psi_1} \quad 1/2(-\psi_1 + \psi_2) \quad \overline{\psi_2}\right| \\ &= 1/2\left|(\psi_1 + \psi_2) \quad \overline{\psi_1} \quad (\psi_1 - \psi_2) \quad \overline{\psi_2}\right|\end{aligned}$$

En zo ook voor de andere twee kolommen.