Answers to the Problems in Chapter 8

Problem 8.1.

Let $E_a = 2E\cos\omega$ be aligned along the y axis. Then, if the two waves are 90° out of phase, $E_b = E\cos(90–\omega) = E\sin\omega$. Align E_b along the x axis. Calculate the length of each vector for a series of angles, ω, sum as vectors and plot the sum against ω on a polar plot. (Since the two vectors are always at 90° their sum = $\{E_a^2 + E_b^2\}^{½}$. See table below.

Angle	E_a	E_b	Sum
0	2.0000	0.0000	2.0000
30	1.7321	0.5000	1.8028
60	1.0000	0.8660	1.3229
90	0.0000	1.0000	1.0000
120	-1.0000	0.8660	1.3229
150	-1.7320	0.5000	1.8028
180	-2.0000	0.0000	2.0000
210	-1.7321	-0.5000	1.8028
240	-1.0000	-0.8660	1.3229
270	0.0000	-1.0000	1.0000
300	1.0000	-0.8660	1.3229
330	1.7320	-0.5000	1.8028
360	2.0000	0.0000	2.0000

The plot will be an ellipse. Plane polarised and circularly polarised light represent the two extremes of elliptically polarised light. When plane polarised light passes through an optically active sample not only is the plane of polarisation rotated, because the left and right circularly polarised components of the beam travel at different speeds, but the light becomes elliptically polarised, because the two components are not equally absorbed.

Problem 8.2

We use the following H-atom wavefunctions in atomic units; $e = \mathrm{Z} = \mathrm{a}_0 = 1$.

$\Psi_{1s} = \{1/\pi\}^{1/2}\exp(-r)$
$\Psi_{2px} = \{1/32\pi\}^{1/2}\, r\sin\vartheta\,\cos\phi\ \exp(-r/2)$
$\Psi_{2pz} = \{1/32\pi\}^{1/2}\, r\cos\vartheta\ \exp(-r/2)$

And the transition moment operator $\mathrm{M_x} = r\sin\vartheta\,\cos\phi$

Then

$$\left\langle \Psi_{2px} \middle| \mathrm{M_x} \middle| \Psi_{1s} \right\rangle = \frac{1}{4\sqrt{2}\,\pi}\iiint r\sin\vartheta\cos\phi e^{-r/2}\cdot r\sin\vartheta\cos\phi\cdot \mathrm{e}^{-r}\cdot r^2\sin\vartheta \mathrm{d}r\mathrm{d}\vartheta\mathrm{d}\phi$$

$$= \frac{1}{4\sqrt{2}\,\pi}\int_0^\infty r^4 \mathrm{e}^{-3r/2}\mathrm{d}r\int_0^\pi \sin^3\vartheta \mathrm{d}\vartheta\int_0^{2\pi}\cos^2\phi \mathrm{d}\phi$$

$$= \frac{1}{4\sqrt{2}\,\pi}\cdot 4!\cdot\left(\frac{2}{3}\right)^5\cdot\frac{4}{3}\cdot\pi = 0.7449$$

and

$$\left\langle \Psi_{2pz} \middle| \mathrm{M_x} \middle| \Psi_{1s} \right\rangle = \frac{1}{4\sqrt{2}\,\pi}\iiint r\cos\vartheta e^{-r/2}\cdot r\sin\vartheta\cos\phi\cdot \mathrm{e}^{-r}\cdot r^2\sin\vartheta \mathrm{d}r\mathrm{d}\vartheta\mathrm{d}\phi$$

$$= \frac{1}{4\sqrt{2}\,\pi}\int_0^\infty r^4 \mathrm{e}^{-3r/2}\mathrm{d}r\int_0^\pi \sin^2\vartheta\cos\vartheta \mathrm{d}\vartheta\int_0^{2\pi}\cos\phi \mathrm{d}\phi$$

$$= \frac{1}{4\sqrt{2}\,\pi}\cdot 4!\cdot\left(\frac{2}{3}\right)^5\cdot 0\cdot 0 = 0$$

Thus, a 1s → 2px transition is possible with x-polarised radiation, but a 1s → 2pz transition is not.

Problem 8.3.

From Box 10.3

$$|\Psi_0> = \{\gamma/\pi\}^{1/4}\ \exp(-\tfrac{1}{2}\gamma r^2)$$

and

$$|\Psi_1> = \{\gamma/\pi\}^{1/4}\ \sqrt{(2\gamma)}\ r\ \exp(-\tfrac{1}{2}\gamma r^2)$$

$$\gamma = 4\pi^2\mu\nu_c/h$$

Thus,

$$\begin{aligned}
\langle\Psi_1|\hat{r}|\Psi_0\rangle &= \sqrt{\frac{\gamma}{\pi}}\int_{-\infty}^{+\infty}\sqrt{2\gamma}\cdot r^2\exp(-\gamma r^2)\mathrm{d}r \\
&= 2\sqrt{2\gamma}\sqrt{\frac{\gamma}{\pi}}\int_{0}^{+\infty} r^2\cdot\exp(-\gamma r^2)\mathrm{d}r \\
&= 2\sqrt{2\gamma}\sqrt{\frac{\gamma}{\pi}}\cdot\frac{\sqrt{\pi}}{4\gamma^{3/2}} = \sqrt{\frac{1}{2\gamma}} = \sqrt{\frac{h}{8\pi^2\mu\nu_c}}
\end{aligned}$$

From Box 10.2:

$\mu(^1\text{H}-^{35}\text{Cl}) = 1.6267\times10^{-27}$ kg and $\nu_c(^1\text{H}-^{35}\text{Cl}) = 8.9630\times10^{13}$ Hz

which give: $\langle\Psi_1|\hat{r}|\Psi_0\rangle = 7.588\times10^{-11}$ m

[The standard integral given can be used, but it is not the most useful for this problem. A more suitable choice is:

$$\int_0^{\infty} x^t\exp(-ax^2) = \frac{\Gamma[\frac{1}{2}(t+1)]}{2a^{\frac{1}{2}(t+1)}}$$

The gamma function $\Gamma(z)$ is a generalisation of the factorial function, $z!$

For positive integers $\Gamma(n+1) = n!$

For positive half-integers $\Gamma(n+\frac{1}{2}) = \dfrac{1\cdot3\cdot5\cdot7\cdots(2n-1)}{2^n}\Gamma(\frac{1}{2})$

and $\Gamma(\tfrac{1}{2}) = \pi^{1/2}$]

Problem 8.4.

$$\hat{H}\,\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

If $\Psi = \phi_a\exp(-i\omega_a t)$

$$\hat{H}\,\Psi = i\hbar\frac{\partial}{\partial t}\phi_a\exp(-i\omega_a t)$$

$$= i\hbar\phi_a(-i\omega_a)\exp(-i\omega_a t)$$

$$= +\hbar\omega_a\phi_a\exp(-i\omega_a t)$$

An eigenfunction with eigenvalue $+\hbar\omega_a$.

If $\Psi = \Sigma_a c_a\phi_a\exp(-i\omega_a t)$

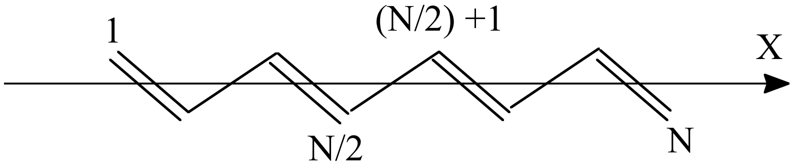
$$\hat{H}\,\Psi = i\hbar\frac{\partial}{\partial t}\sum_a c_a\phi_a\exp(-i\omega_a t)$$

$$= i\hbar\sum_a c_a\phi_a(-i\omega_a)\exp(-i\omega_a t)$$

$$= +\hbar\sum_a c_a\phi_a\omega_a\exp(-i\omega_a t)$$

This is not an eigenfunction because, after the operation, each term in the sum is multiplied by ω_a which changes its value with a.

Problem 8.5.



We require the products of the coefficients at a particular carbon atom, r, in the highest occupied MO and the lowest unoccupied MO.

$$C_{r,\text{hol}} = \sqrt{\frac{2}{N+1}}\,\sin\left(\frac{rN\pi}{2[N+1]}\right) \quad \text{and} \quad C_{r,\text{lul}} = \sqrt{\frac{2}{N+1}}\,\sin\left(\frac{r[\tfrac{1}{2}N+1]\pi}{[N+1]}\right)$$

Therefore,

$$\begin{aligned} C_{r,\text{hol}} \bullet C_{r,\text{lul}} &= \frac{2}{N+1}\sin\left(\frac{rN\pi}{2[N+1]}\right)\bullet\sin\left(\frac{r[N+2]\pi}{2[N+1]}\right) \\ &= -\frac{1}{N+1}\left\{\cos(r\pi)-\cos\left[\frac{r\pi}{N+1}\right]\right\} \end{aligned}$$

This product is the transition density which gives the first line of the table.

If there are N atoms in the chain the centre of the chain lies between atoms ½N and ½N+1 and the distance along x of the n^{th} atom from that centre point, in either direction, is $(n-1)l\cos(30^{\circ}) + \tfrac{1}{2}l\cos(30^{\circ})$ where l is the assumed uniform bond length of 140 pm. Therefore, the x co-ordinate of that atom is $x_n = \pm(n-\tfrac{1}{2})\bullet 140\sqrt{3}/2 = \pm 121.2(n-\tfrac{1}{2})$ pm. With this we can calculate the second line of the table.

The contribution from each atom to the transition moment is simply the product of the two preceding figures in the table. Finally, the contributions are summed and squared.

I find that the values of the squared sum are 13,202 e^2 pm^2, 27,689 e^2 pm^2 and 47,115 e^2 pm^2 for N = 4, 6 and 8 respectively. This is, of course, a very crude calculation but it does show clearly how the increasing length of the conjugated system results in an increasing value of the absorbance.