Answers to the Problems in Chapter 11

Problem 11.1.

We have to evaluate the integral

$$\begin{array}{ccccc} & A & & B & & C & & D & \\ \tfrac{1}{4}\langle \phi_{1s}\alpha(1)\bullet\phi_{2s}\beta(2) - \phi_{2s}\beta(1)\bullet\phi_{1s}\alpha(2) - \phi_{1s}\beta(1)\bullet\phi_{2s}\alpha(2) + \phi_{2s}\alpha(1)\bullet\phi_{1s}\beta(2) & | & e^2/r_{12} & | \\ \phi_{1s}\alpha(1)\bullet\phi_{2s}\beta(2) - \phi_{2s}\beta(1)\bullet\phi_{1s}\alpha(2) - \phi_{1s}\beta(1)\bullet\phi_{2s}\alpha(2) + \phi_{2s}\alpha(1)\bullet\phi_{1s}\beta(2)\rangle & & & & \\ & A' & & B' & & C' & & D' & \end{array}$$

There are sixteen terms in total and we can group them together in the following manner: A/D' $\equiv \langle \phi_{1s}\alpha(1)\bullet\phi_{2s}\beta(2)|e^2/r_{12}|\phi_{2s}\alpha(1)\bullet\phi_{1s}\beta(2)\rangle$

1. The spin of each electron must be the same in the bra and ket. Therefore, the following eight component integrals must be zero.

   A/B', A/C', B/A', B/D', C/A', C/D', D/B', D/C' = 0.

2. There are four Coulomb integrals, e.g.

$\langle \phi_{1s}\alpha(1)\bullet\phi_{2s}\beta(2)|e^2/r_{12}|\phi_{1s}\alpha(1)\bullet\phi_{2s}\beta(2)\rangle = J_{1s,2s}$, namely:

A/A', B/B', C/C', D/D' = $4J_{1s,2s}$ in total.

3. There are four exchange integrals, e.g.

$\langle \phi_{1s}\alpha(1)\bullet\phi_{2s}\beta(2)|e^2/r_{12}|\phi_{2s}\alpha(1)\bullet\phi_{1s}\beta(2)\rangle = K_{1s,2s}$, namely:

A/D', B/C', C/B', D/A' = $4K_{1s,2s}$ in total.

Therefore, the total electron repulsion energy is $\tfrac{1}{4}\{4J_{1s,2s} + 4K_{1s,2s}\}$

$= J_{1s,2s} + K_{1s,2s}$.

Problem 11.2.

We have to evaluate the integral $M_T = e\langle {}^3\Psi_f|r_1 + r_2|{}^1\Psi_i\rangle$ where:

${}^1\Psi_i = \sqrt{\tfrac{1}{2}}\{\phi_{1s}\alpha(1)\bullet\phi_{1s}\beta(2) - \phi_{1s}\beta(1)\bullet\phi_{1s}\alpha(2)\}$

and

${}^3\Psi_f = \sqrt{\tfrac{1}{2}}\{\phi_{1s}\alpha(1)\bullet\phi_{2p}\alpha(2) - \phi_{2p}\alpha(1)\bullet\phi_{1s}\alpha(2)\}$

Therefore,

$$M_T = \tfrac{1}{2}e\langle \phi_{1s}\alpha(1)\bullet\phi_{1s}\beta(2) - \phi_{1s}\beta(1)\bullet\phi_{1s}\alpha(2)|r_1 + r_2| \phi_{1s}\alpha(1)\bullet\phi_{2p}\alpha(2) - \phi_{2p}\alpha(1)\bullet\phi_{1s}\alpha(2)\rangle$$

The most simple and instructive procedure is to focus attention on the spin functions which are the essence of the difference between singlets and triplets. We first note that the operators r_1 and r_2 do not change the spin of the function upon which they operate. Therefore, it is not possible to pair both spins of any function from the bra with any function from the ket. Therefore, all four possible contributions to the integral are zero.

Problem 11.3.
[The π-electron molecular orbitals are given in Figure 11.5]
For the transition $\Psi_3 \rightarrow \Psi_5$

$$\Psi_3 = \{1/\sqrt{(12)}\}\{2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6\}$$
$$\Psi_5 = \{1/2\}\{-\phi_2 + \phi_3 - \phi_5 + \phi_6\}$$

The electron transition density, corresponding to Fig. 11.7, for this transition is shown below. It is clear that the transition is x-polarised and

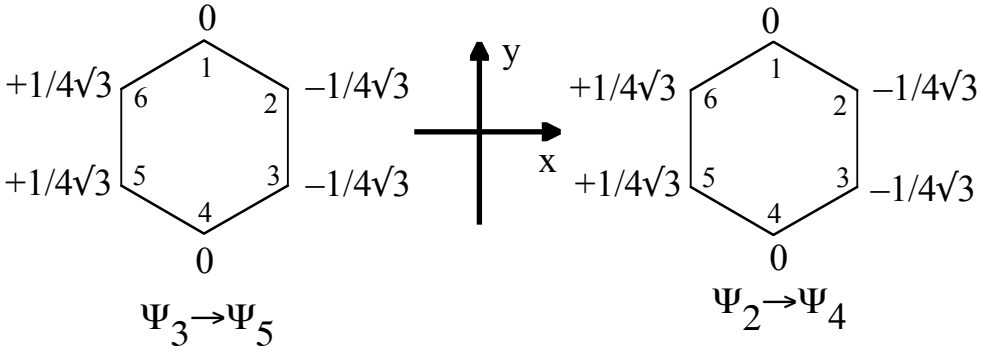
$$T_x = -\{e/4\sqrt{3}\}\times 4\times x = -ex/\sqrt{3}$$

where ±x is the x co-ordinate of the four atoms involved.
For a regular hexagonal benzene ring with C–C bond length = R, x = R√3/2. Thus, the value of T_x is $-eR_x/2$ where the subscript x has been added, as in Section 11.7.2, to indicate that the moment is in the x-direction. This result is equal to the transition moment in the y-direction determined on p. 347 which is what we would expect on account of the high symmetry of benzene.

For the transition $\Psi_2 \rightarrow \Psi_4$

$$\Psi_2 = \{1/2\}\{\phi_2 + \phi_3 - \phi_5 - \phi_6\}$$
$$\Psi_4 = \{1/\sqrt{(12)}\}\{2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6\}$$

The electron transition density, corresponding to Fig. 11.7, for this transition is shown below. It is identical to that for the $\Psi_3 \rightarrow \Psi_5$ transition and gives exactly the same result.



Problem 11.4.

The transition studied in Section 11.7.2 is the $\Psi_2 \rightarrow \Psi_5$. If overlap is included it is helpful to draw up the following array of terms to be considered. Each array element is the product of the y co-ordinate (in units of R, the C-C bond length) of the point of maximum overlap of the orbital functions at the head of the row and column and their overlap. Their sum, multiplied by $\{½\}^2$, is the transition moment.

		Ψ_2			
		$+\phi_2$	$+\phi_3$	$-\phi_5$	$-\phi_6$
	$-\phi_2$	$-½R$	0	0	$½RS_{26}$
Ψ_5	$+\phi_3$	0	$-½R$	$½RS_{35}$	0
	$-\phi_5$	0	$½RS_{35}$	$-½R$	0
	$+\phi_6$	$½RS_{26}$	0	0	$-½R$

It can be seen immediately that the four overlap contributions to the transition moment are of the opposite sign to the others which we found previously. Furthermore, the overlap $S_{26} = S_{35}$ will be very small because of the distance between the carbon atoms involved.

Problem 11.5.

When the p electron of the halogen ion is transferred to the solvent the resulting halogen atom has just 5 p electrons. We normally think of a situation like this as a hole in an otherwise complete p-electron shell, and the spin-orbit coupling which results is extremely similar to that of a single p electron so that states designated $^2P_{1/2}$ and $^2P_{3/2}$ result. (See Section 5.9). Thus, the transfer of the electron gives rise to two excited states separated in energy by $3\zeta/2$, where ζ is the spin-orbit coupling constant. These two states also exist in the gas-phase halogen atom and the data given in the question represent the energy of the transition from the $^2P_{3/2}$ to the $^2P_{1/2}$ state. We therefore expect to find that

$49300 - 45900 = 3400$ cm^{-1} is approximately equal to 3685 cm^{-1} and

$48500 - 40800 = 7700$ cm^{-1} is approximately equal to 7603 cm^{-1}.

The differences in the figures reflect the very different environments of the atoms for the two measurements and also the uncertainty in identifying the peak positions of the very broad CT bands.

Problem 11.6.

λ_{max} ($\pi \rightarrow \pi^*$ ethene) = 162 nm.

Therefore, $\Delta E = h\nu = hc/\lambda = 1.227 \times 10^{-18}$ J.

This energy corresponds to 2β as explained in the question.

Therefore, $2\beta = \Delta E$ or $\beta = \beta_0 = 0.614 \times 10^{-18}$ J.

Therefore, when the bond is twisted 10^o, β

$= \beta_{10} = \beta_0 \cos(10^o) = 0.614 \times 0.985 \times 10^{-18} = 0.605 \times 10^{-18}$ J.

The energy of the absorption band, $\Delta E'$, is now $2\beta_{10} = 1.210 \times 10^{-18}$ J.

And this corresponds to a wavelength of $\lambda = hc/\Delta E' = 164 \times 10^{-9}$ m = 164 nm.

Therefore, the band shift is approximately 2 nm.