Sem 1 (2005/2006) : Chemical Bonding

Q$_6$ (b) Valence Bond Theory accounts for orbital hybridizations of sp^3d and $\overline{sp}^3d^2$.

P : $1s^2 2s^2 2p^6 (3s^2 3p^3) 4s^0 3d^0$
Cl : $1s^2 2s^2 2p^6 3s^2 3p^5$

| ⇅ | ⇅ | ↑ | $3p^5$

__sp³d hybridization__ :

eg. PCl$_5$ molecule.

Valence Bond model proposes that the one 3s, the three 3p and one of the five 3d orbitals of the central P atom mix and form five sp³d hybrid orbitals, which point to the vertices of a trigonal bipyramid. Each hybrid orbital overlaps a 3p orbital of a Cl atom, and the five valence electrons of P, together with one from each of the five Cl atoms, pair up to form five P–Cl bonds.
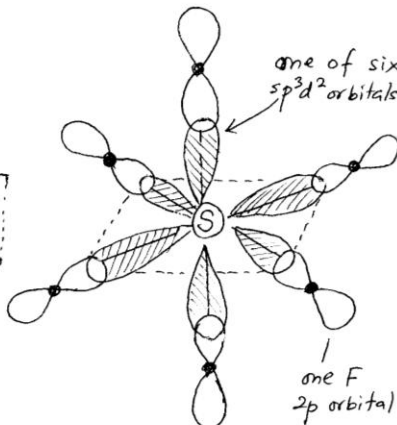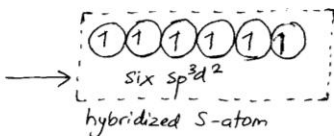

3d → 3d → five sp³d → Hybridized P atom → P, 3p orbital of Cl atom
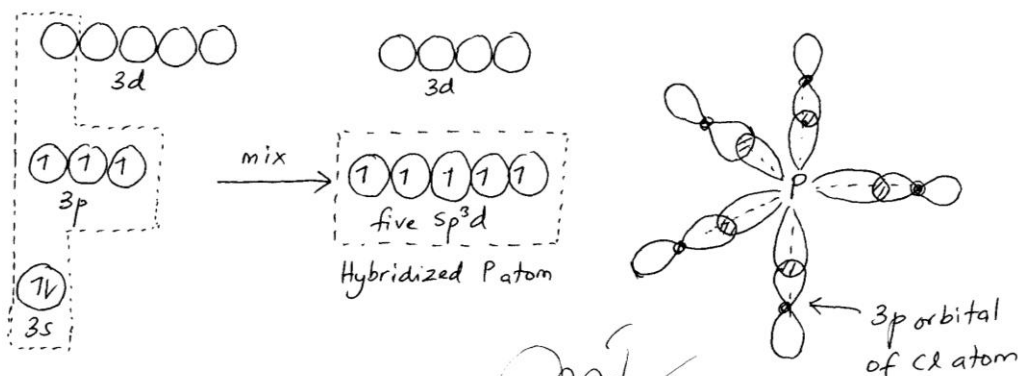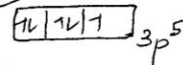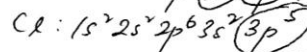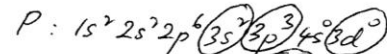
__sp³d² hybridization__ :
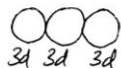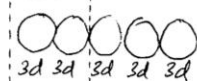
eg. SF$_6$ molecule.

Valence Bond model proposes that the one 3s, the three 3p and two of the five 3d orbitals of the central S atom mix and form six sp³d² hibrid orbitals, which point to the vertices of an octahedron. Each hybrid orbital overlaps a 2p orbital of an F atom, and the six valence electrons of S, together with one from each of the six F atoms, pair up to form six S–F bonds.
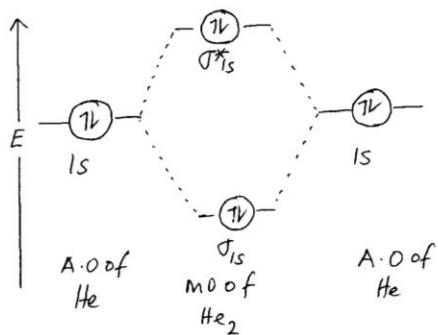
<u>Sem 1 (2005/2006)</u> : Chemical Bonding

Q_6 (b)
Cont.

3d 3d 3d 3d 3d   3d 3d 3d

one of six
sp^3d^2 orbitals

six sp^3d^2
hybridized S-atom

$7b$ 1 1
3p 3p 3p

$7b$
3s

isolated S-atom

one F
2p orbital)

Q_6(d)(i) Molecular orbital energy diagram for He_2, B_2 and O_2

For He_2 (4 electron) : $(\sigma_{1s})^2(\sigma_{1s}^*)^2$

σ_{1s}^*

E

1s   1s

σ_{1s}

A.O of
He

M O of
He_2

A.O of
He

For B_2
B
$1s^2 2s^2 2p^1$

$B_2 : KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p_y})^1(\pi_{2p_z})^1$

σ_{2s}^*

$\pi_{2p_y}^*$ $\pi_{2p_z}^*$

2p   2p

σ_{2p_x}

π_{2p_y} π_{2p_z}

σ_{2s}^*

2s   2s

σ_{2s}

E

A.O
of B

MO of B_2

A.O of
B
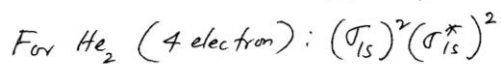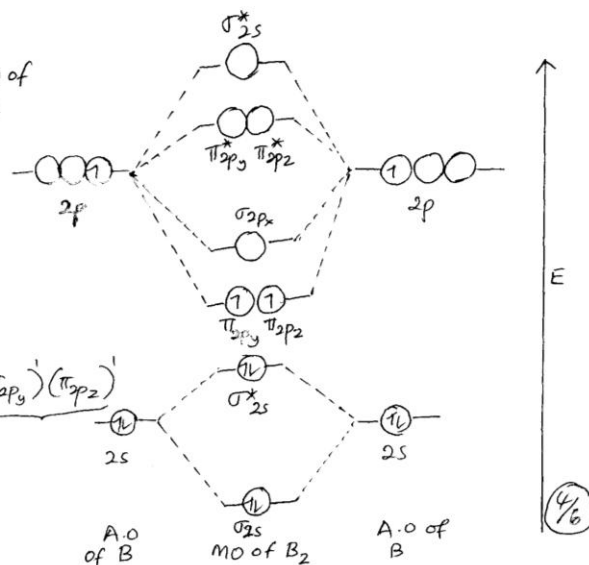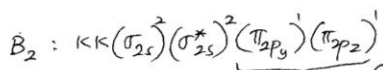
(4/6)

Sem 1 (2005/2006) : Chemical Bonding

$Q_6(d)(i)$ MO energy diagram for O_2 :

O : $1s^2 2s^2 2p^4$ (6 valence electrons)

O_2 : KK $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p_x})^2 [(\pi_{2p_y})^2 (\pi_{2p_z})^2] [(\pi_{2p_y}^*)^1 (\pi_{2p_z}^*)^1]$

(12e⁻)
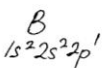
$\sigma_{2p_x}^*$

$\pi_{2p_y}^* \; \pi_{2p_z}^*$

$\pi_{2p_y} \; \pi_{2p_z}$

σ_{2p_x}

σ_{2s}^*

2s   2s

σ_{2s}

A.O of   M.O of   A.O of
O O_2 O
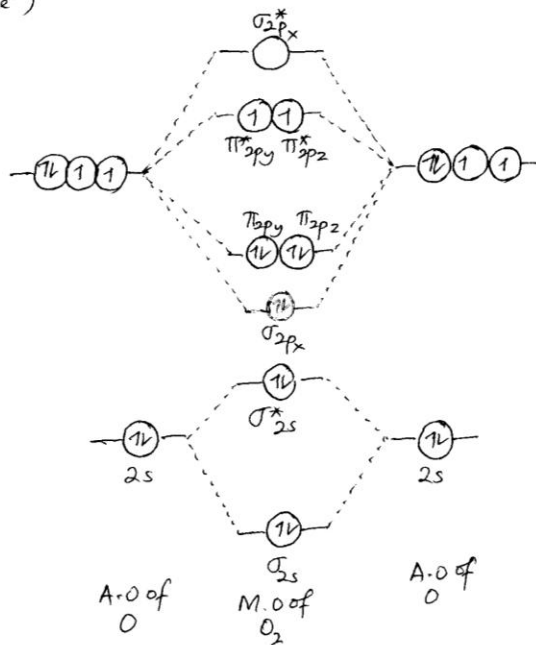
(Notes)

✳ In M.O. of O_2 : Energy of $\sigma_{2p_x} < [(\pi_{2p_y})(\pi_{2p_z})]$ ← small atom

In M.O of B_2 Energy of $\sigma_{2p_x} > [(\pi_{2p_y})(\pi_{2p_z})]$ ← larger atom.

Reason   O : $1s^2 2s^2 2p^4$ ⟨↑↓⟩⟨↑⟩⟨↑⟩   — start to pair up.

• Strong repulsions occur as the 2p electrons pair-up. These repulsions raise the energy of the 2p orbitals high enough above the energy of the 2s orbitals to minimize orbital mixing.

B : $1s^2 2s^2 2p^1$ ⟨↑⟩◯◯

• In contrast, B atom is large and when the 2p AOs (atomic orbitals) are half-filled, the repulsions are relatively small, so the 2p energies are much closer to the 2s-energy. As a result, some mixing occurs between the 2s orbital of one atom and the end-on 2p orbital of the other. This orbital mixing lowers the energy of the σ_{2s} and σ_{2s}^* MOs and raises the energy of the σ_{2p} and σ_{2p}^* MOs, but the π MOs are not affected.

– The only change is the energy order of the σ_{2p_x} and π_{2p_y}, π_{2p_z}.

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$Q_{6(d)(ii)}$ Bond order, BO $= \frac{1}{2}\left(\begin{array}{c}\text{no. of } e^- \text{ in bonding} \\ \text{MO}\end{array}\right) - \left(\begin{array}{c}\text{no. of } e^- \text{ in} \\ \text{antibonding MO}\end{array}\right)$

For He_2 : Bond order $= \frac{1}{2}(2-2) = 0$ $\therefore$ Covalent He_2 molecule does not exist.

For B_2 : Bond order $= \frac{1}{2}(4-2) = 1$

For O_2 : Bond order $= \frac{1}{2}(8-4) = 2$

Bond order $\propto$ Bond energy

B.O of O_2 > B.O of B_2

$\therefore$ O_2 is more stable than B_2 molecule.

He_2 = diamagnetic properties (no unpaired electron)

B_2 and O_2 = paramagnetic properties (2 unpaired electrons)

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