Problem Set 3 Answers
On Separation of Variables

1. (a) $\{-(\hbar^2/2M_1R^2)\partial^2/\partial\phi_1^2 \; -(\hbar^2/2M_2R^2)\, \partial^2/\partial\phi_2^2\}\, \Psi(\phi_1, \phi_2) = E\Psi(\phi_1, \phi_2)$

Let $\Psi(\phi_1, \phi_2) = \psi(\phi_1)\bullet\, \psi(\phi_2)$

$\{-(\hbar^2/2M_1R^2)\partial^2/\partial\phi_1^2 \; - (\hbar^2/2M_2R^2)\, \partial^2/\partial\phi_2^2\}\psi(\phi_1)\bullet\, \psi(\phi_2) = E\psi(\phi_1)\bullet\, \psi(\phi_2)$

$\psi(\phi_2)\{-(\hbar^2/2M_1R^2)\partial^2/\partial\phi_1^2\, \psi(\phi_1)\} + \psi(\phi_1)\{-\, (\hbar^2/2M_2R^2)\, \partial^2/\partial\phi_2^2\psi(\phi_2)\} = E\psi(\phi_1)\bullet\, \psi(\phi_2)$

Dividing both sides by $\psi(\phi_1)\bullet\, \psi(\phi_2)$

$$\frac{\{-(\hbar^2/2M_1R^2)\partial^2/\partial\phi_1^2\psi(\phi_1)\}}{\psi(\phi_1)} + \frac{\{-\, (\hbar^2/2M_2R^2)\, \partial^2/\partial\phi_2^2\psi(\phi_2)\}}{\psi(\phi_2)} = E$$

Since ϕ_1 and ϕ_2 are independent variables, then the first term has nothing to do with the second, so the only way the sum can equal a constant E is if the first term is equal to a constant E_1 and the second term is equal to a constant E_2 such that $E_1+E_2 = E$

Therefore

$$\frac{\{-(\hbar^2/2M_1R^2)\partial^2/\partial\phi_1^2\psi(\phi_1)\}}{\psi(\phi_1)} = E_1$$

$$\frac{\{-\, (\hbar^2/2M_2R^2)\, \partial^2/\partial\phi_2^2\psi(\phi_2)\}}{\psi(\phi_2)} = E_2$$

Solving,

$\{-(\hbar^2/2M_1R^2)\partial^2/\partial\phi_1^2\, \psi(\phi_1)\} \qquad = E_1\psi(\phi_1)$

we find $\psi_{k1}(\phi_1) = (1/\sqrt{2\pi})\, \exp[i\, k_1\phi_1]$ satisfies this equation with eigenvalues $k_1^2\hbar^2/2M_1R^2$

Therefore

$\Psi(\phi_1, \phi_2) = (1/\sqrt{2\pi})\, \exp[i\, k_1\phi_1]\bullet(1/\sqrt{2\pi})\, \exp[i\, k_2\phi_2]$.

$E = k_1^2\hbar^2/2M_1R^2 + k_2^2\hbar^2/2M_2R^2$

2. Similarly for 6 electrons:

(a) $\{-(\hbar^2/2m_eR^2)\partial^2/\partial\phi_1^2 \; -(\hbar^2/2M_2R^2)\, \partial^2/\partial\phi_2^2 -(\hbar^2/2m_eR^2)\partial^2/\partial\phi_3^2 \; -(\hbar^2/2m_eR^2)\, \partial^2/\partial\phi_4^2 -(\hbar^2/2m_eR^2)\partial^2/\partial\phi_5^2 \; -(\hbar^2/2m_eR^2)\, \partial^2/\partial\phi_6^2\}\, \Psi(\phi_1, \phi_2, \phi_3, \phi_4, \phi_5, \phi_6) = E\Psi(\phi_1, \phi_2, \phi_3, \phi_4, \phi_5, \phi_6)$

(b) $\Psi(\phi_1, \phi_2, \phi_3, \phi_4, \phi_5, \phi_6) = \psi(\phi_1)\bullet\, \psi(\phi_2)\, \bullet\psi(\phi_3)\bullet\, \psi(\phi_4)\, \bullet\psi(\phi_5)\bullet\, \psi(\phi_6)$

$\Psi(\phi_1, \phi_2, \phi_3, \phi_4, \phi_5, \phi_6) = (1/\sqrt{2\pi})\, \exp[i\, k_1\phi_1]\bullet(1/\sqrt{2\pi})\, \exp[i\, k_2\phi_2]\bullet\, (1/\sqrt{2\pi})\, \exp[i\, k_3\phi_3]\bullet(1/\sqrt{2\pi})\, \exp[i\, k_4\phi_4]\bullet\, (1/\sqrt{2\pi})\, \exp[i\, k_5\phi_5]\bullet(1/\sqrt{2\pi})\, \exp[i\, k_6\phi_6]$

$E = k_1^2\hbar^2/2m_eR^2 + k_2^2\hbar^2/2m_eR^2 + k_3^2\hbar^2/2m_eR^2 + k_4^2\hbar^2/2m_eR^2 + k_5^2\hbar^2/2m_eR^2 + k_6^2\hbar^2/2m_eR^2$

where $k_1 = 0, \pm 1, \pm 2, ...$, similarly for k_2 , etc.

(c) Invoking the condition that no two electrons can have the same k value, the lowest energy can be $(k_1\ k_2\ k_3\ k_4\ k_5\ k_6) = (0011\text{-}1\text{-}1)$ with total energy given by $(0+0+1+1+1+1)\ \hbar^2/2m_eR^2 = 4\ \hbar^2/2m_eR^2$

The next lowest energy will be given by $(k_1\ k_2\ k_3\ k_4\ k_5\ k_6) = (0011\text{-}12)$ or $(0011\text{-}1\text{-}2)$ or $(0012\text{-}1\text{-}1)$ or $(001\text{-}2\text{-}1\text{-}1)$ [not including permuting the electron's numbers] with energy $(0+0+1+1+1+4)\ \hbar^2/2m_eR^2 = 7\ \hbar^2/2m_eR^2$

The next lowest energy will be given by $(k_1\ k_2\ k_3\ k_4\ k_5\ k_6) = (011\text{-}1\text{-}12)$ or $(011\text{-}1\text{-}1\text{-}2)$ with energy $(0+1+1+1+1+4)\ \hbar^2/2m_eR^2 = 8\ \hbar^2/2m_eR^2$

(d) $\int \psi_k{}^* \, x \, \psi_{k'} \, d\tau$ where $x = R\cos\phi =$

The peak intensity depends on the square of the integral:

$$\int\!\!\int\!\!\int\!\!\int\!\!\int\!\!\int \Psi^*(\phi_1, \phi_2, \phi_3, \phi_4, \phi_5, \phi_6)\, R[\cos\phi_1 + \cos\phi_2 + \cos\phi_3 + \cos\phi_4 + \cos\phi_5 + \cos\phi_6] \, \Psi'(\phi_1, \phi_2, \phi_3, \phi_4, \phi_5, \phi_6) d\phi_1\, d\phi_2\, d\phi_3\, d\phi_4\, d\phi_5\, d\phi_6$$

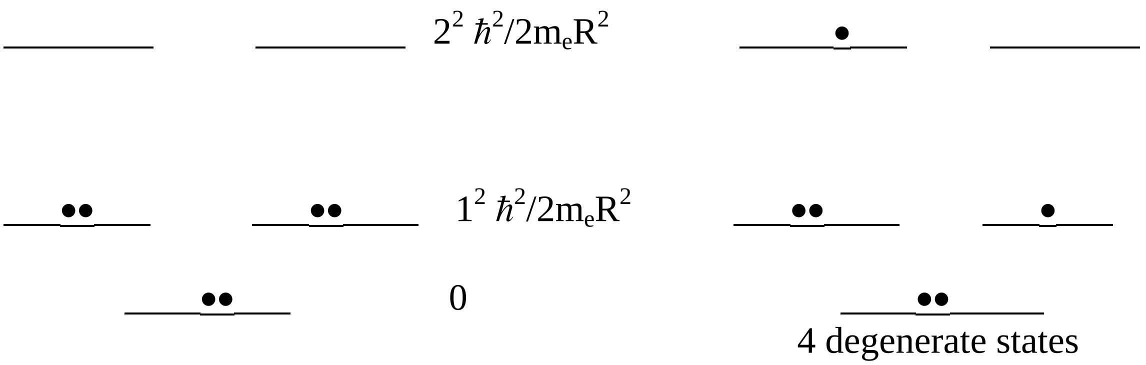
This integral leads to a sum of integrals:

$$\begin{aligned}
&\delta(k_2,k_2')\bullet\ \delta(k_3,k_3')\bullet\ \delta(k_4,k_4')\bullet\ \delta(k_5,k_5')\bullet\ \delta(k_6,k_6')\bullet\int\psi^*_{k1}(\phi_1)\ R\cos\phi_1\psi'_{k1'}(\phi_1)d\phi_1\\
&+\delta(k_1,k_1')\bullet\ \delta(k_3,k_3')\bullet\ \delta(k_4,k_4')\bullet\ \delta(k_5,k_5')\bullet\ \delta(k_6,k_6')\bullet\int\psi_{k2}{}^*(\phi_2)\ R\cos\phi_2\psi'_{k2'}(\phi_2)d\phi_2\\
&+\delta(k_1,k_1')\bullet\ \delta(k_2,k_2')\bullet\ \delta(k_4,k_4')\bullet\ \delta(k_5,k_5')\bullet\ \delta(k_6,k_6')\bullet\int\psi_{k3}{}^*(\phi_3)\ R\cos\phi_3\psi'_{k3'}(\phi_3)d\phi_3\\
&+\delta(k_1,k_1')\bullet\ \delta(k_1,k_1')\bullet\ \delta(k_3,k_3')\bullet\ \delta(k_5,k_5')\bullet\ \delta(k_6,k_6')\bullet\int\psi_{k4}{}^*(\phi_4)\ R\cos\phi_4\psi'_{k4'}(\phi_4)d\phi_4\\
&+\delta(k_1,k_1')\bullet\ \delta(k_2,k_2')\bullet\ \delta(k_3,k_3')\bullet\ \delta(k_4,k_4')\bullet\ \delta(k_6,k_6')\bullet\int\psi_{k5}{}^*(\phi_5)\ R\cos\phi_5\psi'_{k5'}(\phi_5)d\phi_5\\
&+\delta(k_1,k_1')\bullet\ \delta(k_2,k_2')\bullet\ \delta(k_3,k_3')\bullet\ \delta(k_4,k_4')\bullet\ \delta(k_5,k_5')\bullet\int\psi_{k6}{}^*(\phi_6)\ R\cos\phi_6\psi'_{k6'}(\phi_6)d\phi_6
\end{aligned}$$

where the delta function $\delta(k_2,k_2') = 1$ if $k_2=k_2'$ and 0 otherwise. These delta functions result from the fact that the eigenfunctions are orthonormal.

The only term that can survive is when $k_i=k_i'$ <u>for all except</u> that corresponding to the operator $R\cos\phi_j$. This means that a transition is only possible between 6-electron states $\Psi(\phi_1, \phi_2, \phi_3, \phi_4, \phi_5, \phi_6)$ that differ by no more than one electron's quantum number, and it is that one for which the integral $\int\psi^*_{kj}(\phi_j)\ R\cos\phi_j\psi'_{kj'}(\phi_j)d\phi_j$ has to be evaluated. In turn, this latter integral is evaluated by using the identity $\cos\phi = \frac{1}{2}[\exp(i\phi) + \exp(-i\phi)]$

$\int (1/\sqrt{2\pi})\ \exp[-i\ k_1\phi_1]\bullet\ \frac{1}{2}[\exp(i\phi_1) + \exp(-i\phi_1)]\bullet(1/\sqrt{2\pi})\ \exp[i\ k'_1\phi_1]\ d\phi_1 =$
$(1/4\pi)[\delta(k_1,k_1'+1)+\ \delta(k_1,k_1'-1)]$,   that is k_1 and k_1' have to differ by 1.



Total energy = (4) $\hbar^2/2m_eR^2$ Total energy = (7) $\hbar^2/2m_eR^2$

(e) perimeter of the circle is 6(1.394) Å = $2\pi R$; R = 1.331 Å. The longest wavelength corresponds to transition from ground $(4)\hbar^2/2m_eR^2$ to excited state $(7)\hbar^2/2m_eR^2$ with transition energy = $3\,\hbar^2/2m_eR^2$. Convert this energy to wavelength by $\Delta E = hc/\lambda$ or $\lambda = (8\pi^2 m_e R^2 c/3h)$

electron mass = $9.10938188 \times 10^{-28}$ g, R = 1.331 Å, c = $3\text{x}10^{10}$ cm s^{-1}

$$\lambda = \frac{8\pi^2 9.10938188\times10^{-28}(1.331\times10^{-8})^2 3\text{x}10^{10}}{3\text{x}6.62618\text{x}10^{-27}}$$

$\lambda = 1920\ \text{x}10^{-8}$ cm

(f) Two condensed rings outer perimeter = 10(1.394) Å = $2\pi R$.
For N_r rings, $[6+4(N_r - 1)](1.394) = 2\pi R$;
The radius of the equivalent "circle" is $R= [6+4(N_r - 1)](1.394)/ 2\pi$
The number of electrons is $6+4(N_r - 1)$.
The ground state energy is $4+4(2^2)+ 4(3^2) + 4(4^2) + ...$
For N_r=2: $E_{grd} = [4+4(2^2)]\,\hbar^2/2m_e(10\text{x}1.394/2\pi)^2$
For N_r=3: $E_{grd} = [4+4(2^2) + 4(3^2)]\,\hbar^2/2m_e(14\text{x}1.394/2\pi)^2$
For N_r=4: $E_{grd} = [4+4(2^2) + 4(3^2) + 4(4^2)]\,\hbar^2/2m_e(18\text{x}1.394/2\pi)^2$

For the lowest excited states:
For N_r=2: $E_{excited} = [4+3(2^2)+ 3^2\,]\,\hbar^2/2m_e(10\text{x}1.394/2\pi)^2$
For N_r=3: $E_{excited} = [4+4(2^2) + 3(3^2)+ 4^2]\,\hbar^2/2m_e(14\text{x}1.394/2\pi)^2$
For N_r=4: $E_{excited} = [4+4(2^2) + 4(3^2) + 3(4^2) + 5^2]\,\hbar^2/2m_e(18\text{x}1.394/2\pi)^2$

The energy of the transition is
For N_r=2: $\Delta E = [3^2 - 2^2]\,\hbar^2/2m_e(10\text{x}1.394/2\pi)^2$
For N_r=3: $\Delta E = [4^2 - 3^2]\,\hbar^2/2m_e(14\text{x}1.394/2\pi)^2$
For N_r=4: $\Delta E = [5^2 - 4^2]\,\hbar^2/2m_e(18\text{x}1.394/2\pi)^2$

$\Delta E = hc/\lambda$

$\lambda = (2m_e 1.394^2 c/h)(10)^2 / [3^2 - 2^2]$ for $N_r = 2$

$\lambda = (2m_e 1.394^2 c/h)(14)^2 / [4^2 - 3^2]$ for $N_r = 3$

$\lambda = (2m_e 1.394^2 c/h)(18)^2 / [5^2 - 4^2]$ for $N_r = 4$

$$(2m_e 1.394^2 c/h) = \frac{2x9.10938188 \times 10^{-28} (1.394 \times 10^{-8})^2 3x10^{10}}{6.62618x10^{-27}} = 16.03x10^{-7}$$

$\lambda = 16.03x10^{-7} \ (6)^2 / [2^2 - 1^2] = 16.03x10^{-7} x12 = 1920$ Å for $N_r = 1$

$\lambda = 16.03x10^{-7} \ (10)^2 / [3^2 - 2^2] = 16.03x10^{-7} x20 = 3210$ Å for $N_r = 2$

$\lambda = 16.03x10^{-7} \ (14)^2 / [4^2 - 3^2] = 16.03x10^{-7} x28 = 4490$ Å for $N_r = 3$

$\lambda = 16.03x10^{-7} \ (18)^2 / [5^2 - 4^2] = 16.03x10^{-7} x36 = 5770$ Å for $N_r = 4$

The number of rings determine the radius of the “circle” and also the number of electrons. The net result is $\lambda = 160.3\ [12+8(N_r - 1)]$ Å

3.

$$x_{mn} = \frac{4a\, mn\{ (-1)^{m-n} - 1 \}}{\pi^2 \{ m^2 - n^2 \}^2} \quad \text{for } m \neq n$$

m\n	1	2	3	4	5	6	7	...
1	/////	2/9	0	4/225	0	6/1225	0	...
2	2/9	/////	6/25	0	10/441	0	14/2025	...
3	0	6/25	/////	12/49	0	18/729	0	...
4	4/225	0	12/49	/////	20/81	0	28/1089	...
5 $-(8a/\pi^2)$	0	10/441	0	20/81	/////	30/121	0	...
6	6/1225	0	18/729	0	30/121	/////	42/169	...
7	0	14/2025	0	28/1089	0	42/169	/////	...
8	8/3969	0	24/3025	0	40/1521	0	56/225	...
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	

///// although the integral is non-zero, when initial and final states are the same it does not correspond to a transition, instead an expectation value of x, $\langle x \rangle = a/2$.

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

for butadiene —1═2—3═4—

$a = 5(1.40\,\text{Å}) \qquad = 7.00\,\text{Å}$ (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

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

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

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

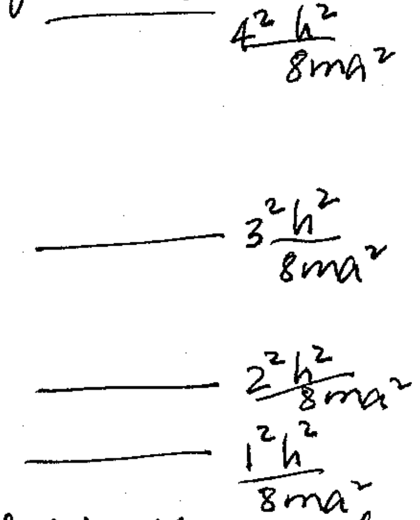
$$E_{n_1} = \frac{n_1^2 h^2}{8ma^2}$$

The others are of the same form, .

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

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

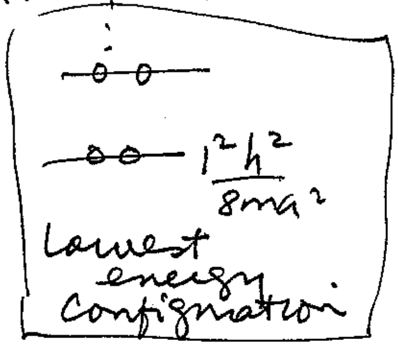
For particle 1 we have: Similarly for particles 2, 3, and 4



Configurations possible:

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

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

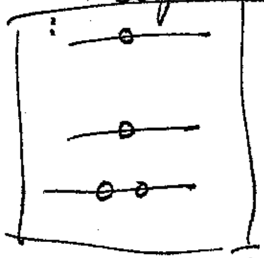


These are the one-electron states

Next energy levels:

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

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



and so on.

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

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

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

Ground: 1122

1st excited 1123 etc.

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

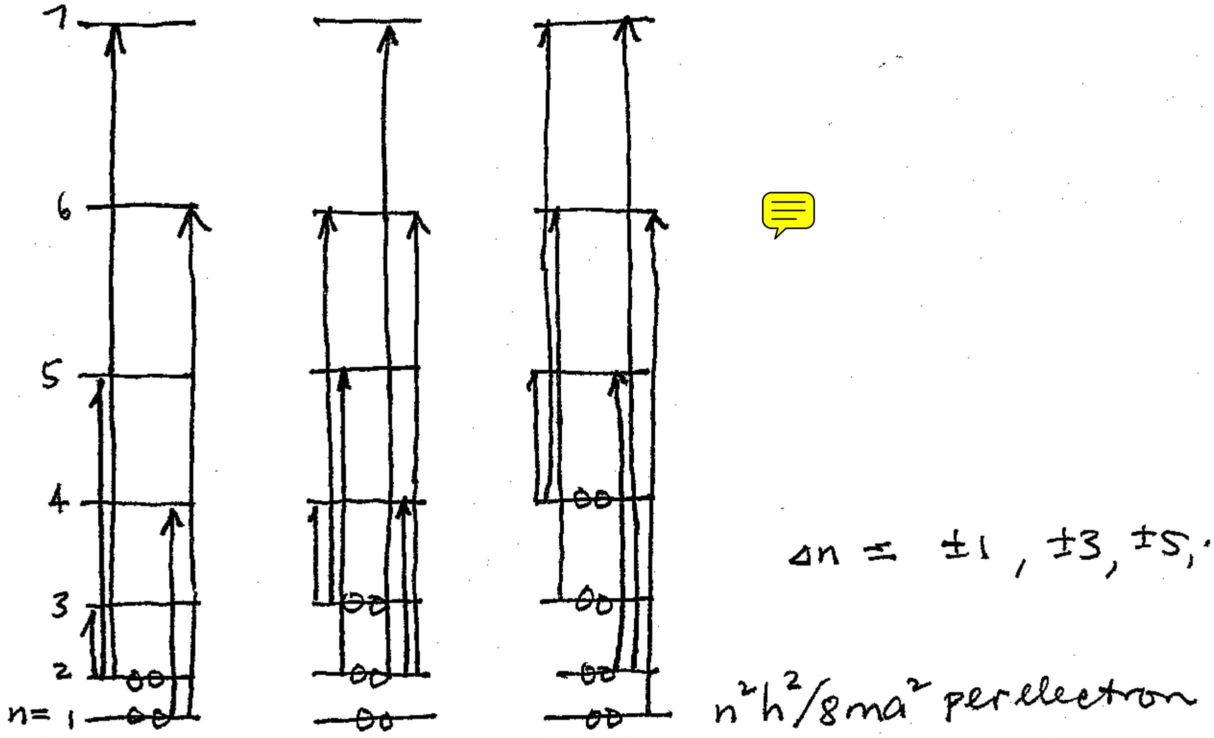
$= -\frac{8a}{\pi^2}\left(\frac{6}{25}\right)$ from page 1 of exam.

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

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, ...



butadiene $a = 7.00\,Å$ hexatriene $a = 9.80\,Å$ octatetraene $a = 12.60\,Å$

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

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

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

$$\lambda = 3234\,Å$$

Oscillator strength $= 1.085 \times 10^{11} \dfrac{X^2}{\lambda} = 1.085 \times 10^{11} \left(\dfrac{6}{25}\right)^2 \left(\dfrac{8}{\pi^2}\right)^2 \dfrac{7^2 \times 10^{-8}}{3234}$

$= 0.622$ etc.

Note that the length L of the polyene is proportional to the number of carbons, m_C if we let the ends of the line extend to (1/2) the C-C bond length beyond the last carbon nuclei. That is, $L = m_C r_{CC}$. Note also that the double occupancy afforded by the Pauli exclusion principle means that the smallest energy transitions corresponds to “from” quantum numbers $m_C/2$ and “to” quantum numbers $1+m_C/2$. That is, the energy of the transition is given by $\Delta E = \{(1+m_C/2)^2 - (m_C/2)^2\}h2/8m_eL^2 = \{(1+m_C/2)^2 - (m_C/2)^2\}h2/8m_e(m_C r_{CC})^2 = hc/\lambda_{abs}$

where the longest wavelength λ_{abs} is given by

$\lambda_{abs} = (m_C)^2/(1+m_C)\ 8cm_e\, r_{CC}{}^2/h$ So we expect the longest wavelength in the absorption spectrum of the polyene having m_C carbons to be proportional to $(m_C)^2/(1+m_C)$, i.e., $4^2/5$, $6^2/7$, $8^2/9$ from butadiene to hexatriene to octatriene. A plot of the longest wavelength versus m_C will not be exactly linear, but nearly so.

Calculation of current densities using gauge-including atomic orbitals

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The current density for hexabenzocoronene is displayed in a plane parallel to the molecular framework and 1 bohr above it.