

Solution Key, PS1 (Coalson), Chem. 2430 [Nov. 2009]

1) a) Consider

$$S_{22} = \int d\vec{r} \chi_2 \chi_2 = \frac{1}{4} \int d\vec{r} [\phi_1 - \phi_2 - \phi_3 + \phi_4][\phi_1 - \phi_2 - \phi_3 + \phi_4] = \frac{1}{4}[1+1+1+1] = 1$$

where we have used the orthonormality properties of $\phi_{1,2,3,4}$. We find similarly that $S_{11} = S_{33} = S_{44} = 1$.

Next examine an off-diagonal overlap matrix element:

$$S_{12} = S_{21} = \int d\vec{r} \chi_1 \chi_2 = \frac{1}{4} \int d\vec{r} [\phi_1 + \phi_2 + \phi_3 + \phi_4][\phi_1 - \phi_2 - \phi_3 + \phi_4] = \frac{1}{4}[1-1-1+1] = 0$$

We find similarly that all off-diagonal overlap elements vanish, i.e., $S_{ij} = 0$; $i \neq j$.

b,c) Consider:

$$\tilde{H}_{22} = \int d\vec{r} \chi_2 \hat{H} \chi_2 = \frac{1}{4} \int d\vec{r} [\phi_1 - \phi_2 - \phi_3 + \phi_4] \hat{H} [\phi_1 - \phi_2 - \phi_3 + \phi_4] = \frac{1}{4}[4\alpha - 2\beta] = \alpha - \frac{1}{2}\beta$$

$$\tilde{H}_{12} = \int d\vec{r} \chi_1 \hat{H} \chi_2 = \frac{1}{4} \int d\vec{r} [\phi_1 + \phi_2 + \phi_3 + \phi_4] \hat{H} [\phi_1 - \phi_2 - \phi_3 + \phi_4] = \frac{1}{4}[-2\beta] = -\frac{1}{2}\beta$$

$$\tilde{H}_{12} = \int d\vec{r} \chi_1 \hat{H} \chi_3 = \frac{1}{4} \int d\vec{r} [\phi_1 + \phi_2 + \phi_3 + \phi_4] \hat{H} [\phi_1 + \phi_2 - \phi_3 - \phi_4] = 0$$

Continuing in this fashion, we obtain:

$$\tilde{\mathbf{H}} = \begin{bmatrix} \alpha + 3\beta/2 & -\beta/2 & 0 & 0 \\ -\beta/2 & \alpha - \beta/2 & 0 & 0 \\ 0 & 0 & \alpha + \beta/2 & \beta/2 \\ 0 & 0 & \beta/2 & \alpha - 3\beta/2 \end{bmatrix}$$

Finding the eigenvectors/values of the χ_1, χ_2 block gives:

$$(i) \quad E_{MO} = \alpha + \frac{\beta}{2}[1 + \sqrt{5}]; \quad \bar{c} = \frac{1}{\sqrt{10 + 4\sqrt{5}}} \begin{pmatrix} 2 + \sqrt{5} \\ -1 \end{pmatrix} = \begin{pmatrix} 0.973 \\ -0.23 \end{pmatrix}$$

$$(ii) \quad E_{MO} = \alpha + \frac{\beta}{2}[1 - \sqrt{5}]; \quad \bar{c} = \begin{pmatrix} 0.23 \\ 0.973 \end{pmatrix}$$

where the corresponding molecular orbitals are given by $\psi = c_1\chi_1 + c_2\chi_2$.

Likewise, finding the eigenvectors/values of the χ_3, χ_4 block gives:

$$(iii) \quad E_{MO} = \alpha + \frac{\beta}{2}[-1 + \sqrt{5}]; \quad \bar{c} = \begin{pmatrix} 0.923 \\ 0.23 \end{pmatrix}$$

$$(iv) \quad E_{MO} = \alpha + \frac{\beta}{2}[-1 - \sqrt{5}]; \quad \bar{c} = \begin{pmatrix} -0.23 \\ 0.973 \end{pmatrix}$$

where the corresponding molecular orbitals are given by $\psi = c_1\chi_3 + c_2\chi_4$.

d) i) The four MO energy levels obtained above are identical to the energy levels obtained by direct processing of the Hückel Hamiltonian for butadiene, without employing symmetry adapted basis functions. (See Atkins, p. 270-271).

ii) Consider MO i) above, which corresponds to the energy eigenfunction $\psi = 0.973\chi_1 - 0.23\chi_2$.

Invoking the definitions of $\chi_{1,2}$ as linear combinations of $\phi_{1,2,3,4}$ [cf. Fig. 1], we can write this wavefunction equivalently as:

$$\psi = 0.372\phi_1 + 0.602\phi_2 + 0.602\phi_3 + 0.372\phi_4 \quad ,$$

which is precisely the standard Hückel theory prediction for the lowest energy MO of butadiene (see Atkins, p. 271). In a similar fashion, the three other MOs obtained above can also be converted exactly into the corresponding MOs obtained via standard Hückel theory.

2) a) For $\beta_1 = \beta_2$, Eq. [3] reduces to:

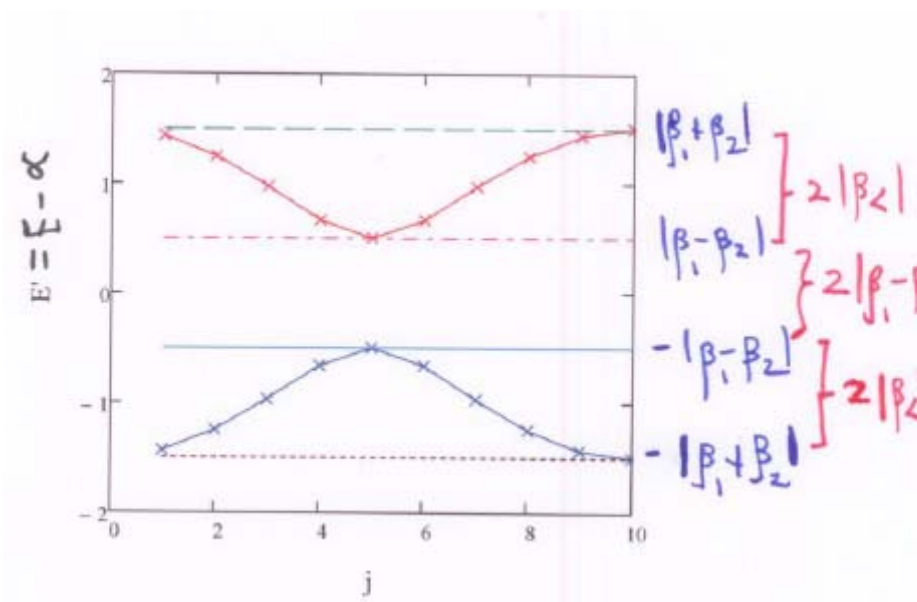
$$E_j' = \pm\sqrt{2}\beta[1 + \cos(4\pi j / N)]^{1/2} \quad ; \quad j = 1, 2, \dots, N/2 \quad [A1]$$

This generates exactly the same N energy eigenvalues as the formula for Hückel MO energies of (single- β) cyclic hydrocarbons given in class or in Atkins (p. 273). For the case that $N=8$, we find numerically from formula [A1]:

$$E_j / \beta = -2, -1.414, -1.414, 0, 0, 1.414, 1.414, 2$$

Note that 3 of these energy levels are doubly degenerate. Exactly the same 8 Hückel MO energy levels are obtained from the standard formula for cyclic hydrocarbons.

b) The range of allowed energy levels in each band is effectively determined by the allowed range of the cosine function. The following boundaries are obtained:



[Note: The curves in this figure are based on the values $\beta_1 = -0.5, \beta_2 = -1.0$]

Thus:

i) for both bands, band width = $2|\beta_{<}|$, where $|\beta_{<}|$ is the lesser of $|\beta_{1,2}|$.

ii) band gap = $2|\beta_1 - \beta_2|$.

8.3 Denote ψ_a by a and ψ_b by b .

$$\begin{aligned}\psi_{\pm} &= (a \pm b)/[2(1 \pm S)]^{1/2} \\ |\psi_{\pm}|^2 &= (a^2 + b^2 \pm 2ab)/2(1 \pm S) \\ \rho_{\pm} &= \{(a^2 + b^2 \pm 2ab)/2(1 \pm S)\} - \frac{1}{2}(a^2 + b^2) \\ &= \pm[ab - \frac{1}{2}S(a^2 + b^2)]/(1 \pm S)\end{aligned}$$

$S = (1 + s + \frac{1}{3}s^2)e^{-s}$, $s = R/a_0 = 2.46$ when $R = 130$ pm; hence $S = 0.469$.

$a \rightarrow \psi_a = (1/\pi a^3)^{1/2}e^{-r_a/a}$; $b \rightarrow \psi_b = (1/\pi a^3)^{1/2}e^{-r_b/a}$

$$(1/\pi a^3) = 2.148 \times 10^{-6} \text{ pm}^{-3}$$

$$\begin{aligned}\rho_+ &= (1.462 \times 10^{-6} \text{ pm}^{-3}) \left\{ e^{-(r_a+r_b)/a} - 0.235(e^{-2r_a/a} + e^{-2r_b/a}) \right\} \\ \rho_- &= -(4.045 \times 10^{-6} \text{ pm}^{-3}) \left\{ e^{-(r_a+r_b)/a} - 0.235(e^{-2r_a/a} + e^{-2r_b/a}) \right\}\end{aligned}$$

Note that $\rho_- = -2.767\rho_+$, so it is sufficient to plot one. We plot

$$\rho \equiv e^{-(r_a+r_b)/a} - 0.235(e^{-2r_a/a} + e^{-2r_b/a})$$

For all points on a line joining the two nuclei and lying beyond b , $r_b = r_a - R$, we have

$$\rho = (e^s - 0.235 - 0.235e^{2s})e^{-2r_a/a} = -20.73e^{-2r_a/a}$$

For points on the same line, but lying between the nuclei, $r_b = R - r_a$, so

$$\begin{aligned}\rho &= e^{-s} - 0.235(e^{-2r_a/a} + e^{-2s}e^{2r_a/a}) \\ &= 0.0854 - 0.235(e^{-2r_a/a} + 0.00730 e^{2r_a/a})\end{aligned}$$

(Note that the two expressions for ρ are equal at $r_a = R$.) ρ is plotted in Fig. 1.

Exercise: Plot the difference density for points either side of $R = 130$ pm, e.g. at $R = 80$ pm and 180 pm, and also for points in a plane bisecting and perpendicular to the internuclear distance (with $R = 130$ pm).

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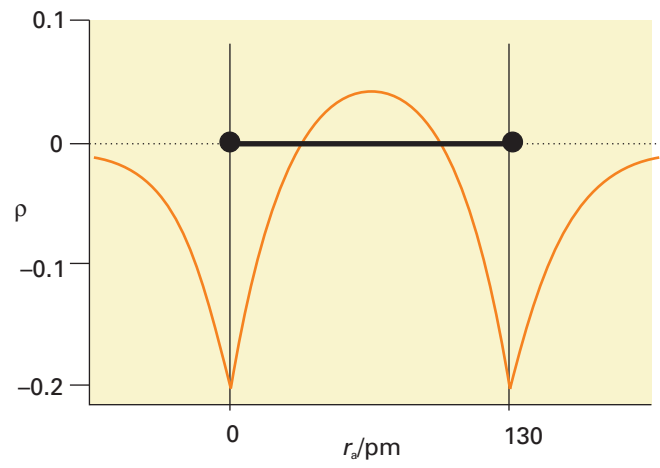


Figure 1: The difference density calculated in Problem 8.3.

8.4

$$k = (d^2E/dR^2)_0 = (1/a_0^2)(d^2E/dx^2)_0 \quad [x = R/a_0]$$

The 0 indicates the minimum of the curve, which occurs at close to $x = 2.5$ [Section 8.3, Fig. 8.12 of the text].

$$\begin{aligned} E &= E_{1s} + j_0/xa_0 - \left(\frac{j' + k'}{1 + S} \right) \quad [\text{eqn 8.25}] \\ &= E_{1s} + j_0/xa_0 - \frac{(j_0/xa_0)\{1 - (1+x)e^{-2x}\} + (j_0/a_0)(1+x)e^{-x}}{1 + (1+x + \frac{1}{3}x^2)e^{-x}} \\ &= E_{1s} + \frac{j_0}{a_0} \left\{ \frac{1}{x} - \frac{(1/x)\{1 - (1+x)e^{-2x}\} + (1+x)e^{-x}}{1 + (1+x + \frac{1}{3}x^2)e^{-x}} \right\} \\ k &= \left(\frac{j_0}{a_0^3} \right) \frac{d^2}{dx^2} \{ \dots \} \text{ evaluated at } x = 2.5 \\ &= 0.061884j_0/a_0^3 \quad [\text{mathematical software second derivative evaluator}] \end{aligned}$$

The vibrational frequency is therefore

$$\begin{aligned} \omega &= \left(\frac{2k}{m_H} \right)^{1/2} = \left(\frac{0.061884e^2}{2\pi\epsilon_0 m_H a_0^3} \right)^{1/2} \\ &= \left(\frac{2 \times 0.061884\hbar^2}{m_e m_H a_0^4} \right)^{1/2} [a_0 = 4\pi\epsilon_0\hbar^2/m_e e^2] = \frac{0.35181\hbar}{(m_e m_H)^{1/2} a_0^2} \\ &= \underline{3.41 \times 10^{14} \text{ s}^{-1}} \quad (\nu = 54.3 \text{ THz}) \end{aligned}$$

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8.7

$$\begin{aligned}
 \psi^2(1, 2) &= \{1/4(1+S)^2\}\{a(1)a(2) + b(1)b(2) + a(1)b(2) + b(1)a(2)\}^2 \\
 &= \{1/4(1+S)^2\}\{a^2(1)a^2(2) + b^2(1)b^2(2) + a^2(1)b^2(2) + b^2(1)a^2(2) \\
 &\quad + 2a(1)b(1)a(2)b(2) + 2a^2(1)a(2)b(2) + 2a(1)b(1)a^2(2) \\
 &\quad + 2b(1)a(1)b^2(2) + 2b^2(1)a(2)b(2) + 2a(1)b(1)b(2)a(2)\}
 \end{aligned}$$

$$\begin{aligned}
 \rho_1 &\equiv \int \psi^2(1, 2) d\tau_2 \\
 &= \{1/4(1+S)^2\}\{2a^2(1) + 2b^2(1) + 2a(1)b(1)S + 2a^2(1)S \\
 &\quad + 2a(1)b(1) + 2a(1)b(1) + 2b^2(1)S + 2a(1)b(1)S\} \\
 &= \{1/2(1+S)\}\{a^2(1) + b^2(1) + 2a(1)b(1)\}
 \end{aligned}$$

It follows that

$$\begin{aligned}
 \delta\rho &\equiv \rho_1 - \frac{1}{2}\{a^2(1) + b^2(1)\} \\
 &= \{1/2(1+S)\}\{a^2(1) + b^2(1) + 2a(1)b(1) - a^2(1)(1+S) - b^2(1)(1+S)\} \\
 &= \{1/2(1+S)\}\{2a(1)b(1) - a^2(1)S - b^2(1)S\}
 \end{aligned}$$

As in Problem 8.3, outside the nuclei but on the line of centres, $r_b = r_a - R$, whereas between the nuclei, $r_b = R - r_a$. Since

$$a = (1/\pi a_0^3)^{1/2} e^{-r_a/a_0},$$

and likewise for b , and since

$$S = (1 + s + \frac{1}{3}s^2)e^{-s} = 0.75 \text{ when } R = 74 \text{ pm}$$

we have:

Outside the nuclei:

$$\begin{aligned}
 2\pi a_0^3 \delta\rho &= \{2e^{-2r_a/a_0+s} - 0.75e^{-2r_a/a_0}(1 + e^{2s})\}/1.75 \\
 &= -2.82e^{-2r_a/a_0}
 \end{aligned}$$

Between the nuclei:

$$\begin{aligned}
 2\pi a_0^3 \delta\rho &= \{2e^{-s} - 0.75e^{-2r_a/a_0} - 0.75e^{2r_a/a_0-2s}\}/1.75 \\
 &= 0.282 - 0.429e^{-2r_a/a_0} - 0.026e^{2r_a/a_0}
 \end{aligned}$$

The two components (which coincide at $r_a = R$) are plotted in Fig. 1.

Exercise: Plot the difference density for different bond lengths (e.g. $R=50$ pm, 100 pm).

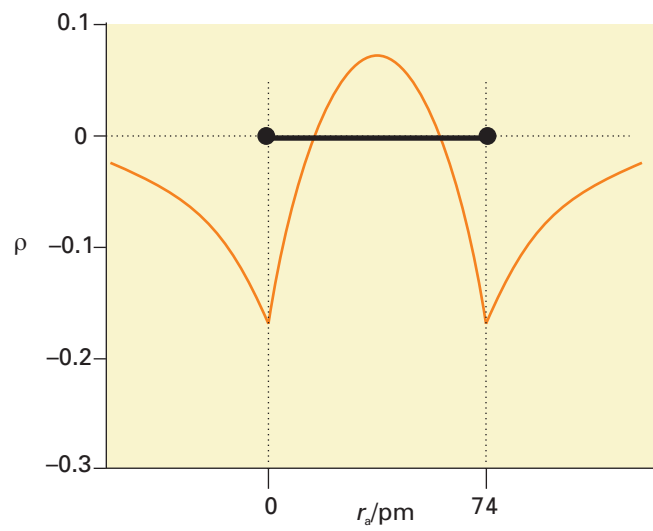


Figure 1: The difference density calculated in Problem 8.7.

8.8 The question refers to $\psi = c_1\Psi_1 + c_3\Psi_3$ [in the notation of Section 8.5]. Therefore, noting that the spin factors are common to Ψ_1 and Ψ_3 , so ignoring them for the present,

$$\begin{aligned}
 \psi &= c_1 1\sigma(1)1\sigma(2) + c_3 2\sigma(1)2\sigma(2) \\
 &= \frac{1}{2}c_1\{a(1) + b(1)\}\{a(2) + b(2)\} + \frac{1}{2}c_3\{a(1) - b(1)\}\{a(2) - b(2)\} \\
 &\quad [a = \phi_a, b = \phi_b, \text{ and } 1\sigma = (a + b)/\sqrt{2}, 2\sigma = (a - b)/\sqrt{2}] \\
 &= \frac{1}{2}c_1\{a(1)a(2) + b(1)b(2) + a(1)b(2) + b(1)a(2)\} \\
 &\quad + \frac{1}{2}c_3\{a(1)a(2) + b(1)b(2) - a(1)b(2) - b(1)a(2)\} \\
 &= \frac{1}{2}(c_1 + c_3)\{a(1)a(2) + b(1)b(2)\} + \frac{1}{2}(c_1 - c_3)\{a(1)b(2) + b(1)a(2)\}
 \end{aligned}$$

as required.

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