CHEMISTRY 542

Second Exam

November 10, 2003

①

$$\mathbb{H} = \frac{\hbar}{2}\begin{bmatrix} a_1+a_2 & & & \\ & a_1-a_2 & & \\ & & -a_1+a_2 & \\ & & & -a_1-a_2 \end{bmatrix}$$

$$\mathcal{H} = \begin{bmatrix} 5+10+1 & & & \\ & 5-10-1 & 2 & \\ & 2 & -5+10-1 & \\ & & & -5-10+1 \end{bmatrix}$$

$$\text{or} \begin{bmatrix} \boxed{16} & & & 0 \\ & -6 & 2 & \\ & 2 & 4 & \\ 0 & & & \boxed{-14} \end{bmatrix}$$

$E_1 = 16 \quad E_4 = -14$ Solve the 2x2 det $\det\begin{vmatrix} -6-E & 2 \\ 2 & 4-E \end{vmatrix} = 0$ or $(-6-E)(4-E) = 4$

$$E^2 + 2E - 28 = 0$$

$$E = -\frac{2}{2} \pm \frac{1}{2}\sqrt{4+112} = -1 \pm 5.38516$$

$E_2 = -6.38516 \qquad E_3 = +4.38516$

(2) By inspection,

$E_1^{(0)} = 1 \quad E_1^{(1)} = 3\alpha \quad E_1^{(2)} = -\frac{(1)(1)\alpha^2}{\epsilon_4 - \epsilon_1} - \frac{(-1)(-1)\alpha^2}{\epsilon_5 - \epsilon_1}$

$= -\frac{\alpha^2}{5-1} - \frac{\alpha^2}{8-1}$

$E_2^{(0)} = 2 \quad E_2^{(1)} = 5\alpha \quad E_2^{(2)} = 0$

$E_3^{(0)} = 3 \quad E_3^{(1)} = -\alpha \quad E_3^{(2)} = -\frac{(2)(2)\alpha^2}{\epsilon_4 - \epsilon_3} = -\frac{4\alpha^2}{5-3}$

$E_4^{(0)} = 5 \quad E_4^{(1)} = 2\alpha \quad E_4^{(2)} = -\frac{(1)(1)\alpha^2}{\epsilon_1 - \epsilon_4} - \frac{(2)(2)\alpha^2}{\epsilon_3 - \epsilon_4}$

$= -\frac{\alpha^2}{1-5} - \frac{4\alpha^2}{3-5}$

$E_5^{(0)} = 8 \quad E_5^{(1)} = 0 \quad E_5^{(2)} = -\frac{(-1)(-1)\alpha^2}{\epsilon_1 - \epsilon_5} = -\frac{\alpha^2}{1-8}$

Energies: correct to second order

$E_1 = 1 + 3\alpha - \frac{\alpha^2}{4} - \frac{\alpha^2}{7}$

$E_2 = 2 + 5\alpha$

$E_3 = 3 - \alpha - \frac{4\alpha^2}{2}$

$E_4 = 5 + 2\alpha + \frac{\alpha^2}{4} + \frac{4\alpha^2}{2}$

$E_5 = 8 + \frac{\alpha^2}{7}$

Wavefunctions: correct to first order

$\psi_1 = \phi_1 - \frac{\alpha}{4}\phi_4 - \frac{(-\alpha)}{7}\phi_5 = \phi_1 - \frac{\alpha}{4}\phi_4 + \frac{\alpha}{7}\phi_5$

$\psi_2 = \phi_2$

$\psi_3 = \phi_3 - \frac{2\alpha}{2}\phi_4 = \phi_3 - \alpha\phi_4$

$\psi_4 = \phi_4 - \frac{\alpha}{-4}\phi_1 - \frac{2\alpha}{-2}\phi_3 = \phi_4 + \frac{\alpha}{4}\phi_1 + \alpha\phi_3$

$\psi_5 = \phi_5 - \frac{(-\alpha)}{-7}\phi_1 = \phi_5 - \frac{\alpha}{7}\phi_1$

③ (a) $x_{mn} = \int_0^a \Psi_m^*(x)\; x\; \Psi(x)\, dx$

$$= \frac{2}{a}\int_0^a \sin\left(\frac{m\pi}{a}x\right) x \sin\left(\frac{n\pi}{a}x\right) dx$$

$$= \frac{1}{a}\int_0^a \left\{ \begin{array}{l} x\cos\left[(m-n)\frac{\pi}{a}x\right] \\ -x\cos\left[(m+n)\frac{\pi}{a}x\right] \end{array} \right\} dx$$

$$= \frac{1}{a}\left[\begin{array}{l} x\sin(m-n)\frac{\pi}{a}x + \dfrac{\cos(m-n)\frac{\pi}{a}x}{(m-n)^2\pi^2/a^2} \\ -x\sin(m+n)\frac{\pi}{a}x - \dfrac{\cos(m+n)\frac{\pi}{a}x}{(m+n)^2\pi^2/a^2} \end{array} \right]_0^a$$

sin is zero at both ends so we have:

$$= \frac{1}{a}\left\{ \frac{\cos(m-n)\pi - 1}{(m-n)^2\pi^2/a^2} - \frac{\cos(m+n)\pi - 1}{(m+n)^2\pi^2/a^2} \right\}$$

For $m = 2 \quad n = 1$

$$x_{21} = \frac{1}{a}\left(\frac{a^2(\cos\pi - 1)}{1^2\pi^2} - \frac{a^2(\cos 3\pi - 1)}{3^2\pi^2} \right)$$

$$= \frac{a}{\pi^2}\left(\frac{-2}{1^2} - \frac{-2}{3^2} \right) = \frac{-8a}{\pi^2}\left(2/9 \right)$$

(b) $H = \dfrac{-\hbar^2}{2m}\left(\dfrac{\partial^2}{\partial x_1^2} + \dfrac{\partial^2}{\partial x_2^2} + \dfrac{\partial^2}{\partial x_3^2} + \dfrac{\partial^2}{\partial x_4^2}\right)$

for butadiene —1═2—3═4—

$a = 5(1.40\,Å) \qquad = 7.00\,Å$ (given)

$$H(x_1, x_2, x_3, x_4)\,\Psi(x_1, x_2, x_3, x_4) = E\,\Psi(x_1, x_2, x_3, x_4)$$

Use separation of variables:

Let $\Psi(x_1, x_2, x_3, x_4) = \psi(x_1)\cdot\psi(x_2)\cdot\psi(x_3)\cdot\psi(x_4)$

$$\{H(x_1) + H(x_2) + H(x_3) + H(x_4)\}\,\psi(x_1)\cdot\psi(x_2)\cdot\psi(x_3)\cdot\psi(x_4)$$
$$= E\,\psi(x_1)\cdot\psi(x_2)\cdot\psi(x_3)\cdot\psi(x_4)$$

$$\frac{H(x_1)\psi(x_1)}{\psi(x_1)} + \frac{H(x_2)\psi(x_2)}{\psi(x_2)} + \frac{H(x_3)\psi(x_3)}{\psi(x_3)} + \frac{H(x_4)\psi(x_4)}{\psi(x_4)} = E$$

Therefore, each of the terms must be equal to some constant such that the sum of the four different constants sum to E.

But we already know the answers to

$$H(x_1)\psi(x_1) = E_{n_1}\psi(x_1)$$

$\dfrac{-\hbar^2}{2m}\dfrac{d^2}{dx_1^2}\psi(x_1) = E_{n_1}\psi(x_1)$ has solutions

$$\psi(x_1) = \sqrt{\frac{2}{a}}\sin\left(\frac{n_1\pi}{a}x_1\right)$$

$$E_{n_1} = \frac{n_1^2 h^2}{8ma^2}$$

The others are of the same form.

$$\Psi(x_1, x_2, x_3, x_4) = \sqrt{\frac{2}{a}}\sin\frac{n_1\pi}{a}x_1\cdot\sqrt{\frac{2}{a}}\sin\frac{n_2\pi}{a}x_2\cdot\sqrt{\frac{2}{a}}\sin\frac{n_3\pi}{a}x_3\cdot\sqrt{\frac{2}{a}}\sin\frac{n_4\pi}{a}x_4$$

and $E = \dfrac{n_1^2 h^2}{8ma^2} + \dfrac{n_2^2 h^2}{8ma^2} + \dfrac{n_3^2 h^2}{8ma^2} + \dfrac{n_4^2 h^2}{8ma^2}$

For particle 1 we have: Similarly for particles 2, 3, and 4

$\dfrac{4^2 h^2}{8ma^2}$

$\dfrac{3^2 h^2}{8ma^2}$

$\dfrac{2^2 h^2}{8ma^2}$

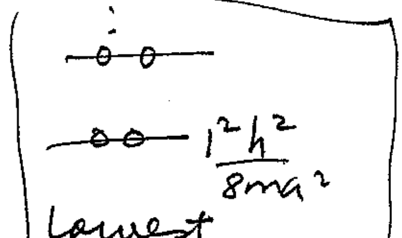
$\dfrac{1^2 h^2}{8ma^2}$

These are the one-electron states

Configurations possible:

$n_1 = 1 \quad n_2 = 1 \quad n_3 = 2 \quad n_4 = 2$

(lowest energy — no more than two in a one-electron state)

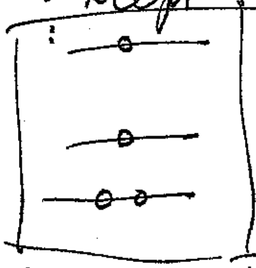


Lowest energy configuration

Next energy levels:

$n_1 = 1 \quad n_2 = 1 \quad n_3 = 2 \quad n_4 = 3$ etc.

(can assign all possible n values to each except that no more than two can have the same n value.



and so on.

$$E_{excited} = [2(1^2) + 1(2^2) + 1(3^2)]\, h^2/8ma^2$$ and so on.

(c) The transitions depend on square of the integral:

$$\int_0^a \cdots \int_0^a \underbrace{\psi_{n_1}(x_1)\psi_{n_2}(x_2)\psi_{n_3}(x_3)\psi_{n_4}(x_4)}_{\text{initial state}} (x_1 + x_2 + x_3 + x_4) \underbrace{\psi_{n_1'}(x_1)\psi_{n_2'}(x_2)\psi_{n_3'}(x_3)\psi_{n_4'}(x_4)}_{\text{final state}} dx_i \cdots$$

Ground: 1122 $\qquad$ 1st excited 1123 etc.

$= 0 + 0 + 0 + x_{23}$ because of ORTHONORMAL condition.

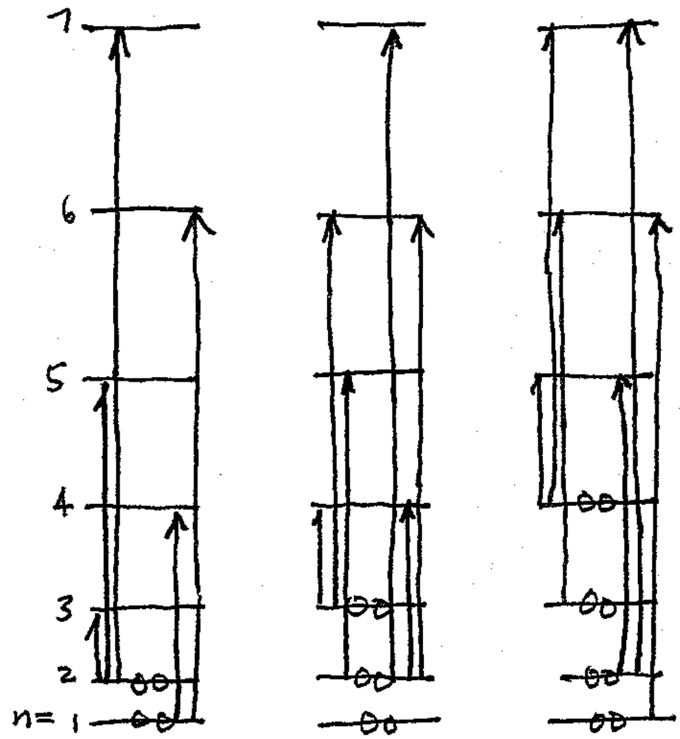
$= \dfrac{-8a}{\pi^2}\left(\dfrac{6}{25}\right)$ from page 1 of exam.

square of the integral $= \left(\dfrac{-8a}{\pi^2}\dfrac{6}{25}\right)^2$

We see from the matrix X given on page 1 of the exam, that the only transitions allowed are only those in which

a. ONLY one electron has a different n in the ground and excited states

b. the n values in the ground and excited configurations have to be those that have non-zero matrix elements in the X matrix on page 1 e.g., 12, 14, 16, ... 21, 23, 25, 27, ...



$\Delta n = \pm 1, \pm 3, \pm 5, \dots$

$n^2h^2/8ma^2$ per electron

butadiene $a = 7.00$ Å

hexatriene $a = 9.80$ Å

octatetraene $a = 12.60$ Å

$$\Delta E = \frac{(3^2-2^2)h^2}{8ma^2} \qquad \Delta E = \frac{(4^2-3^2)h^2}{8ma^2} \qquad \Delta E = \frac{(5^2-4^2)h^2}{8ma^2}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{8mc}{h}\frac{a^2}{3^2-2^2} \qquad \lambda = 330\left(\frac{9.80^2}{7}\right) \qquad \lambda = 330\left(\frac{12.60^2}{9}\right)$$

$$= 330\ \text{Å}^{-1}\ \frac{(7\text{Å})^2}{5} \qquad \lambda = 4528\ \text{Å} \qquad \lambda = 5821\ \text{Å}$$

$$\lambda = 3234\ \text{Å}$$

oscillator strength $= 1.085\times10^{11}\dfrac{X^2}{\lambda} = 1.085\times10^{11}\left(\dfrac{6}{25}\right)^2\left(\dfrac{8}{\pi^2}\right)^2\dfrac{7^2\times10^{-8}}{3234}$

$= 0.622$ etc.