

1. Hund's first rule states that an atom with an unfilled shell in its ground state adopts an electronic configuration with the greatest number of unpaired electrons. The purpose of this question is to provide a justification for this important rule.

a) Consider the two 2p electrons in an oxygen atom. We could try writing

$$\Psi = 2p_x(\vec{r}_1)2p_y(\vec{r}_2)$$

for the wave function describing these electrons. Give three reasons why is Ψ unacceptable as a wave function.

b) The following four wave functions are acceptable.

$$\Psi_+ = \frac{1}{\sqrt{2}}[2p_x(\vec{r}_1)2p_y(\vec{r}_2) + 2p_y(\vec{r}_1)2p_x(\vec{r}_2)] \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

$$\Psi'_- = \frac{1}{\sqrt{2}}[2p_x(\vec{r}_1)2p_y(\vec{r}_2) - 2p_y(\vec{r}_1)2p_x(\vec{r}_2)][\alpha(1)\alpha(2)]$$

$$\Psi''_- = \frac{1}{\sqrt{2}}[2p_x(\vec{r}_1)2p_y(\vec{r}_2) - 2p_y(\vec{r}_1)2p_x(\vec{r}_2)][\beta(1)\beta(2)]$$

$$\Psi'''_- = \frac{1}{\sqrt{2}}[2p_x(\vec{r}_1)2p_y(\vec{r}_2) - 2p_y(\vec{r}_1)2p_x(\vec{r}_2)] \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

Show that Ψ_+ is a product of a spatially symmetric function and an antisymmetric spin function. Show that Ψ'_- , Ψ''_- and Ψ'''_- are products of a spatially antisymmetric function and symmetric spin functions. Why must the symmetry of the spatial function be opposite to that of the spin function?

c) Show that Ψ_+ corresponds to a singlet state, while Ψ'_- , Ψ''_- and Ψ'''_- correspond to a triplet state.

d) According to Hund's first rule, the triplet state (higher spin multiplicity) has lower energy than the ground state. To understand *why*, notice that the probability of finding the two electrons at the same point in space for the triplet state is zero with parallel (unpaired) spins. For the singlet, on the other hand, notice the electrons can be located at the same point in space. Use this observation to justify the lower energy of the triplet state.

2. For "light" atoms (Z less than about 40), the interactions between the orbital angular momentum and spin angular momentum is sufficiently weak to be ignored in calculating the total angular momentum. This is the key assumption in the Russell-Saunders scheme for determining atomic term symbols.

The interaction between orbital and spin angular momentum, though very small, is not zero. When an electron has orbital angular momentum, a small magnetic dipole and a correspondingly weak magnetic field are generated. This magnetic field interacts with the electron spin magnetic moment and produces a very small change in the energy.

The magnitude of spin-orbit interaction energy is proportional to the dot product of the orbital and spin angular momentum vectors

$$\Delta E_{\text{spin-orbit}} = c \vec{L} \cdot \vec{S}$$

c is a proportionality constant.

a) Use the expression

$$\vec{J} \cdot \vec{J} = [\vec{L} + \vec{S}] \cdot [\vec{L} + \vec{S}] = \vec{L}^2 + \vec{S}^2 + 2\vec{L} \cdot \vec{S}$$

for the square of the total angular momentum and

$$\vec{J} \cdot \vec{J} = J(J+1)\hbar^2$$

$$\vec{L} \cdot \vec{L} = \ell(\ell+1)\hbar^2$$

$$\vec{S} \cdot \vec{S} = S(S+1)\hbar^2$$

to derive

$$\Delta E_{\text{spin-orbit}} = c[J(J+1) - \ell(\ell+1) - S(S+1)]$$

for the energy change caused by spin orbit coupling. (In the notation used here, note that J , ℓ and S are quantum numbers, not the magnitudes of the angular momentum vectors.)

b) Experiments give $c \approx 0.000023 Z^4$ eV. Why does this result imply the break-down of the Russell-Saunders scheme for heavy atoms?

c) If ℓ is zero, show that the predicted energy change caused by spin-orbit coupling is zero. Give a physical explanation for this result.

d) The Rydberg equation gives

$$E_n = -\frac{109677.6 \text{ cm}^{-1}}{n^2}$$

for the energy levels of the hydrogen atom. According to this result, the energy depends only on the principal quantum number n . Spin-orbit coupling, however, can produce small energy differences for states with the same n value. In tutorial #2, we showed that the $2p^1$ configuration of the hydrogen atom has $^2P_{1/2}$ and $^2P_{3/2}$ states. Calculate the changes in energies of these states (in units of cm^{-1}) caused by spin-orbit coupling. Confirm that these energy changes are very small compared to E_2 .

e) Show that your answer to c) is consistent with Hund's third rule.

f) The two transitions for the famous yellow doublet in the emission spectrum of sodium atoms are

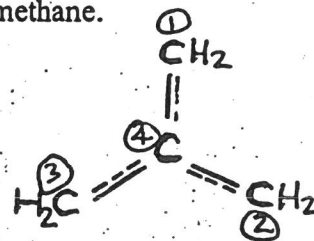


Using the $Z = 2.51$ for the effective atomic number experienced by sodium 3s electrons, calculate the splitting (small difference in energy) between these transitions caused by spin-orbit coupling. (The experimental value is 17.2 cm^{-1} .) Which transition is higher in energy?

3. Write out the MO configurations for Na_2 through Ar_2 (ignoring the filled 1s, 2s and 2p shells). Is Mg_2 predicted to exist?

4. Determine the ground-state electron configurations for NO^+ and NO . Compare the bond orders of the two species.

5. a) Use Hückel theory to calculate the energy of the π electrons in trimethylenemethane.



b) Calculate the stabilization energy relative to two ethylene molecules.

c) Show that Hund's first rule predicts a triplet for the trimethylenemethane ground state.

d) Calculate the wavelength of a photon required for a transition to the first excited state.

6. Three sp^2 orbitals are formed by taking linear combinations of the atomic 2s and the two 2p orbitals:

$$\varphi_{A(i)} = \frac{1}{\sqrt{3}}(2s + \sqrt{2}p_x)$$

$$\varphi_{A(ii)} = \frac{1}{\sqrt{3}}\left(2s - \frac{1}{\sqrt{2}}2p_x + \frac{\sqrt{3}}{\sqrt{2}}2p_y\right)$$

$$\varphi_{A(iii)} = \frac{1}{\sqrt{3}}\left(2s - \frac{1}{\sqrt{2}}2p_x - \frac{\sqrt{3}}{\sqrt{2}}2p_y\right)$$

Show that the three hybrid orbitals constructed in this manner lie in the x - z plane with lobes pointing in directions separated by 120° . (Hint: $\vec{a} \cdot \vec{b} = |\vec{a}||\vec{b}|\cos\theta$)

7. The Hückel determinant for the π electrons in benzene is

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha - E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha - E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha - E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha - E & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0$$

Solve this equation to obtain the four different energy levels (two of which are doubly degenerate):

$$E_6 = \alpha - 2\beta$$

$$E_4 \text{ and } E_5 = \alpha - \beta \quad (\text{LUMO, doubly degenerate})$$

$$E_2 \text{ and } E_3 = \alpha + \beta \quad (\text{HOMO, doubly degenerate})$$

$$E_1 = \alpha + 2\beta$$

8. Optional! Show that the wave functions ψ_1 and ψ_2 for the ground state and first excited state of the π electrons in butadiene are orthonormal.

$$\psi_1 = 0.3717p_{1,1} + 0.6015p_{2,2} + 0.6015p_{3,3} + 0.3717p_{4,4}$$

$$\psi_2 = 0.6015p_{1,1} + 0.3717p_{2,2} - 0.3713p_{3,3} - 0.6015p_{4,4}$$

① a) $\Psi = 2p_x(\vec{r}_1)2p_y(\vec{r}_2)$ is unacceptable as a wave function because: it is not antisymmetric with respect to interchange of electrons 1 and 2, the electrons are distinguishable (1 in p_x and 2 in p_y orbitals), spin functions are not included

b) Interchanging electrons 1 and 2 in $\frac{1}{2}[2p_x(\vec{r}_1)2p_y(\vec{r}_2) + 2p_y(\vec{r}_1)2p_x(\vec{r}_2)]$ gives the same spatial function $\frac{1}{2}[2p_x(\vec{r}_2)2p_y(\vec{r}_1) + 2p_y(\vec{r}_2)2p_x(\vec{r}_1)]$

interchanging electrons 1 and 2 in $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$ give the original spin function multiplied by minus one = $\frac{1}{\sqrt{2}}[\alpha(2)\beta(1) - \beta(2)\alpha(1)] = -\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$

vice versa for $\Psi_+^I, \Psi_+^{II}, \Psi_+^{III}$

c) the spin function for Ψ_+ has zero spin angular momentum ($\uparrow\downarrow$ or $\downarrow\uparrow$) $S=0$ $2S+1=1$

the spin functions for $\Psi_-^I, \Psi_-^{II}, \Psi_-^{III}$ have $\uparrow\uparrow$ ($M_S=1$), $\uparrow\downarrow$ or $\downarrow\uparrow$ ($M_S=0$), or $\downarrow\downarrow$ ($M_S=-1$) corresponding to $S=1$ $2S+1=3$ (triplet)

$$d) \Psi_+(\vec{r}_1, \vec{r}_2 = \vec{r}_1) = \frac{1}{\sqrt{2}} [2p_x(\vec{r}_1)2p_y(\vec{r}_1) + 2p_y(\vec{r}_1)2p_x(\vec{r}_1)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \neq 0$$

$\Psi_-^{I, II, III}(\vec{r}_1, \vec{r}_2 = \vec{r}_1) = 0$ less probable for electrons 1 and 2 to be close together, less repulsion energy for electrons 1 and 2, therefore lower energy

$$\textcircled{2} \quad \text{a) } \vec{L} \cdot \vec{S} = \frac{1}{2} [\vec{J} \cdot \vec{J} - \vec{L} \cdot \vec{L} - \vec{S} \cdot \vec{S}]$$

$$= \frac{1}{2} [J(J+1)\hbar^2 - l(l+1)\hbar^2 - s(s+1)\hbar^2]$$

$$\Delta E_{\text{spin-orbit}} \propto \vec{L} \cdot \vec{S} \propto [J(J+1) - l(l+1) - s(s+1)]$$

$$\boxed{\Delta E_{\text{spin-orbit}} = c [J(J+1) - l(l+1) - s(s+1)]}$$

$$\text{b) empirically, } c = 0.000023 Z^4 \text{ eV}$$

for $Z = 40$ (where Russell-Saunders treatment of \vec{L} and \vec{S} as independent starts to break down)

$$\Delta E_{\text{spin-orbit}} \approx 0.000023 (40)^4 \text{ eV} \approx 58.8 \text{ eV}$$

This is significant compared to electron energies e.g., first ionization energies in the 5 to 15 eV range)

$$\text{c) } l=0, \text{ then } \vec{L} = 0 \text{ and } \vec{J} = \vec{L} + \vec{S} = \vec{S}$$

$$\vec{J} \cdot \vec{J} = \vec{S} \cdot \vec{S}$$

quantum number $J = S$

$$\Delta E_{\text{spin-orbit}} = c [J(J+1) - l(l+1) - s(s+1)]$$

$$= c [J(J+1) - 0(1) - J(J+1)] = 0$$

for $l=0$, there is no orbital angular momentum to generate a magnetic field to interact with the spin magnetic moment

(2 cont.)

d) $2P_{1/2}$ state $2S+1 = 2$ $S = \frac{1}{2}$
 $l = 1$ (P state) $J = \frac{1}{2}$

$$\begin{aligned}\Delta E_{\text{spin-orbit}} &= c [J(J+1) - l(l+1) - s(s+1)] \quad (z=1 \text{ (hydrogen)}) \\ &= c \left[\frac{1}{2} \left(\frac{3}{2} \right) - 1(2) - \frac{1}{2} \left(\frac{3}{2} \right) \right] \\ &= -2c z^4 \\ &= -2(0.000023) \text{ eV} \\ &= -0.000046 \text{ eV} \\ &= -0.000046 \text{ eV} \left(\frac{109677.6 \text{ cm}^{-1}}{13.6 \text{ eV}} \right) \\ &= \boxed{-0.37 \text{ cm}^{-1}} \quad (0.0013\% \text{ of } E_2)\end{aligned}$$

$2P_{3/2}$ state $S = \frac{1}{2}$ $l = 1$ $J = \frac{3}{2}$ $z = 1$

$$\begin{aligned}\Delta E_{\text{spin-orbit}} &= c \left[\frac{3}{2} \frac{5}{2} - 1(2) - \frac{1}{2} \frac{3}{2} \right] = c \left[\frac{15 - 8 - 3}{4} \right] \\ &= c \\ &= 0.000023 \text{ eV} \left(\frac{109677.6 \text{ cm}^{-1}}{13.6 \text{ eV}} \right) (1)^4 \\ &= \boxed{0.18 \text{ cm}^{-1}} \quad (0.00066\% \text{ of } E_2)\end{aligned}$$

these spin-orbit energy changes are tiny compared to the energy of a 2p electron in a hydrogen atom

$$E_2 = \frac{-109667.6}{4} \text{ cm}^{-1} = -27416.9 \text{ cm}^{-1}$$

e) for the same values of L and S and shell < half-filled, the state with lower J has lower energy

(2 cont.)

f) $3p$ ${}^2P_{1/2}$ state $s = \frac{1}{2}$ $l = 1$ $J = \frac{1}{2}$

$$\Delta E_{\text{spin-orbit}} = c \left[\frac{1}{2} \frac{3}{2} - 1(2) - \frac{1}{2} \frac{3}{2} \right]$$

$$= -2c = -2(0.000023) Z^4$$

$$= -2(0.000023)(2.5)^4 \text{ eV} \frac{109667.6 \text{ cm}^{-1}}{13.6 \text{ eV}}$$

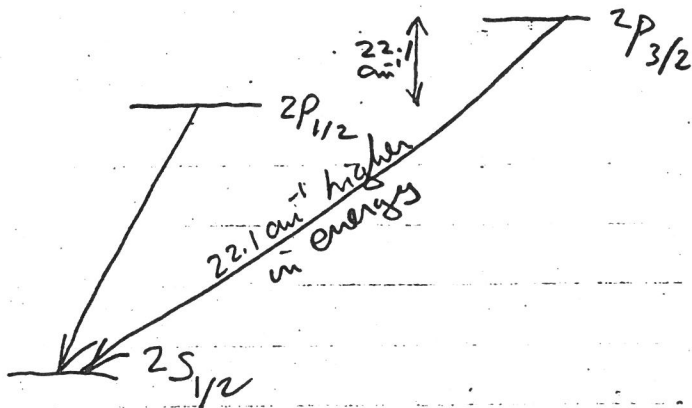
$$= -14.7 \text{ cm}^{-1}$$

$3p$ ${}^2P_{3/2}$ $s = \frac{1}{2}$ $l = 1$ $J = \frac{3}{2}$

$$\Delta E_{\text{spin-orbit}} = c \left[\frac{3}{2} \frac{5}{2} - 1(2) - \frac{1}{2} \frac{3}{2} \right]$$

$$= c$$

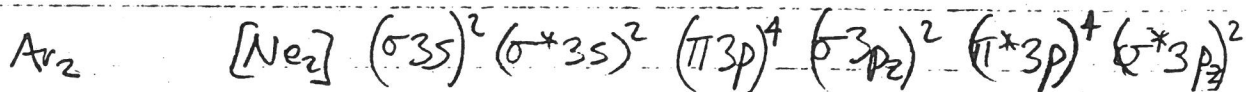
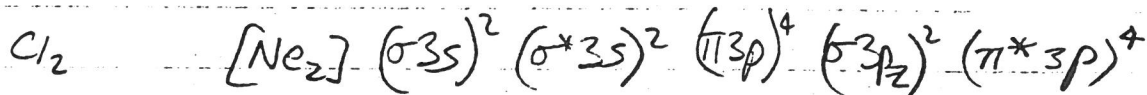
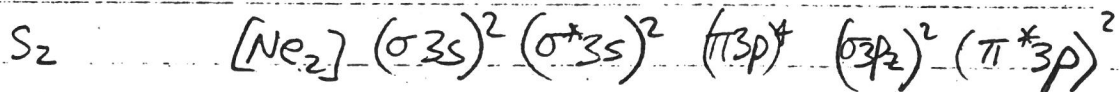
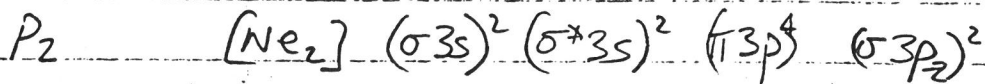
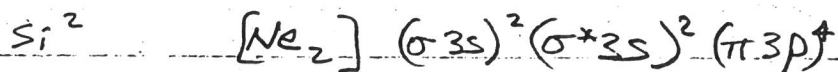
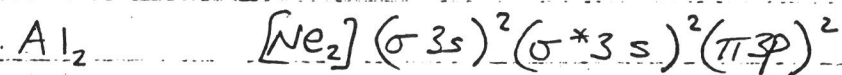
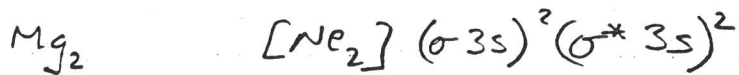
$$= 7.4 \text{ cm}^{-1}$$



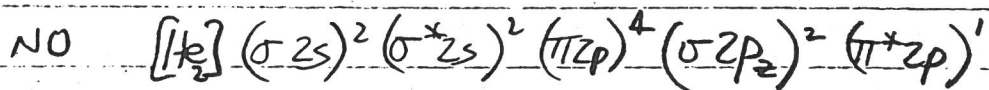
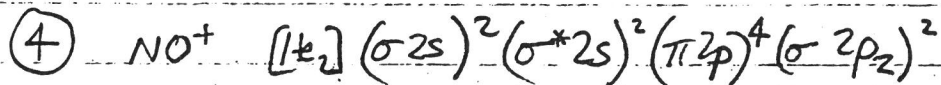
The ${}^2P_{3/2}$ state goes up in energy by 7.4 cm^{-1} , the ${}^2P_{1/2}$ state drops 14.7 cm^{-1}

$$\text{total difference} = 22.1 \text{ cm}^{-1}$$

small compared to $\bar{\nu}$ for visible light ($\approx 5890 \text{ cm}^{-1}$ for yellow light)



Mg_2 (and Ar_2) are predicted to be unstable (no excess of bonding electrons)

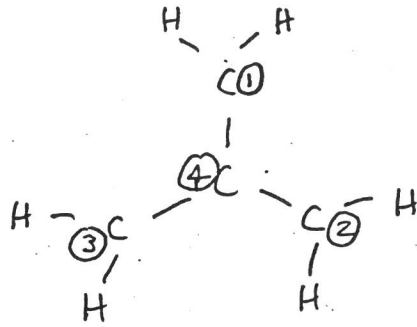


NO^+ ; net $4+2=6$ bonding electrons \Rightarrow triple bond

NO ; $4+2-1=5$ bonding electrons $\Rightarrow 2\frac{1}{2}$ bonds

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5



σ framework
(sp^2 hybridization on each carbon)

one electron per carbon atom
is "leftover" for π bonding

carbon atom #4 is the central atom in this numbering scheme

a) Hückel determinant used to calculate the π electron energy:

$$\begin{vmatrix} \alpha - E & 0 & 0 & \beta \\ 0 & \alpha - E & 0 & \beta \\ 0 & 0 & \alpha - E & \beta \\ \beta & \beta & \beta & \alpha - E \end{vmatrix} = 0$$

define $x = \frac{\alpha - E}{\beta}$

$$\begin{vmatrix} x & 0 & 0 & 1 \\ 0 & x & 0 & 1 \\ 0 & 0 & x & 1 \\ 1 & 1 & 1 & x \end{vmatrix} = 0$$

$$x \begin{vmatrix} x & 0 & 1 \\ 0 & x & 1 \\ 1 & 1 & x \end{vmatrix} - 0 + 0 - (1) \begin{vmatrix} 0 & x & 0 \\ 0 & 0 & x \\ 1 & 1 & 1 \end{vmatrix}$$

$$= x x \begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} + x(1) \begin{vmatrix} 0 & x \\ 1 & 1 \end{vmatrix} = (1)(-x) \begin{vmatrix} 0 & x \\ 1 & 1 \end{vmatrix}$$

$$0 = x^2(x^2 - 1) + x(0 - x) + x(0 - x) = x^4 - 3x^2 = x^2(x^2 - 3)$$

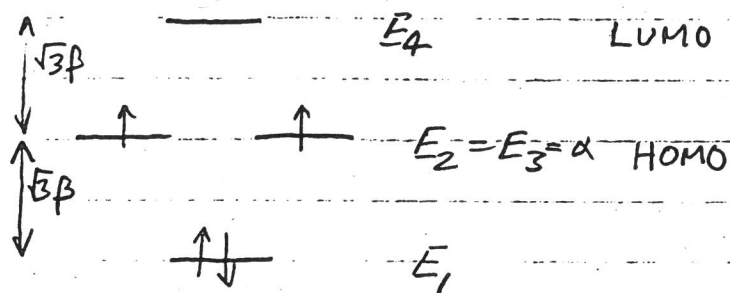
(5 cont.)

the roots of the equation $x^2(x^2-3)=0$ are:

$$\frac{\alpha-E}{\beta} = -\sqrt{3}, 0, 0, \sqrt{3}$$

$$\alpha - E = -\sqrt{3}\beta, \alpha, \alpha, \sqrt{3}\beta$$

$$\begin{aligned} E_4 &= \alpha - \sqrt{3}\beta \\ E_2 = E_3 &= \alpha \text{ (doubly degenerate)} \\ E_1 &= \alpha + \sqrt{3}\beta \end{aligned}$$

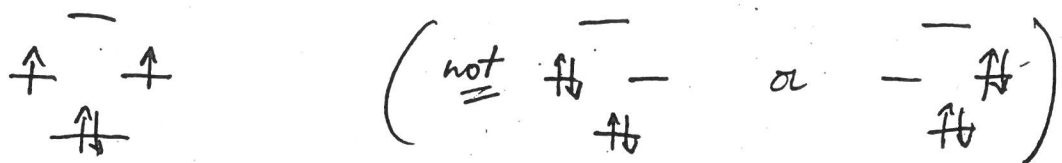


$$\begin{aligned} \pi \text{ electron energy} &= 2E_1 + 2E_2 = 2E_1 + 2E_3 \\ &= 2(\alpha + \sqrt{3}\beta) + 2\alpha \\ &= 4\alpha + 2\sqrt{3}\beta \end{aligned}$$

$$\begin{aligned} \text{b) stabilization energy} &= (4\alpha + 2\sqrt{3}\beta) - \left(\begin{array}{l} \pi \text{ electron energy} \\ \text{for two ethylene molecules} \end{array} \right) \\ &= 4\alpha + 2\sqrt{3}\beta - (4\alpha + 4\beta) \\ &= 2(\sqrt{3}-2)\beta = -0.536\beta \\ &\approx (-0.536)(-75 \text{ kJ mol}^{-1}) = +40 \text{ kJ mol}^{-1} \end{aligned}$$

(5 cont.)

c) According to Hund's rule # 1, the number of unpaired electrons is maximized in the ground state, so we have



two unpaired electrons \Rightarrow triplet $(2s+1=3)$

d) photon energy = $E_2 - E_1$

$$\Delta E = -\sqrt{3}\beta = h\nu$$

$$\begin{aligned} \nu &= \frac{\sqrt{3} (75 \text{ kJ mol}^{-1})}{6.022 \times 10^{23} \text{ mol}^{-1}} \frac{1}{6.626 \times 10^{-34} \text{ J s}} \frac{1000}{\text{kJ}} \\ &= 3.256 \times 10^{14} \text{ Hz} \end{aligned}$$

$$\lambda = c/\nu = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{3.256 \times 10^{14} \text{ s}^{-1}} = 921 \text{ nm (IR)}$$

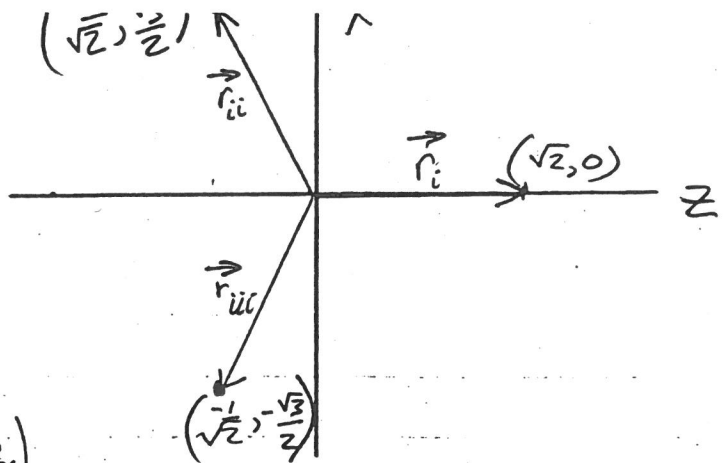
⑥ In $\varphi_{A(i)}$ = $\frac{1}{\sqrt{3}} (2s + \sqrt{2} p_z)$ the p orbital lies

along the z axis. $\vec{r}_{(i)} = (z_{(i)}, x_{(i)}) = (\sqrt{2}, 0) \equiv (1.414, 0)$

In $\varphi_{A(ii)}$ = $\frac{1}{\sqrt{3}} (2s - \frac{1}{\sqrt{2}} 2p_z + \frac{\sqrt{3}}{\sqrt{2}} 2p_x)$

the composite p orbital (a mixture of p_z and p_x) points in the direction $\vec{r}_{(ii)} = (z_{(ii)}, x_{(ii)}) = (-\frac{1}{\sqrt{2}}, \frac{\sqrt{3}}{\sqrt{2}}) \approx (-0.707, 1.225)$

(6 cont.)



$$\ln \Phi_{A(ii)} = \frac{1}{\sqrt{3}} \left(2s - \frac{1}{\sqrt{2}} 2p_z - \frac{3}{\sqrt{2}} 2p_x \right)$$

the composite $2p$ orbital has

$$\text{the direction } \vec{r}_{iii} = (z_{iii}, x_{iii}) = \left(-\frac{1}{\sqrt{2}}, -\frac{\sqrt{3}}{\sqrt{2}} \right)$$

$$\vec{r}_{iii} \approx (-0.707, -1.225)$$

angle between \vec{r}_i and \vec{r}_{ii} :

$$\cos \theta = \frac{\vec{r}_i \cdot \vec{r}_{ii}}{|\vec{r}_i| |\vec{r}_{ii}|} = \frac{(\sqrt{2}, 0) \cdot \left(-\frac{1}{\sqrt{2}}, \frac{\sqrt{3}}{\sqrt{2}} \right)}{\sqrt{(\sqrt{2})^2 + 0^2} \cdot \sqrt{\left(-\frac{1}{\sqrt{2}} \right)^2 + \left(\frac{\sqrt{3}}{\sqrt{2}} \right)^2}}$$

$$= \frac{-\frac{\sqrt{2}}{\sqrt{2}} + 0}{\sqrt{2} \sqrt{2}} = -\frac{1}{2} \quad \text{arc cos} \left(-\frac{1}{2} \right) = 120^\circ$$

angle between \vec{r}_{ii} and \vec{r}_{iii} :

$$\cos \theta = \frac{\vec{r}_{ii} \cdot \vec{r}_{iii}}{|\vec{r}_{ii}| |\vec{r}_{iii}|} = \frac{\left(-\frac{1}{\sqrt{2}}, \frac{\sqrt{3}}{\sqrt{2}} \right) \cdot \left(-\frac{1}{\sqrt{2}}, -\frac{\sqrt{3}}{\sqrt{2}} \right)}{\sqrt{\frac{1}{2} + \frac{3}{2}} \sqrt{\frac{1}{2} + \frac{3}{2}}}$$

$$= \frac{\frac{1}{2} - \frac{3}{2}}{\sqrt{2} \sqrt{2}} = \frac{-1}{2} \quad \theta = 120^\circ$$

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Benzene Hückel determinant equation

$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix}$$

(using $x = \frac{\alpha - E}{\beta}$)

$$= x \begin{vmatrix} x & 1 & 0 & 0 & 0 \\ 1 & x & 1 & 0 & 0 \\ 0 & 1 & x & 1 & 0 \\ 0 & 0 & 1 & x & 1 \\ 0 & 0 & 0 & 1 & x \end{vmatrix} - \begin{vmatrix} 1 & 1 & 0 & 0 & 0 \\ 0 & x & 1 & 0 & 0 \\ 0 & 1 & x & 1 & 0 \\ 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 1 & x \end{vmatrix} - \begin{vmatrix} 1 & x & 1 & 0 & 0 \\ 0 & 1 & x & 1 & 0 \\ 0 & 0 & 1 & x & 1 \\ 0 & 0 & 0 & 1 & x \\ 1 & 0 & 0 & 0 & 1 \end{vmatrix}$$

$$= \begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} - \begin{vmatrix} 1 & 1 & 0 & 0 \\ 0 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} + \begin{vmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & x & 0 \\ 0 & 0 & 1 & x \\ 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 \end{vmatrix}$$

$$= x(x) \begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} - x \begin{vmatrix} 1 & 1 & 0 & 0 \\ 0 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix}$$

$$- \begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} + \begin{vmatrix} 0 & 1 & 0 & 0 \\ 0 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 1 & 0 & 1 & x \end{vmatrix}$$

$$+ \begin{vmatrix} 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \\ x & 1 & 0 & 0 \end{vmatrix} + \begin{vmatrix} 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \\ 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 \end{vmatrix}$$

(6 roots)

$$= x^2 \left| \begin{array}{cccc|c} x & 1 & 0 & 0 & \\ 1 & x & 1 & 0 & \\ 0 & 1 & x & 1 & -x \\ 0 & 0 & 1 & x & \end{array} \right| \left| \begin{array}{ccc} 1 & 1 & 0 \\ 0 & x & 1 \\ 0 & 1 & x \\ 0 & 0 & 1 \end{array} \right|$$

$$-2 \left| \begin{array}{cccc|c} x & 1 & 0 & 0 & \\ 1 & x & 1 & 0 & \\ 0 & 1 & x & 1 & + \\ 0 & 0 & 1 & x & \end{array} \right| \left| \begin{array}{ccc} 0 & 1 & 0 \\ 0 & x & 1 \\ 0 & 1 & x \\ 1 & 0 & 1 \end{array} \right| \left| \begin{array}{ccc} 0 & 0 & 1 \\ 0 & 0 & 1 \\ 0 & 1 & x \\ 1 & x & 1 \end{array} \right|$$

$$= x^3 \left| \begin{array}{ccc|c} x & 1 & 0 & \\ 1 & x & 1 & -x^2 \\ 0 & 1 & x & \end{array} \right| \left| \begin{array}{ccc} 1 & 1 & 0 \\ 0 & x & 1 \\ 0 & 1 & x \end{array} \right| \left| \begin{array}{ccc} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{array} \right| \left| \begin{array}{ccc} 0 & 1 & 0 \\ 0 & x & \\ 0 & 1 & x \end{array} \right|$$

$$-2x \left| \begin{array}{ccc|c} x & 1 & 0 & \\ 1 & x & 1 & +2 \\ 0 & 1 & x & \end{array} \right| \left| \begin{array}{ccc} 1 & 1 & 0 \\ 0 & x & 1 \\ 0 & 1 & x \end{array} \right| \left| \begin{array}{ccc} 0 & 1 & 0 \\ 0 & x & 1 \\ 1 & 1 & x \end{array} \right| \left| \begin{array}{ccc} 0 & 0 & 1 \\ 0 & 1 & x \\ 1 & x & 1 \end{array} \right|$$

$$= x^4(x^2-1) - x^3(x-0) - x^2(x^2-1) + x^2(0) - x^2(x^2-1) + x^2$$

$$-x(0) - 2x^2(x^2-1) + 2x^2 + 2(x^2-1) - 2(0) + (-1) + (-1)$$

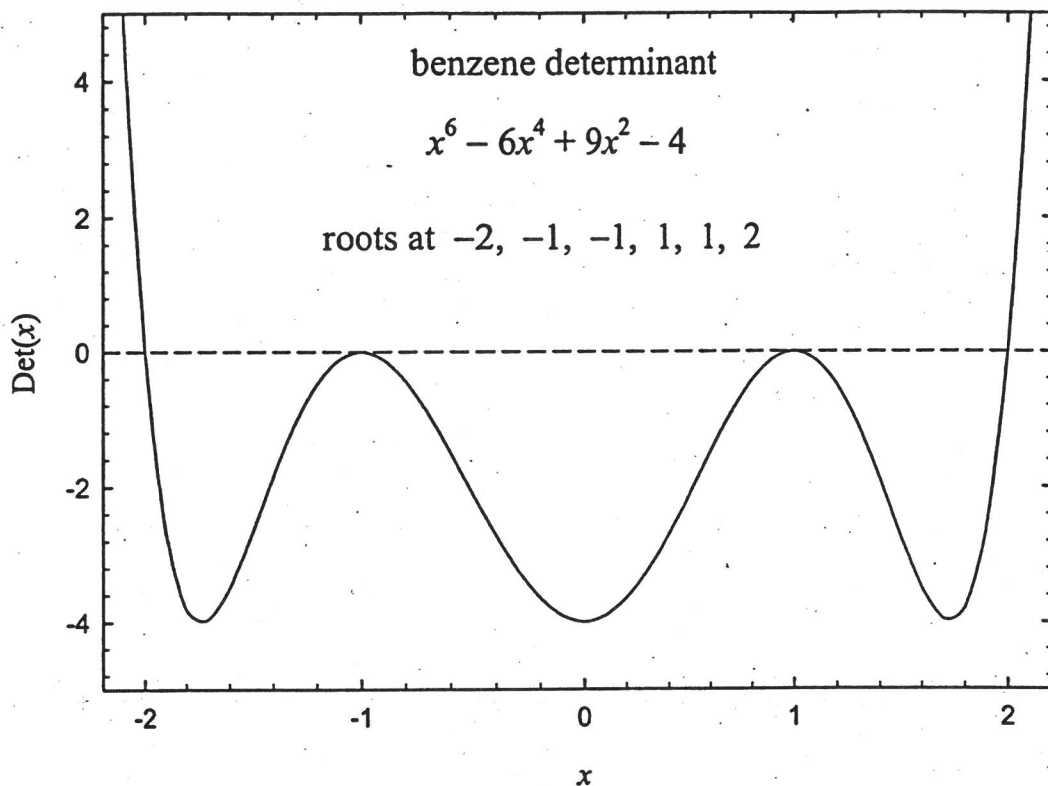
$$0 = x^6 - x^4 - x^4 - x^4 + x^2 - x^4 + x^2 + x^2 - 2x^4 + 2x^2 + 2x^2 + 2x^2 - 2$$

$$\boxed{x^6 - 6x^4 + 9x^2 - 4 = 0} \leftarrow \text{find the 6 roots!}$$

6-10-25-4

(6 cont.)

One way to search for the roots a polynomial is to plot it, and locate the values of x where the polynomial is zero.



$x^2 - 6x^4 + 9x^2 - 4$ appears to be zero at

$$x = -2, -1, 1, 2$$

next step \rightarrow try factoring out $x^2 - 4, x^2 - 1$

(6 cont.)

$$\begin{array}{r} x^4 - 2x^2 + 1 \\ \hline x^2 - 4 \overline{) x^6 - 6x^4 + 9x^2 - 4} \\ \underline{x^6 - 4x^4} \\ -2x^4 \\ \underline{-2x^4 + 8x^2} \\ x^2 \\ \underline{x^2 - 4} \\ 0 \end{array}$$

evaluation of

$$\frac{x^6 - 6x^4 + 9x^2 - 4}{x^2 - 4}$$

$$0 = (x^6 - 6x^4 + 9x^2 - 4) = (x^2 - 4)(x^4 - 2x^2 + 1)$$

$$0 = (x^2 - 4)(x^2 - 1)^2$$

roots $x = -2, 2$

roots $x = -1, 1$ (twice)

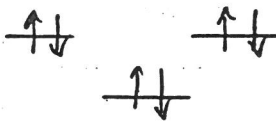
\therefore six roots: $-2, -1, -1, 1, 1, 2 = \frac{\alpha - E}{\beta}$

$$E_6 = \alpha - 2\beta$$

$$E_4 = E_5 = \alpha - \beta$$

$$E_2 = E_3 = \alpha + \beta$$

$$E_1 = \alpha + 2\beta$$



$$\int P_{zi}^* P_{zi} d\tau = 1 \quad \int P_{zi}^* P_{zk} = 0 \quad \text{if } i \neq k$$

$$(8) \int \psi_1^* \psi_1 d\tau$$

$$= \int (0.3717 P_{z1} + 0.6015 P_{z2} + 0.6015 P_{z3} + 0.3717 P_{z4})^* (0.3717 P_{z1} + 0.6015 P_{z2} + 0.6015 P_{z3} + 0.3717 P_{z4}) d\tau$$

$$= 0.3717^2 \int P_{z1}^* P_{z1} d\tau + 0.6015^2 \int P_{z2}^* P_{z2} d\tau + 0.6015^2 \int P_{z3}^* P_{z3} d\tau + 0.3717^2 \int P_{z4}^* P_{z4} d\tau \quad \left. \begin{array}{l} \text{MAIN} \\ \text{TERMS} \\ i=k \end{array} \right\}$$

$$+ \cancel{0.3717(0.6015) \int P_{z1}^* P_{z2} d\tau} + \cancel{0.3717(0.6015) \int P_{z1}^* P_{z3} d\tau} + \cancel{0.3717(0.3717) \int P_{z1}^* P_{z4} d\tau}$$

$$+ \cancel{0.6015(0.3717) \int P_{z2}^* P_{z1} d\tau} + \cancel{0.6015(0.6015) \int P_{z2}^* P_{z3} d\tau} + \cancel{0.6015(0.3717) \int P_{z2}^* P_{z4} d\tau} \quad \left. \begin{array}{l} \text{CROSS} \\ \text{TERMS} \\ i \neq k \end{array} \right\}$$

$$+ \cancel{0.6015(0.3717) \int P_{z3}^* P_{z1} d\tau} + \cancel{0.6015(0.6015) \int P_{z3}^* P_{z2} d\tau} + \cancel{0.6015(0.3717) \int P_{z3}^* P_{z4} d\tau}$$

$$+ \cancel{0.3717(0.3717) \int P_{z4}^* P_{z1} d\tau} + \cancel{0.3717(0.6015) \int P_{z4}^* P_{z2} d\tau} + \cancel{0.3717(0.6015) \int P_{z4}^* P_{z3} d\tau} \quad \left. \begin{array}{l} \text{all} \\ \text{zero} \end{array} \right\}$$

$$= 0.3717^2 + 0.6015^2 + 0.6015^2 + 0.3717^2$$

$$= 0.1382 + 0.3618 + 0.3618 + 0.1382 = 1.0000$$

Similarly $\int \psi_2^* \psi_2 d\tau = 1$

$$\int \psi_1^* \psi_2 d\tau$$

$$= \int (0.3717 P_{z1} + 0.6015 P_{z2} + 0.6015 P_{z3} + 0.3717 P_{z4})^* (0.6015 P_{z1} + 0.3717 P_{z2} - 0.3717 P_{z3} - 0.6015 P_{z4}) d\tau$$

$$= 0.3717(0.6015) \int P_{z1}^* P_{z1} d\tau + 0.6015(0.3717) \int P_{z2}^* P_{z2} d\tau - 0.6015(0.3717) \int P_{z3}^* P_{z3} d\tau - 0.3717(0.6015) \int P_{z4}^* P_{z4} d\tau$$

$$+ \text{cross terms (all zero) such as } 0.3717(0.3717) \int P_{z1}^* P_{z2} d\tau + \dots$$

$$= 0.3717(0.6015) + 0.6015(0.3717) - 0.6015(0.3717) - 0.3717(0.6015)$$

$$= 0$$