HYBRIDIZATION

Definition: The phenomenon of mixing up of atomic orbitals of similar energies and formation of equivalent number of entirely new orbitals of identical shape and energy is known as "hybridization" and the new orbitals so formed is called as "hybrid orbitals".

Important points for understanding the hybridization:

(i) The number of hybrid orbitals generated is equal to the number of pure atomic orbitals that participate in hybridization process.

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(iii) Covalent bonds is polyatomic molecules are formed by the overlap of hybrid orbitals or of hybrid orbitals with unhybridized ones.

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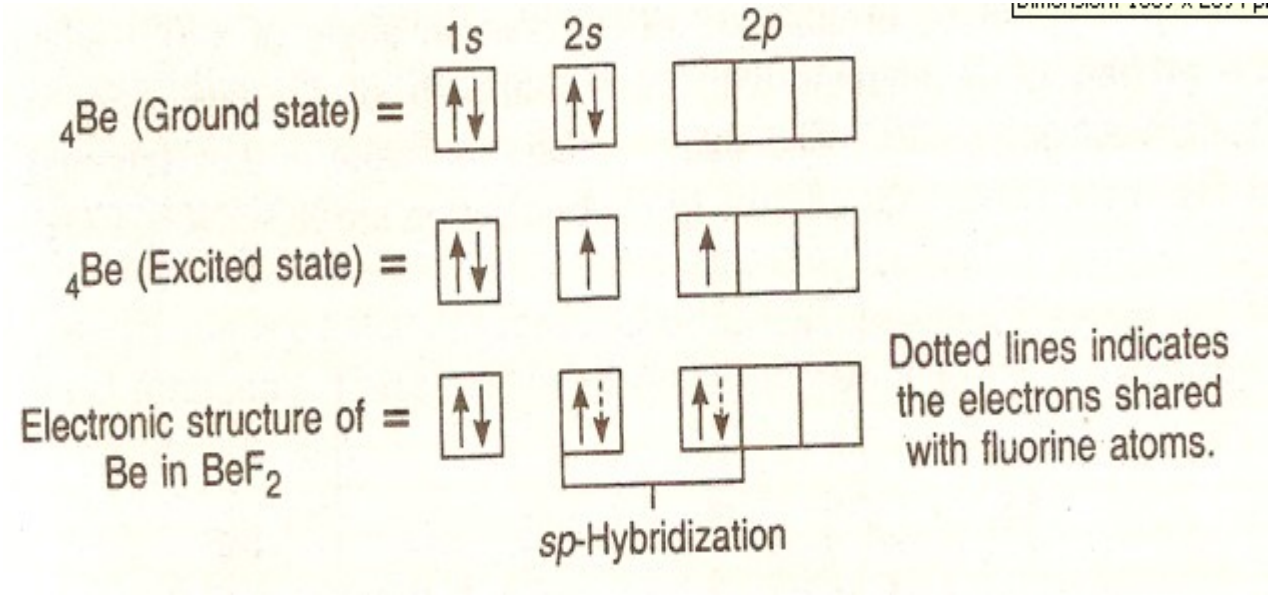
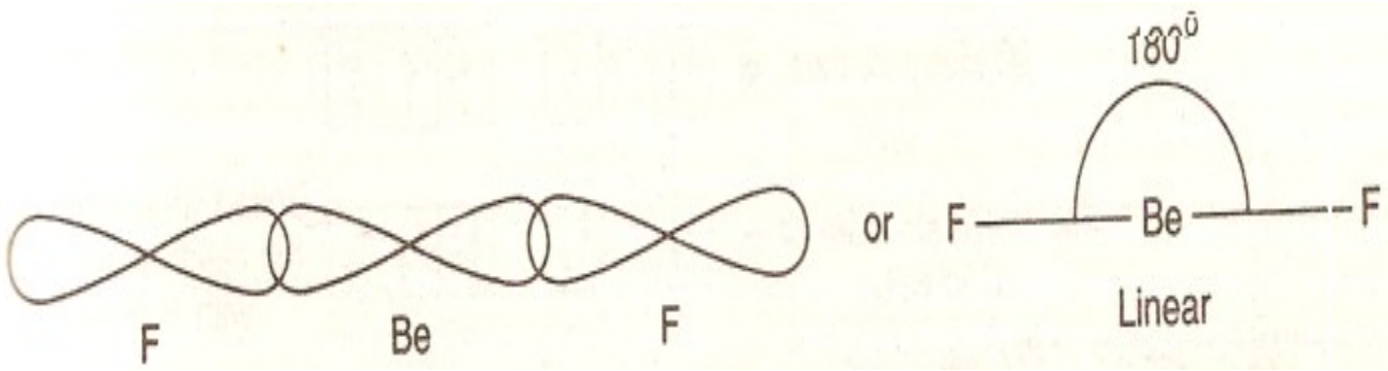
Example: In BeF_2 Molecule the sp-hybridized orbitals of Be overlap with the half-filled orbitals of two fluorine atoms to give a **linear shape.**

HYBRIDIZATION

Structure of BeF_2 Molecule

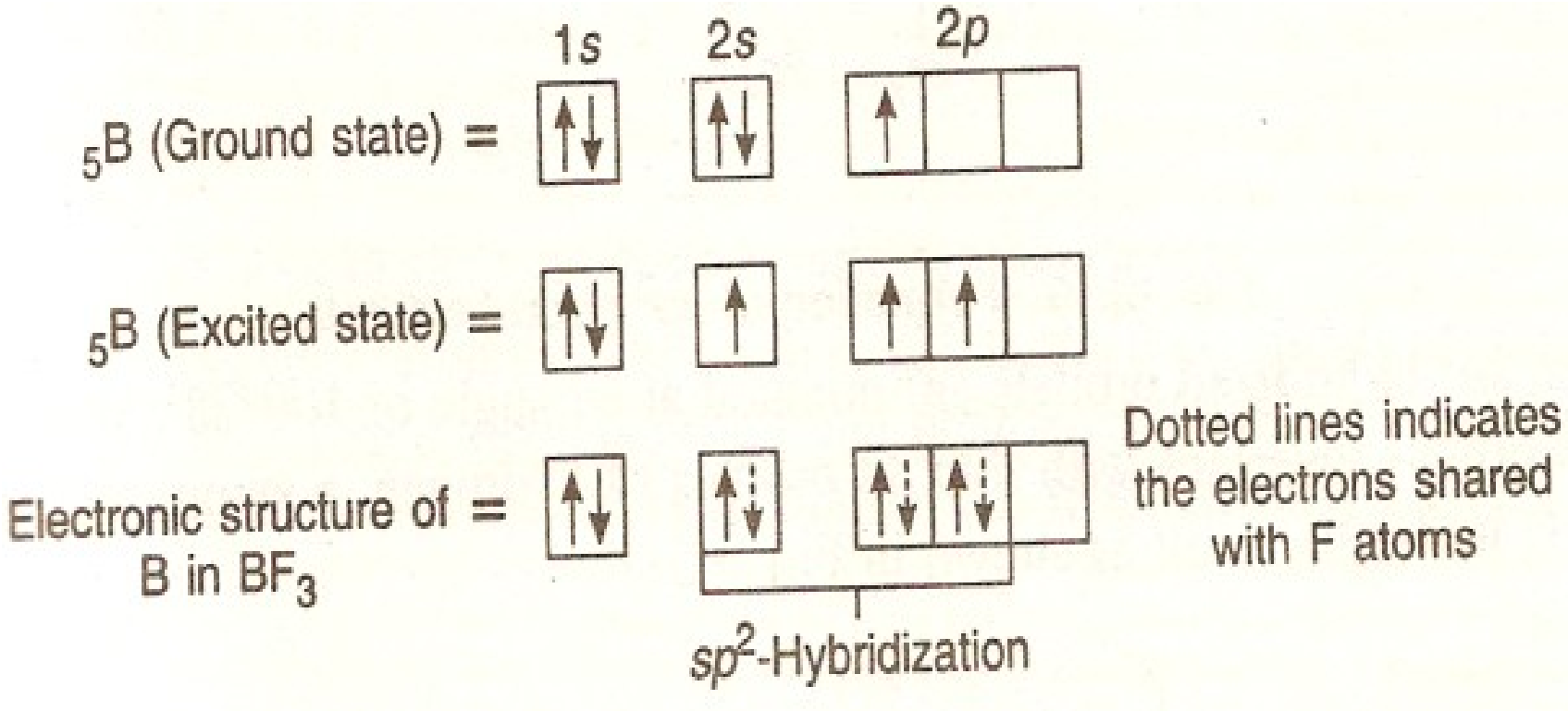




HYBRIDIZATION

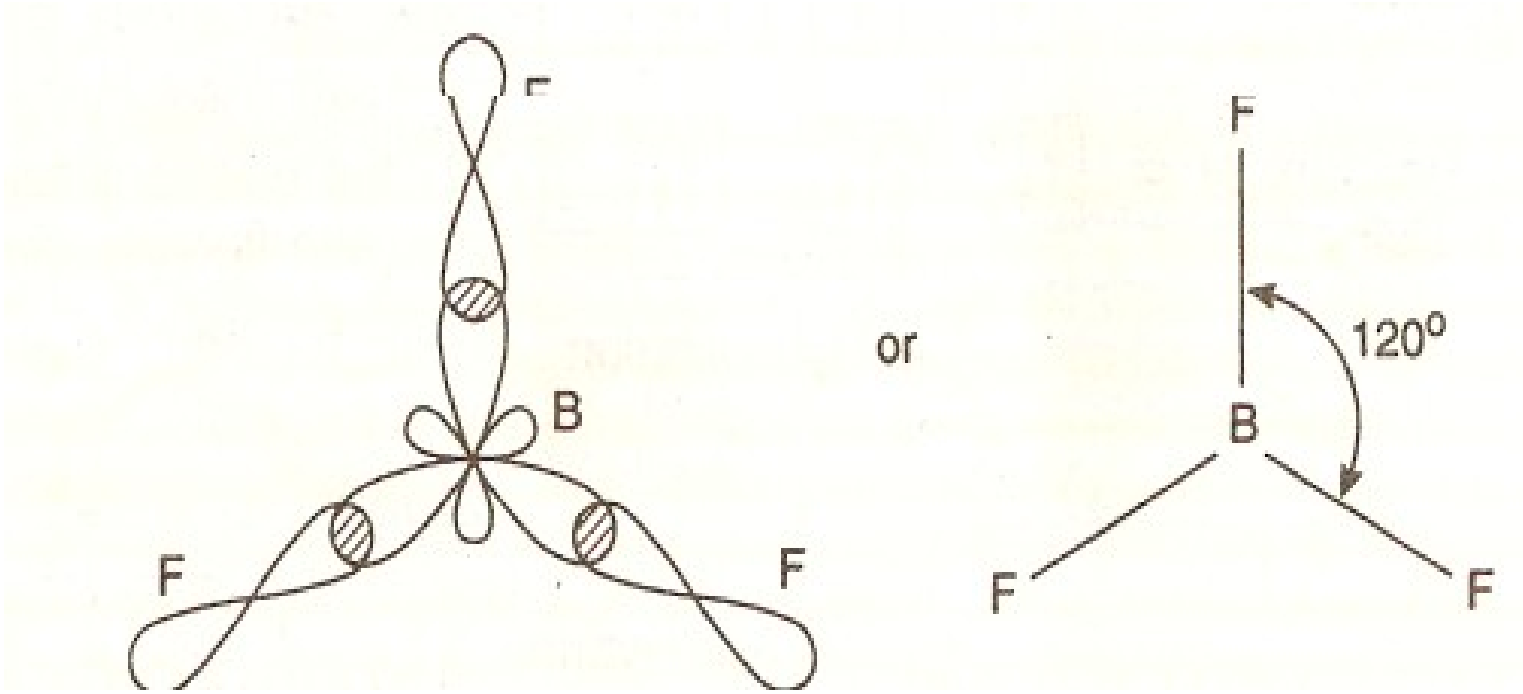
sp^2-hybridization: The combination of one s and two p-orbitals to form three hybrid orbitals of equal energy is known as sp^2-hybridization.

Example : BF_3 Molecule.



HYBRIDIZATION

These sp2 hybridized orbitals are oriented at an angle of 120°. When three sp2 hybridized orbitals of B overlaps with three p-orbitals of fluorine, three σ -bonds are formed with bond angle 120°. The shape of BF3 molecule is thus trigonal planar



HYBRIDIZATION

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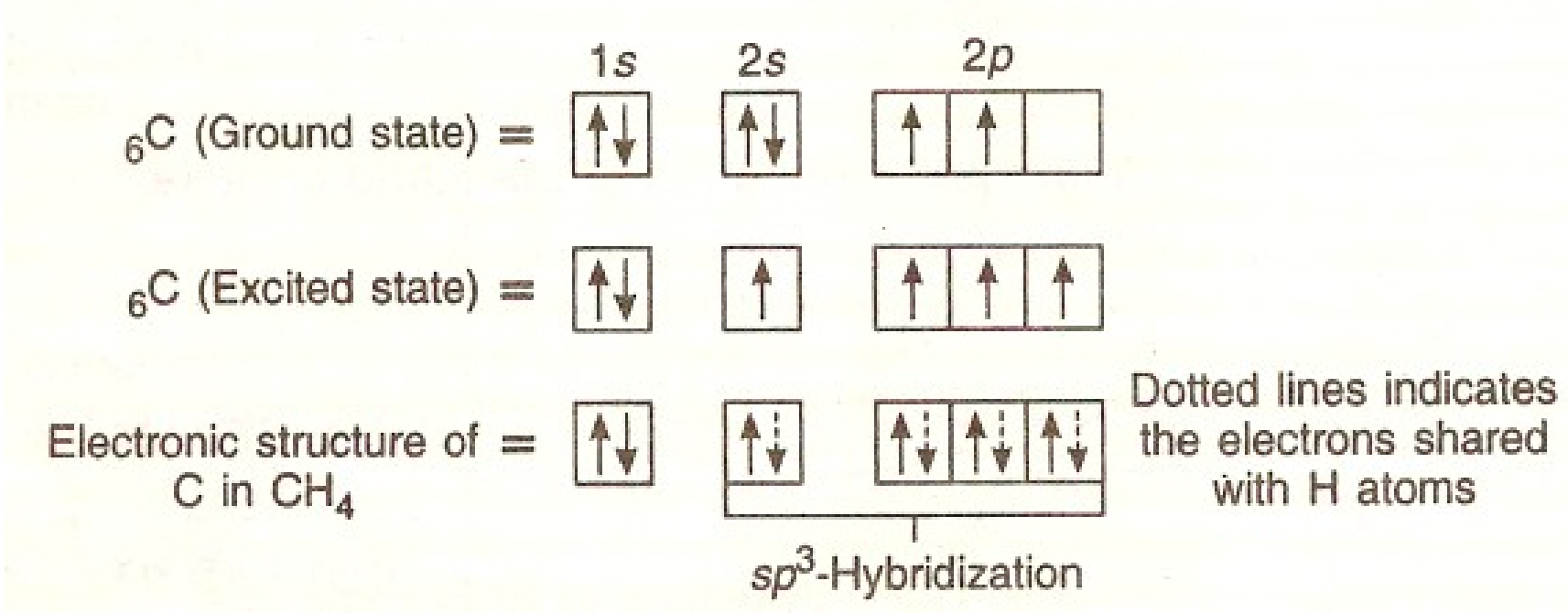
Example: Methane (CH_4) molecule.



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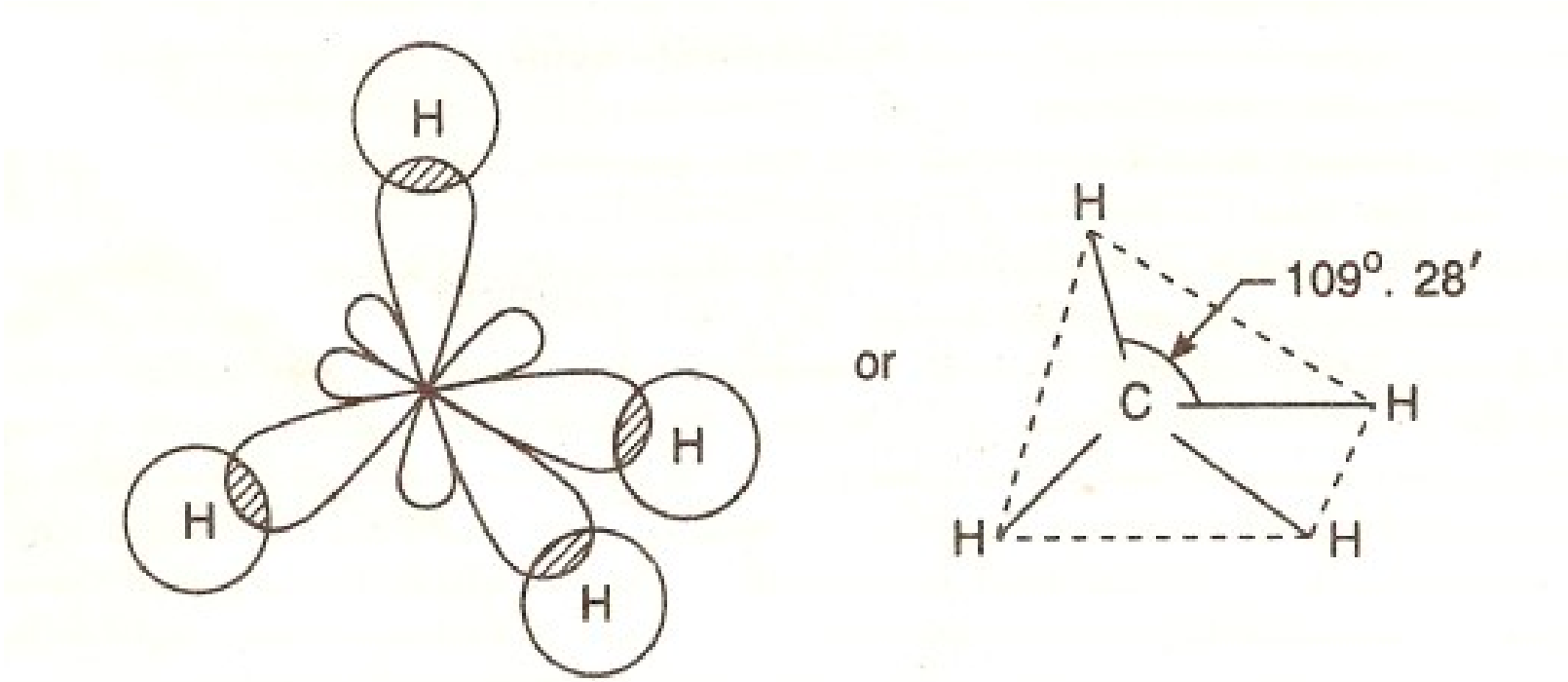
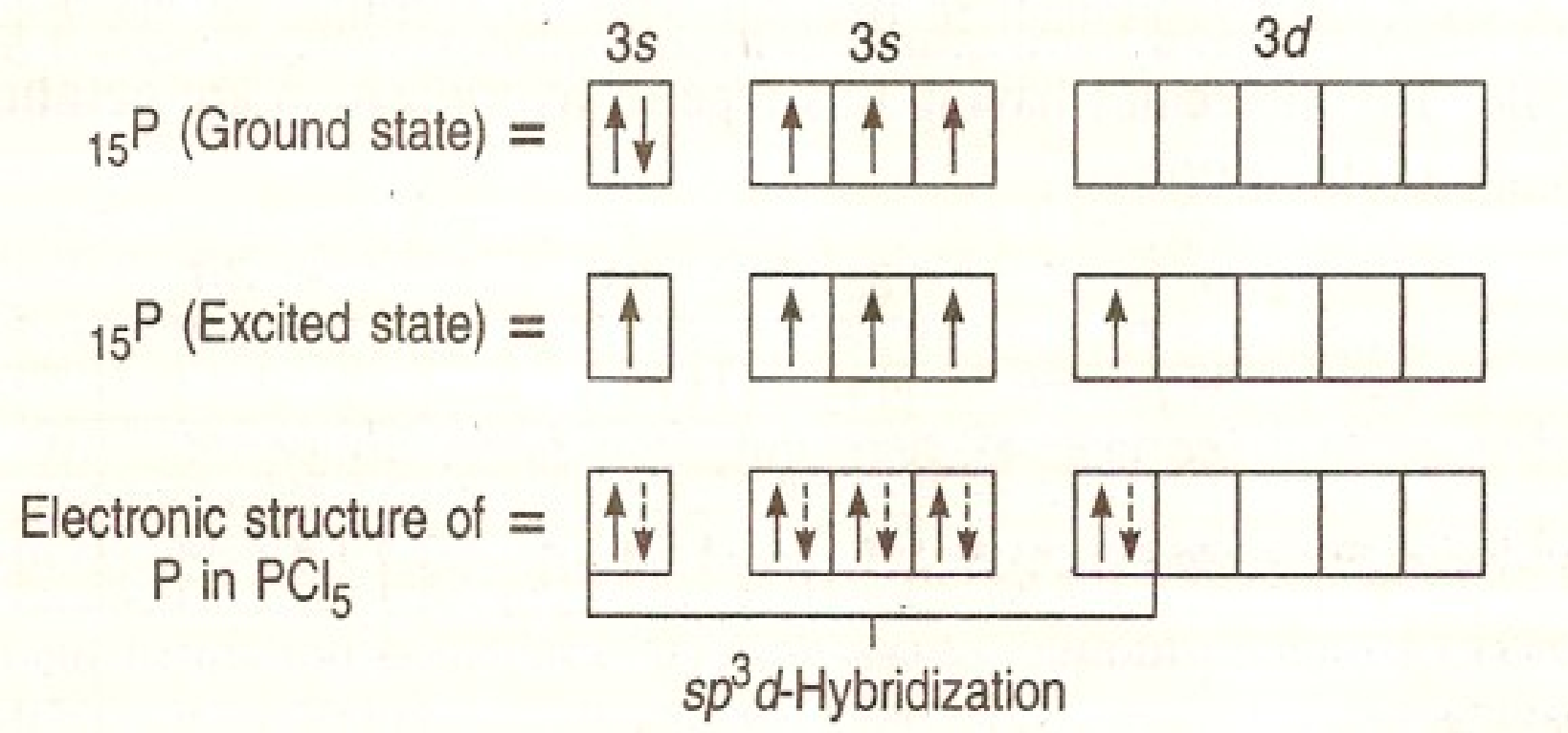
These sp3-hybridized orbitals are oriented at an angle of 109°28'. When these four sp3 hybrid orbitals overlaps with four 1s orbitals of hydrogen, a symmetrical tetrahedral shaped CH4 molecule form.



HYBRIDIZATION

(4) sp3d-hybridization: The combination of one s, three *p* and one d-orbitals to form five hybrid orbitals of equal energy is known as sp3d-hybridization.

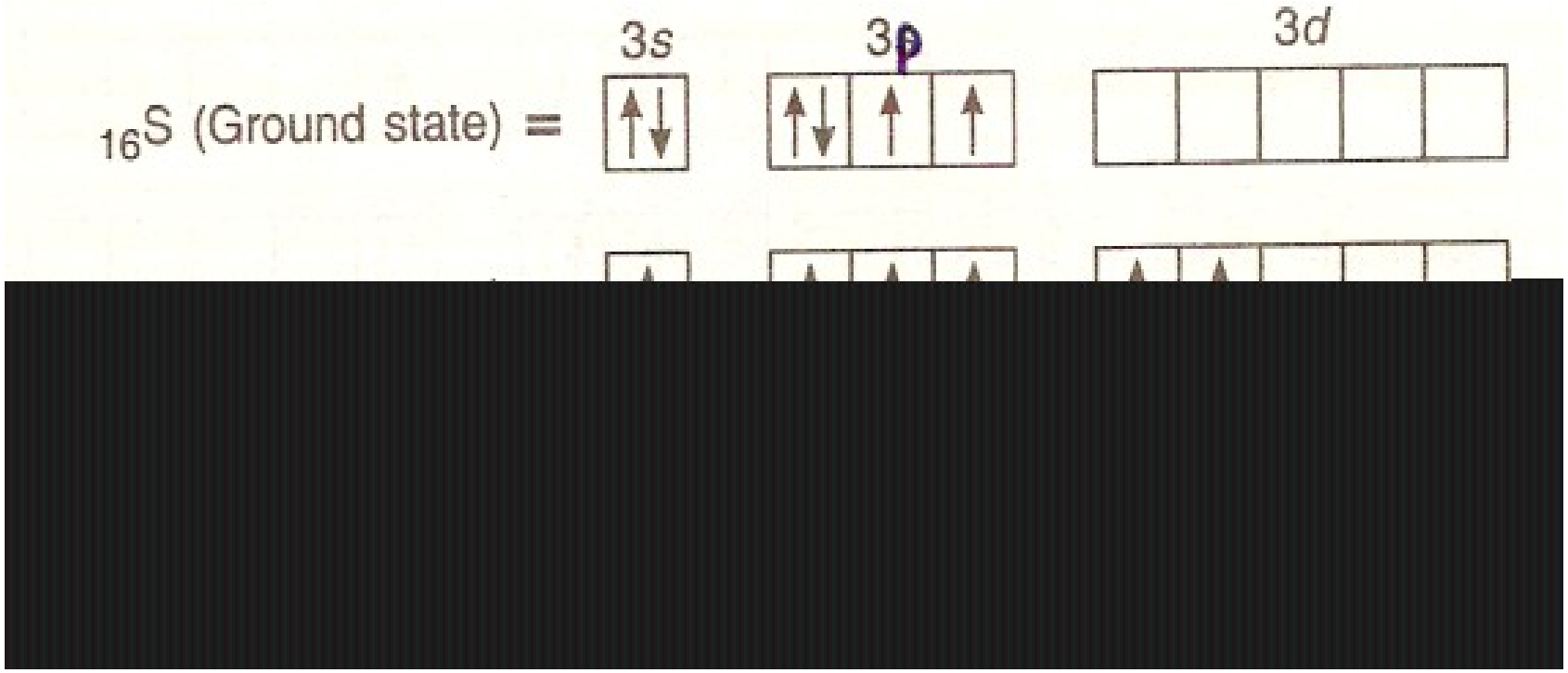
Example: PCl_5 molecule.



HYBRIDIZATION

(5)sp^3d^2-hybridization : The combination of one s, three p and two d-orbitals to form six hybrid orbitals of equal energy is known as sp^3d^2-hybridization.

Examples : SF_6 Molecule.



VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

Definition: The Valence-Shell-Electrons-Pair-Repulsion Theory (VSEPR), proposes that the stereochemistry of an atom in a molecule is determined primarily by the repulsive interactions among all the electron pairs in its valence shell.

Postulates of VSEPR Theory : The main postulates of this theory are :

(1) The shape of the molecule is determined by repulsion between all of the electron pairs present in the valence shell.

VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

(2) A lone pair of electrons takes up more space round the central atom than a bond pair, since the lone pair is attracted to one nucleus whilist the bond pair is shared by two nuclei. It follows that repulsion between two lone pairs is greater than the repulsion between a lone pair and a bond pair, which in turn is greater than the repulsion between two bond pairs. The repulsive interactions decrease in the order :

LP-LP > LP-BP > BP-BP

(3) The magnitude of repulsion between bonding pairs of electrons. depends on the electronegativity difference between the central atom and the other atoms.

VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

(4) Double bonds cause more repulsion than single bonds, and triple bonds cause more repulsion than a double bond. Repulsive forces decrease sharply with increasing bond angle between the electron pairs.

Example: BF_3 Molecule

In BF_3 the central B atom has the configuration : $1s^2$, $2s^2$, $2p_x^1$. During the bond formation one 2s-electron is promoted to vacant 2py orbital. Thus, excited B (configuration: $1s^2$, $2s^1$, $2P_x^1$, $2p_y^1$, $2p_z^0$) has three unpaired electrons for bond formation with three fluorine atoms. The three bonds between B and F atoms should be slightly different strengths, because in one, 2s; while in other, two 2p-orbital electrons are involved. But in fact, all the three bonds is BF3 are of equal strength with bond angle of 120°.

VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

Structure of BF_3 Molecule:

VALENCE BOND THEORY

Introduction: Atoms with unpaired electrons tend to combine with other atoms which also have unpaired electrons. In this way the unpaired electrons are paired up, and the atoms involved all attain a stable electronic arrangement. This in usually a full shell of electrons (i.e., a noble gas configuration). Two electrons shared between two atoms constitute a bond. The number of bonds formed by an atom is usually the same as the number of unpaired electrons in the ground state, i.e., the lowest energy state. However, in some cases the atom may form more bonds than this. This occurs by excitation of the atom (i.e., providing it with energy) when electrons which were paired in the ground state are unpaired and promoted into suitable empty orbitals. This increases the number of unpaired electrons, and hence the number of bonds which can be formed.

VALENCE BOND THEORY

Postulates of Valance Bond Theory :

(i) A molecule is considered to be made up of atoms.

(ii) Electrons in atoms occupy atomic orbitals.

(iii) Orbitals may or may not be hybridized.

(iv) The atomic orbitals (or the hybrid orbitals) are thought to remain even when the atom is chemically bonded in a molecule.

Example: 1. In HF, H has a singly occupied s-orbital that overlaps with a singly filled 2p orbital on F.

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VALENCE BOND THEORY

Limitations of valence Bond Theory :

This theory does not explain :

(i) The directional nature of covalent bond.

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(iv) The structures of odd electron molecules or ions where no pairing of electrons takes place.

MOLECULAR ORBITAL THEORY

Introduction: The molecular orbital theory given by Hund and Mullikens considers that the valency electrons are associated with all the concerned nuclii, *i.e.,* with the molecule as a whole. Thus, in other words, the atomic orbitals combine together to form molecular orbitals in which the identity of both the atomic orbitals is lost.

Postulates of Molecular Orbital Theory :

(a) During the formation of bond, the two half-filled atomic·orbitals with opposite spins combine to form two molecular orbitals (M.O.). One of which is bonding M.O. and other antibonding M.O. The energy of combining atomic orbitals, however, should be of similar magnitude.

MOLECULAR ORBITAL THEORY

(b) A bonding M.O. has lower energy than the atomic orbitals from which it is formed; while antibonding M.O. has higher energy than the atomic orbitals from which it is formed.

(c) Two *s* or p-orbitals can overlap end-to-end to form one sigma bonding molecular orbital (σ) and one sigma antibonding molecular orbital (σ *).

(d) Two p-orbitals can overlap sideways to form one pi (π)-bonding molecular orbital and pi (π *) anti bonding orbital.

(e) The energies of σ -bonding orbitals are lower than those of π -bonding orbitals.

(f) The orbitals of lower energy are filled first. Each orbital may hold up two electrons, provided that they have opposite spins.

MOLECULAR ORBITAL THEORY

(g) When several orbitals have the same energy, *(i.e.,* they are degenerate), electrons will be arranged so as to give the maximum number of unpaired spins (Hund‘s rule).

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The energies of the σ2p and π2p M.Os. are very close together. The order of M.Os shown above is correct for oxygen and heavier elements, but for the lighter elements boron, carbon and nitrogen the $\pi 2p_y$ and $\pi 2p_z$ are probably lower than $\sigma 2p_x$. For these atoms the order is :

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MOLECULAR ORBITAL THEORY

Significance of Bond order

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Combination of Atomic Orbitals

(i) **Combinaltion of s-orbitals:** The combination of two similar 1*s* atomic orbitals gives rise to two molecular orbitals, σ1s and σ *1s. σ1s is the bonding molecular orbital, whereas σ *1s is the antibonding molecular orbital. Similarly, the combination of two 2s atomic orbitals will give rise to σ2s and σ*2s molecular orbitals. These will be of higher energy than σ1s and σ*1s molecular orbitals as they are formed from atomic orbitals of higher energy.

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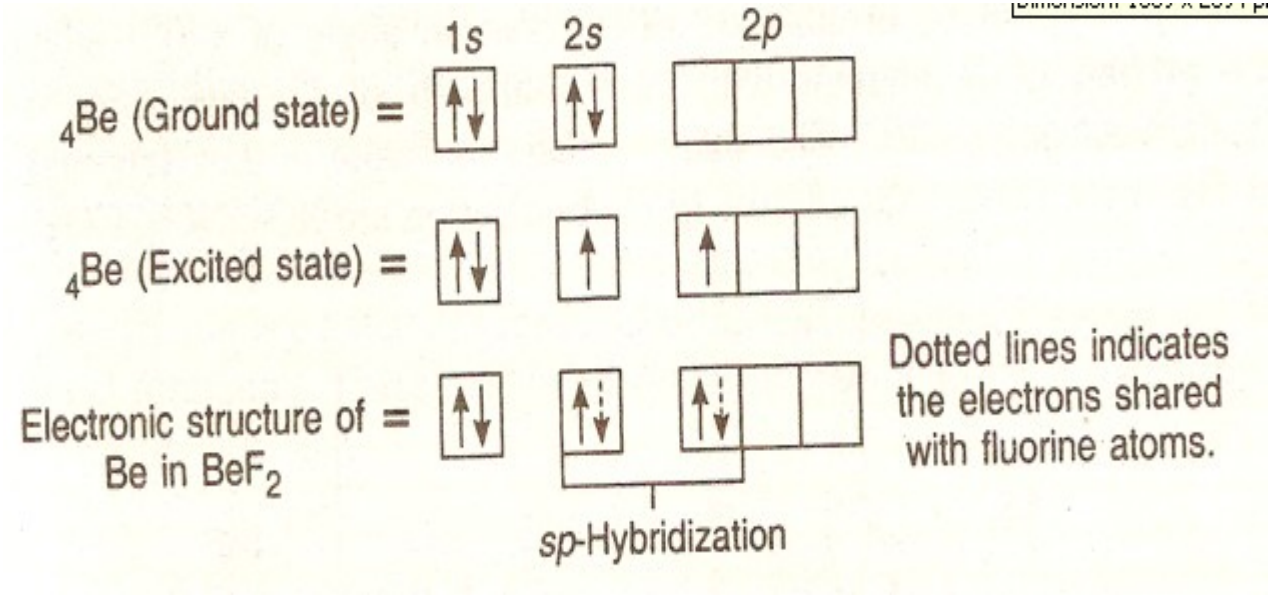

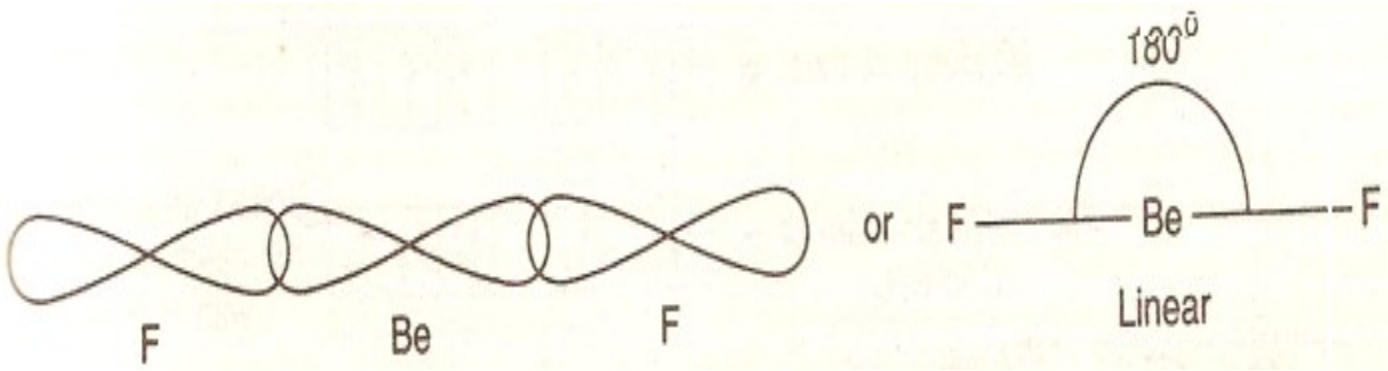

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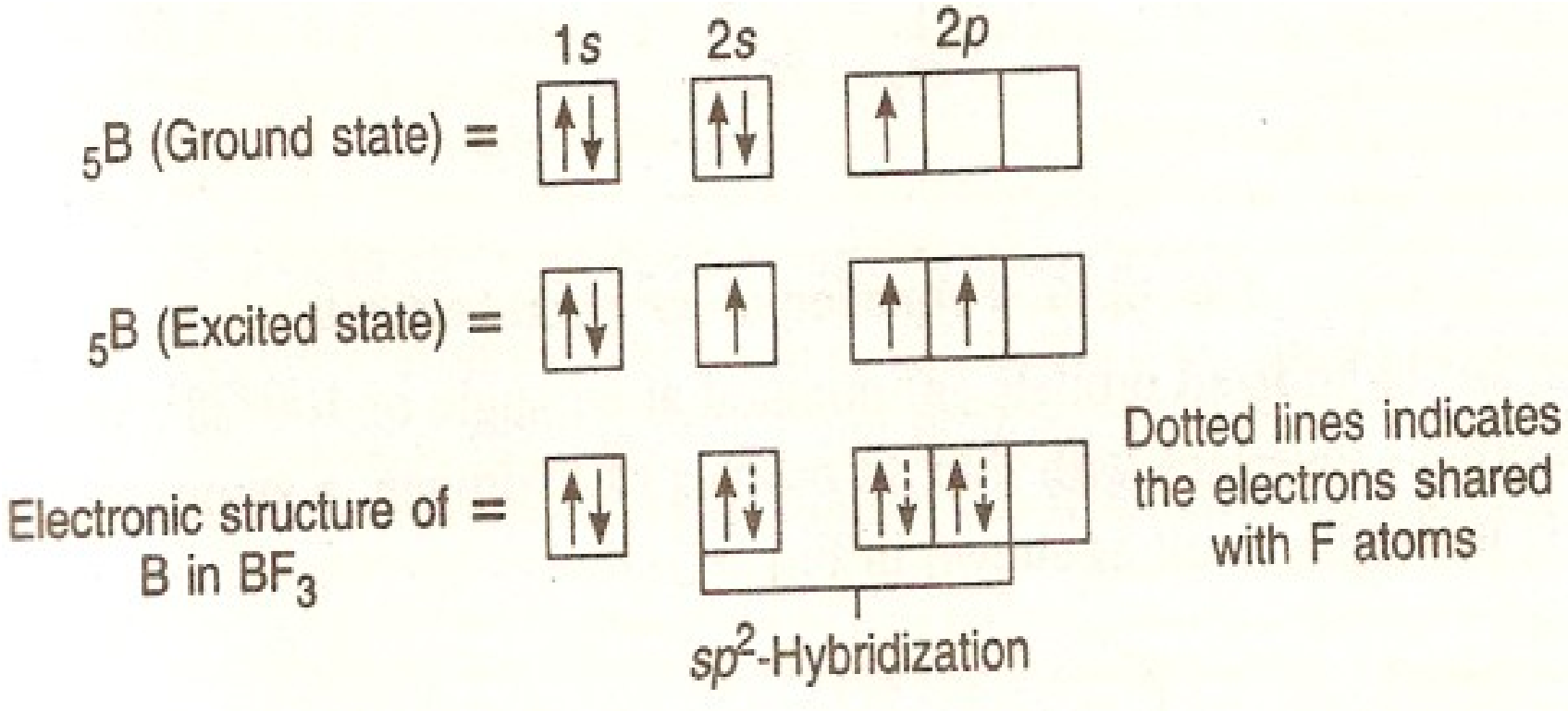

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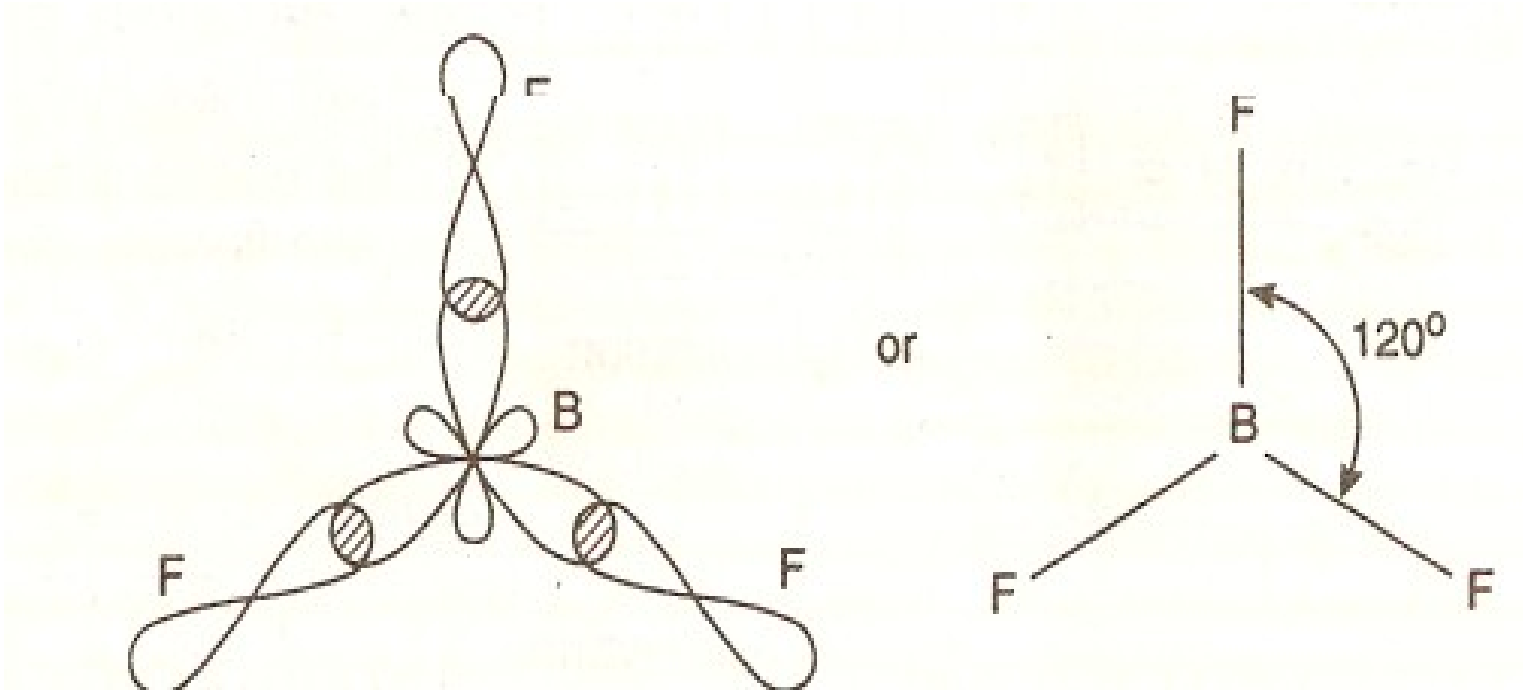

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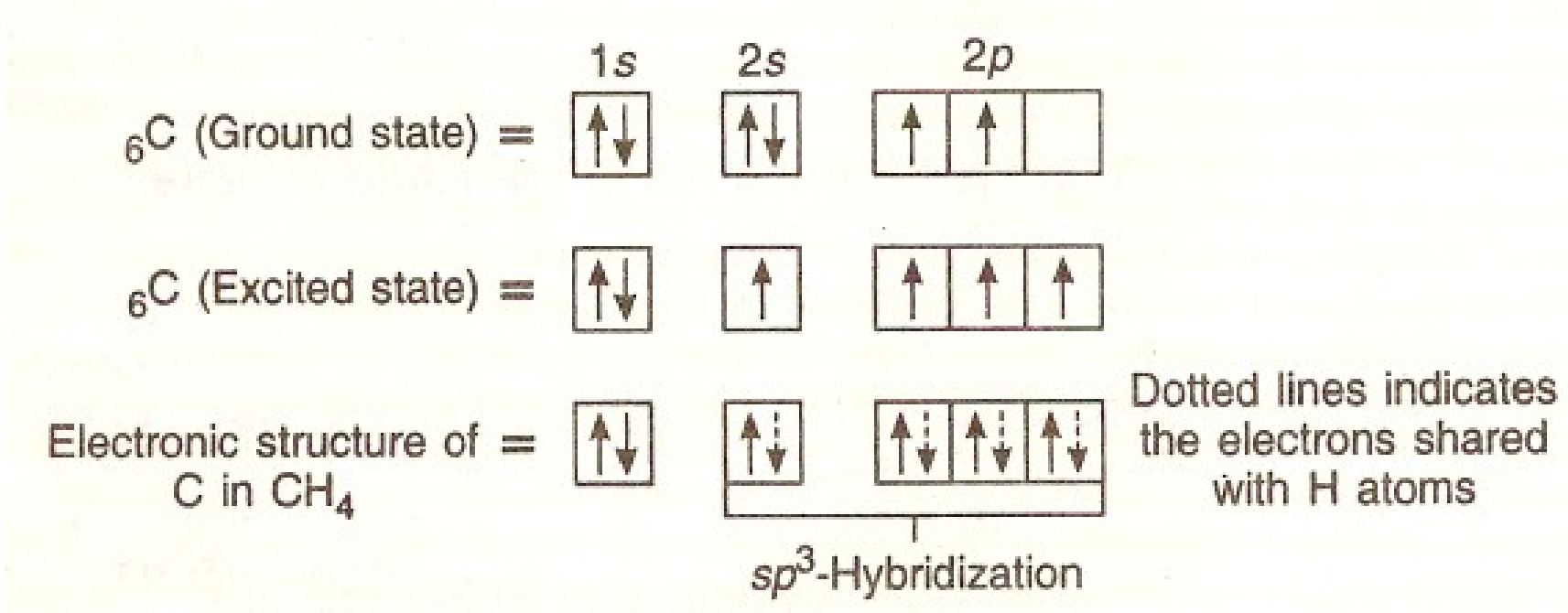

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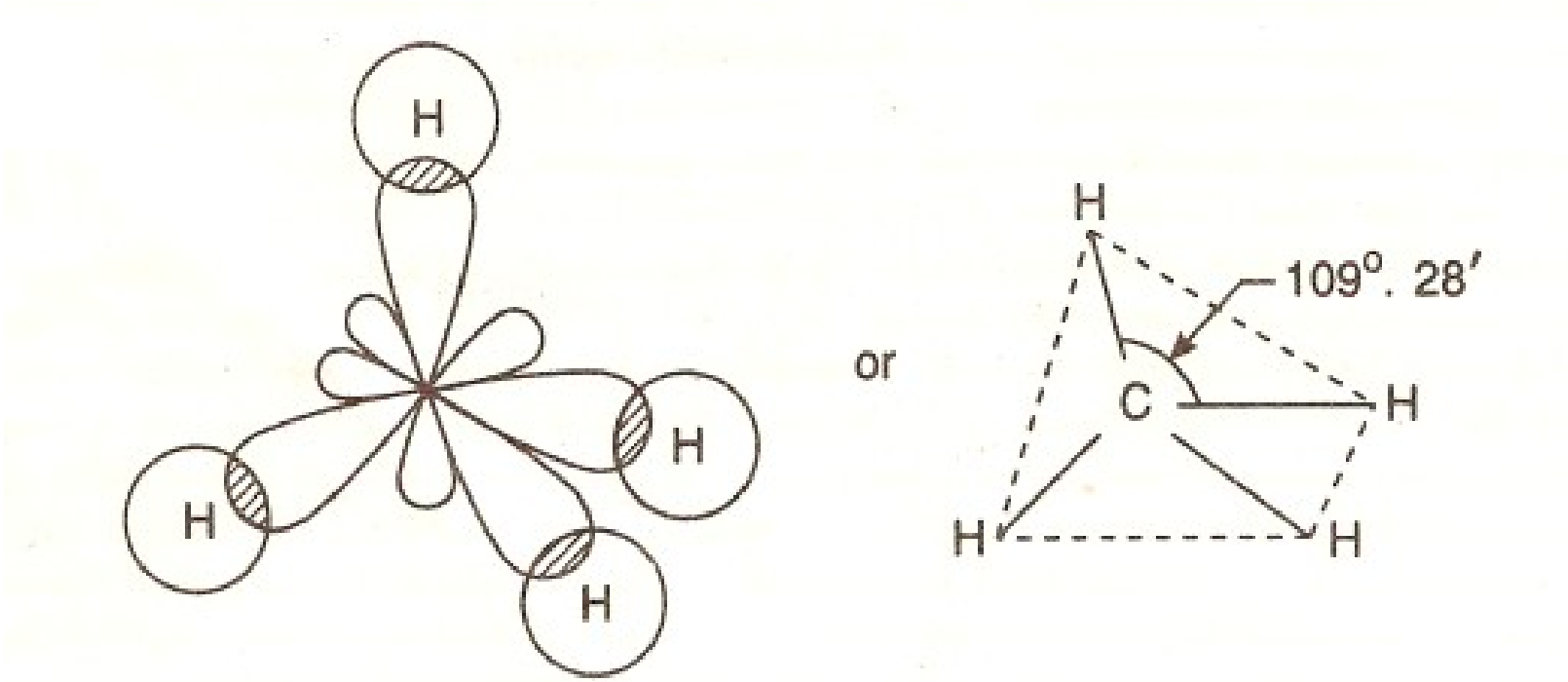

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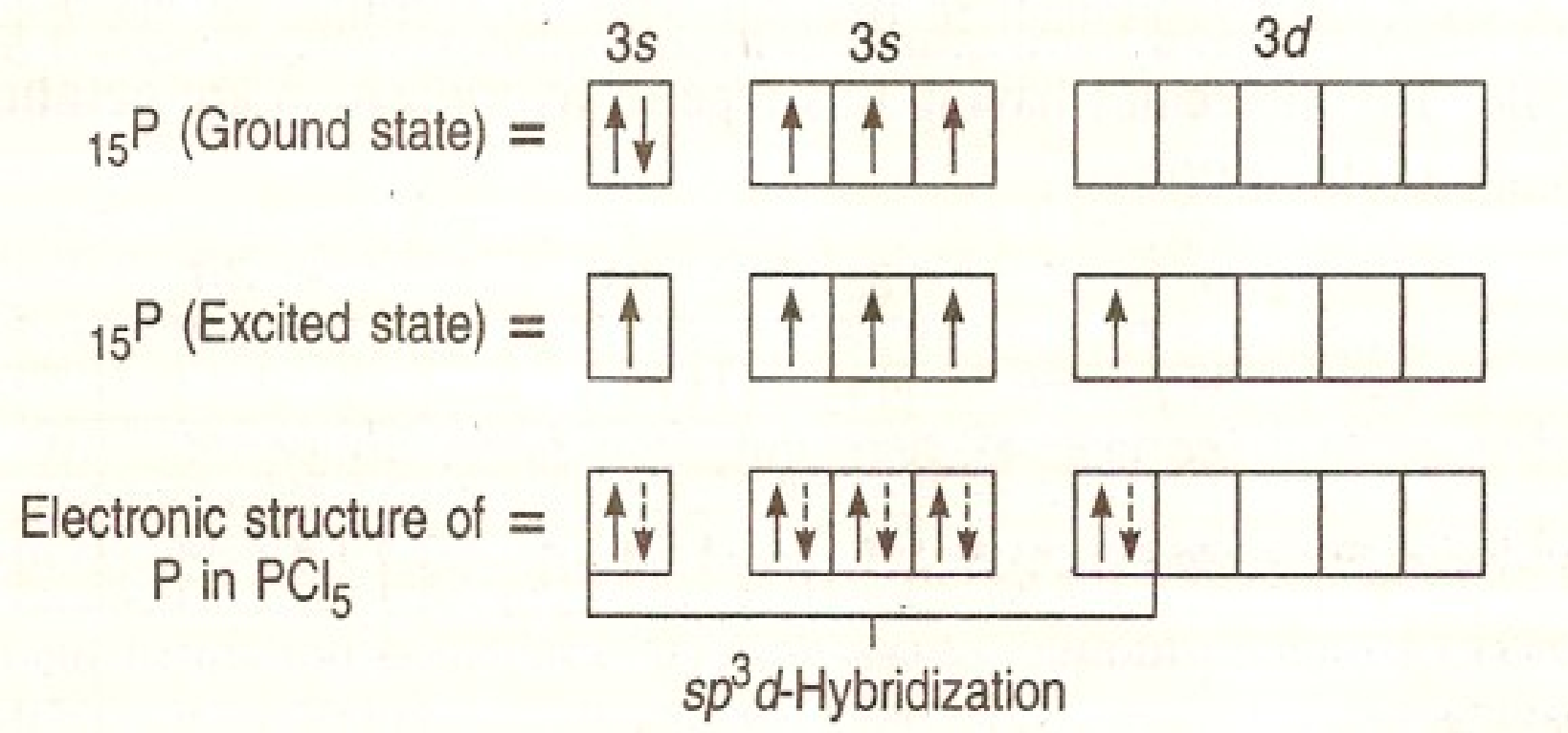

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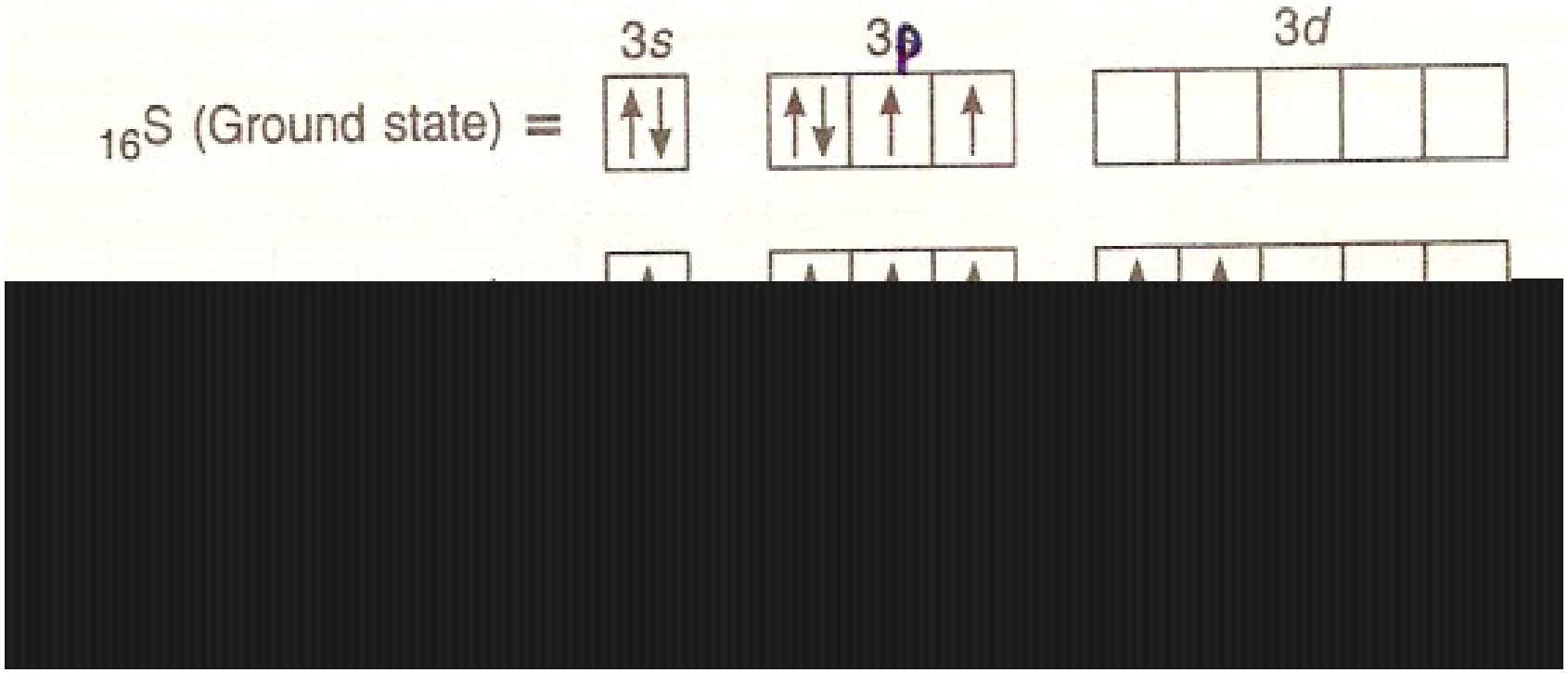

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