Assignment 20

① a) $\Psi^{VB+ionic} \propto \left(C_{cov}\left[\psi_{1s}^{A}(\vec{r}_1)\psi_{1s}^{B}(\vec{r}_2) + \psi_{1s}^{B}(\vec{r}_1)\psi_{1s}^{A}(\vec{r}_2)\right] + C_{ionic}\left[\psi_{1s}^{A}(\vec{r}_1)\psi_{1s}^{A}(\vec{r}_2) + \psi_{1s}^{B}(\vec{r}_1)\psi_{1s}^{B}(\vec{r}_2)\right]\right)$
$\times\left(\alpha(1)\beta(2) - \beta(1)\alpha(2)\right)$

b) $\Psi^{MO+CI} \propto \left(C_{bond}\left[\psi_{1s}^{A}(\vec{r}_1) + \psi_{1s}^{B}(\vec{r}_1)\right]\left[\psi_{1s}^{A}(\vec{r}_2) + \psi_{1s}^{B}(\vec{r}_2)\right]\right.$
$\left. + C_{antibond}\left[\psi_{1s}^{A}(\vec{r}_1) - \psi_{1s}^{B}(\vec{r}_1)\right]\left[\psi_{1s}^{A}(\vec{r}_2) - \psi_{1s}^{B}(\vec{r}_2)\right]\right)\left(\alpha(1)\beta(2) - \beta(1)\alpha(2)\right)$

c) $\Psi^{MO+CI} \propto \left(C_{bond}\left[\cancel{\psi_{1s}^{A}(\vec{r}_1)\psi_{1s}^{A}(\vec{r}_2)} + \psi_{1s}^{A}(\vec{r}_1)\psi_{1s}^{B}(\vec{r}_2) + \psi_{1s}^{B}(\vec{r}_1)\psi_{1s}^{A}(\vec{r}_2) + \cancel{\psi_{1s}^{B}(\vec{r}_1)\psi_{1s}^{B}(\vec{r}_2)}\right]\right.$
$\left. C_{antibond}\left[\cancel{\psi_{1s}^{A}(\vec{r}_1)\psi_{1s}^{A}(\vec{r}_2)} - \psi_{1s}^{A}(\vec{r}_1)\psi_{1s}^{B}(\vec{r}_2) - \psi_{1s}^{B}(\vec{r}_1)\psi_{1s}^{A}(\vec{r}_2) + \cancel{\psi_{1s}^{B}(\vec{r}_1)\psi_{1s}^{B}(\vec{r}_2)}\right]\right)$
$\times\left(\alpha(1)\beta(2) - \beta(1)\alpha(2)\right)$

$= \left(\left[C_{bond} + C_{antibond}\right]\left[\psi_{1s}^{A}(\vec{r}_1)\psi_{1s}^{A}(\vec{r}_2) + \psi_{1s}^{B}(\vec{r}_1)\psi_{1s}^{B}(\vec{r}_2)\right]\right.$
$\left. + \left[C_{bond} - C_{antibond}\right]\left[\psi_{1s}^{A}(\vec{r}_1)\psi_{1s}^{B}(\vec{r}_2) + \psi_{1s}^{B}(\vec{r}_1)\psi_{1s}^{A}(\vec{r}_2)\right]\right)\left(\alpha(1)\beta(2) - \beta(1)\alpha(2)\right) \propto \Psi^{VB+ionic}$

$C_{cov} = \cancel{C_{bond} + C_{antibond}}$ $C_{bond} - C_{antibond}$

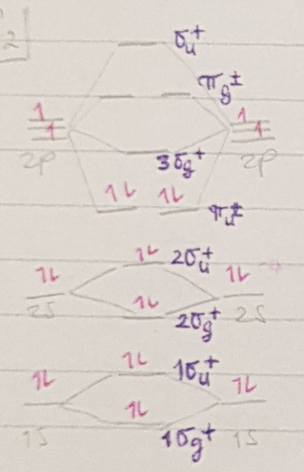
$C_{ionic} = \cancel{C_{bond} - C_{antibond}}$ $C_{bond} + C_{antibond}$

② a)

$$|\Psi_{1\sigma^2 2\sigma^2}\rangle = \frac{1}{\sqrt{4!}}\begin{bmatrix} \phi_{1\sigma}(\vec{r}_1)\alpha(1) & \phi_{1\sigma}(\vec{r}_1)\beta(1) & \phi_{2\sigma}(\vec{r}_1)\alpha(1) & \phi_{2\sigma}(\vec{r}_1)\beta(1) \\ \phi_{1\sigma}(\vec{r}_2)\alpha(2) & \phi_{1\sigma}(\vec{r}_2)\beta(2) & \phi_{2\sigma}(\vec{r}_2)\alpha(2) & \phi_{2\sigma}(\vec{r}_2)\beta(2) \\ \phi_{1\sigma}(\vec{r}_3)\alpha(3) & \phi_{1\sigma}(\vec{r}_3)\beta(3) & \phi_{2\sigma}(\vec{r}_3)\alpha(3) & \phi_{2\sigma}(\vec{r}_3)\beta(3) \\ \phi_{1\sigma}(\vec{r}_4)\alpha(4) & \phi_{1\sigma}(\vec{r}_4)\beta(4) & \phi_{2\sigma}(\vec{r}_4)\alpha(4) & \phi_{2\sigma}(\vec{r}_4)\beta(4) \end{bmatrix}$$

b) $\phi_{2\sigma}(\vec{r}) = c\,\psi_{Li\text{-}2s}(\vec{r}) + \sqrt{1 - |c|^2}\,\psi_{H\text{-}1s}(\vec{r})$

③ C_2



C_2^+

a) $(1\sigma_g^+)^2(1\sigma_u^+)^2(2\sigma_g^+)^2(2\sigma_u^+)^2(\pi_u^+)^2(\pi_u^-)^4$

b) $\frac{1}{2}(7-4) = \frac{3}{2}$

c) doublet

C_2

a) $(1\sigma_g^+)^2(1\sigma_u^+)^2(2\sigma_g^+)^2(2\sigma_u^+)^2(\pi_u^+)^2(\pi_u^-)^2$

b) $\frac{1}{2}(8-4) = 2$

c) singlet

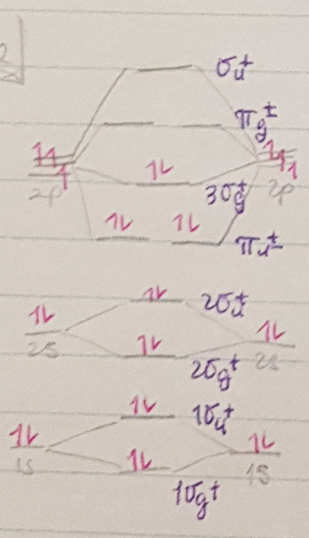
C_2^-

a) $(1\sigma_g^+)^2(1\sigma_u^+)^2(2\sigma_g^+)^2(2\sigma_u^+)^2(\pi_u^+)^2(\pi_u^-)^2(3\sigma_g^+)^4$

b) $\frac{1}{2}(9-4) = \frac{5}{2}$

c) doublet

N_2



N_2^+

a) $(1\sigma_g^+)^2(1\sigma_u^+)^2(2\sigma_g^+)^2(2\sigma_u^+)^2(\pi_u^+)^2(\pi_u^-)^2(3\sigma_g^+)^4$

b) $\frac{1}{2}(9-4) = \frac{5}{2}$

c) doublet

N_2

a) $(1\sigma_g^+)^2(1\sigma_u^+)^2(2\sigma_g^+)^2(2\sigma_u^+)^2(\pi_u^+)^2(\pi_u^-)^2(3\sigma_g^+)^2$

b) $\frac{1}{2}(10-4) = 3$

c) singlet

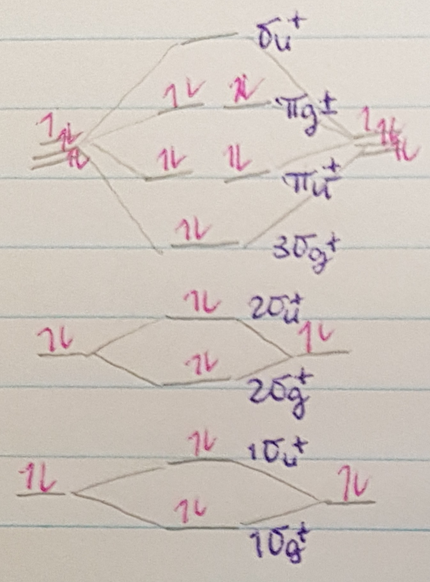
N_2^-

a) $(1\sigma_g^+)^2(1\sigma_u^+)^2(2\sigma_g^+)^2(2\sigma_u^+)^2(\pi_u^+)^2(\pi_u^-)^2(3\sigma_g^+)^2(\pi_g^+)^4$

b) $\frac{1}{2}(10-5) = \frac{5}{2}$

c) doublet.

F_2



F_2^+

a) $(1\sigma_g^+)^2(1\sigma_u^+)^2(2\sigma_g^+)^2(2\sigma_u^+)^2(3\sigma_g^+)^2(\pi_u^+)^2(\pi_u^-)^2(\pi_g^+)^2(\pi_g^-)^4$

b) $\frac{1}{2}(10-7) = \frac{3}{2}$

c) doublet.

F_2

a) $(1\sigma_g^+)^2(1\sigma_u^+)^2(2\sigma_g^+)^2(2\sigma_u^+)^2(3\sigma_g^+)^2(\pi_u^+)^2(\pi_u^-)^2(\pi_g^+)^2(\pi_g^-)^2$

b) $\frac{1}{2}(10-8) = 1$

c) singlet.

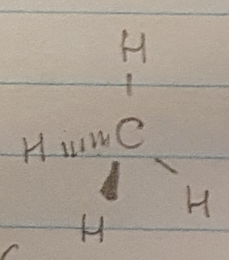
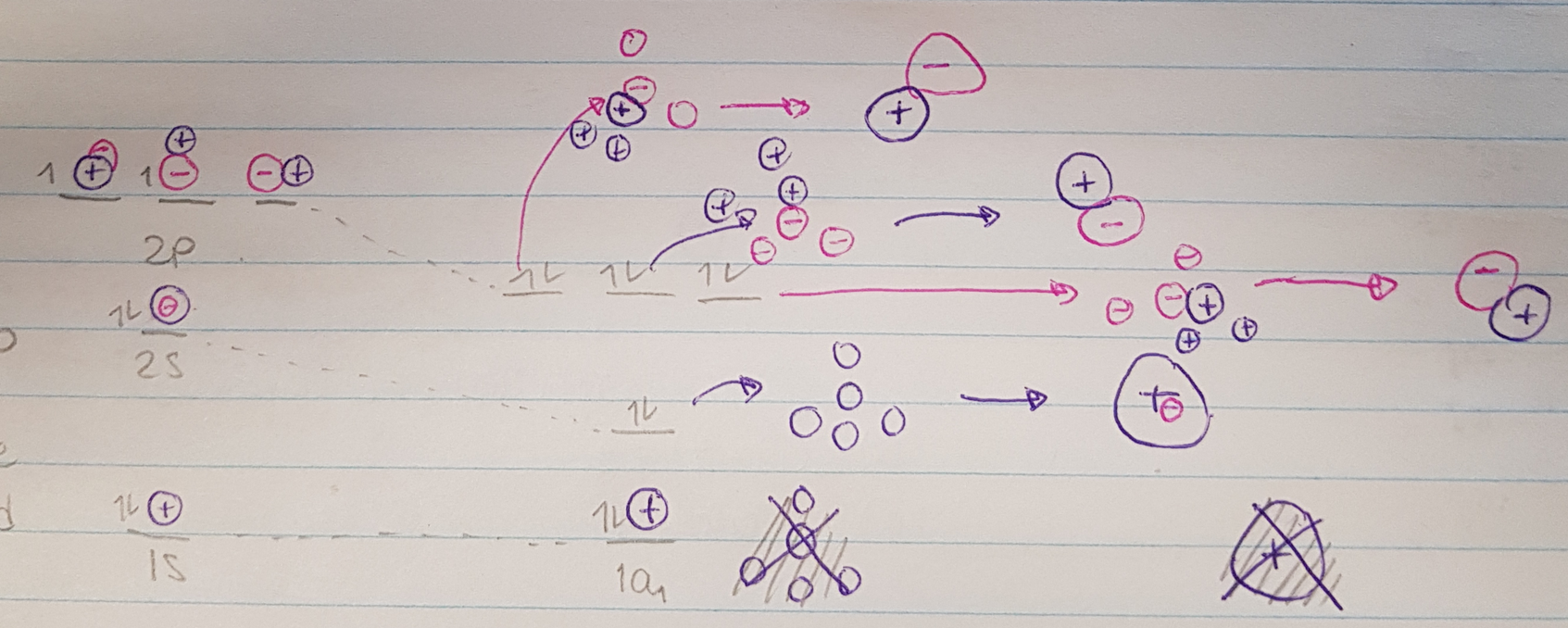
F_2^-

a) $(1\sigma_g^+)^2(1\sigma_u^+)^2(2\sigma_g^+)^2(2\sigma_u^+)^2(3\sigma_g^+)^2(\pi_u^+)^2(\pi_u^-)^2(\pi_g^+)^2(\pi_g^-)^2(3\sigma_u^+)^4$

b) $\frac{1}{2}(10-9) = \frac{1}{2}$

c) doublet.

④ CH_4.



symmetric, so $2p_x, 2p_y, 2p_z$ are degenerate under the ligand field-theory