HW #10 Answers

1. IP K = 4.34 eV, EA Cl = 3.61 eV.
So at R = ∞, $K^+ + Cl^-$ is 0.73 eV (0.027 a.u.) above K + Cl.

At long range $E_{K+Cl} \approx 0$, $E_{K^+Cl^-} \approx 0.027 - 1/R$
The curves cross at $R_c = 37$ a.u. (19.6 Å)
The dipole moment curve will be essentially linear from small R to R_c, and then droop to 0 for $R > R_c$.

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2. Occupied orbitals of planar biphenyl have energies of $\alpha + 2.28\beta$, $\alpha + 1.89\beta$, $\alpha + 1.32\beta$, $\alpha + \beta$, $\alpha + \beta$, $\alpha + 0.70\beta$.
This gives a total π energy of $12\alpha + 16.38\beta$ vs $12\alpha + 16\beta$ for two non-interacting benzene rings
The stabilization due to conjugation is ~ 2eV.
If one considers the H atoms that are close to one another on the two rings and the fact that they carry a charge of ~ 0.3, this gives a repulsion of ~1.4eV. The repulsion is probably greater than this due to the overlap of the charge densities of the relevant H atoms.

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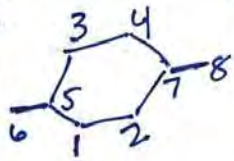
3. Xylylene



Totally symmetric representation

$\chi_1 = \frac{1}{2}(\varphi_1 + \varphi_2 + \varphi_3 + \varphi_4)$
$\chi_2 = \frac{1}{\sqrt{2}}(\varphi_5 + \varphi_6)$
$\chi_3 = \frac{1}{\sqrt{2}}(\varphi_6 + \varphi_8)$

$H_{11} = \alpha + \beta$, $H_{22} = H_{33} = \alpha$
$H_{12} = \sqrt{2}\beta$, $H_{13} = 0$
$H_{23} = \beta$

So the matrix we need to diagonalize is

$$\begin{pmatrix} 1 & \sqrt{2} & 0 \\ \sqrt{2} & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

The eigenvalues are $\alpha + 2.17\beta$, $\alpha + 0.31\beta$, $\alpha - 1.48\beta$

Change sign in vertical plane

$\chi_4 = 1/2(\varphi_1 + \varphi_2 - \varphi_3 - \varphi_4)$

$H_{44} = \alpha + \beta$

(note I actually had the molecule rotated 90° from what is shown above)

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change sign in both planes

$\chi_5 = 1/2(\varphi_1 - \varphi_2 - \varphi_3 + \varphi_4)$

$H_{55} = \alpha - \beta$

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change sign in horizontal plane

$\chi_6 = 1/2(\varphi_1 + \varphi_3 - \varphi_2 - \varphi_4)$

$\chi_7 = 1/\sqrt{2}(\varphi_5 - \varphi_7)$

$\chi_8 = 1/\sqrt{2}(\varphi_6 - \varphi_8)$

$H_{66} = \alpha - \beta$, $H_{67} = \sqrt{2}\beta$

$H_{77} = \alpha$, $H_{68} = 0$

$H_{88} = \alpha$, $H_{78} = -\beta$

Eigenvalues: $\alpha - 2.17\beta$, $\alpha + 1.48\beta$, $\alpha - 0.31\beta$

Planar cyclooctatetraene:

Eigenvalues $\alpha + 2\beta$, $\alpha + 1.41\beta$, $\alpha + 1.41\beta$, $\alpha + 0$, $\alpha + 0$, $\alpha - 1.41\beta$, $\alpha - 1.41\beta$, $\alpha - 2\beta$

Total π energy COT = $8\alpha + 9.64\beta$

Total π energy xylylene = $8\alpha + 9.92\beta$ ← more stable

4. CO_2 in plane π^*  in-plane σ_g

These two orbitals mix when the molecule is bent, with one combination dropping rapidly in energy and the other combination going up in energy as the molecule is bent.