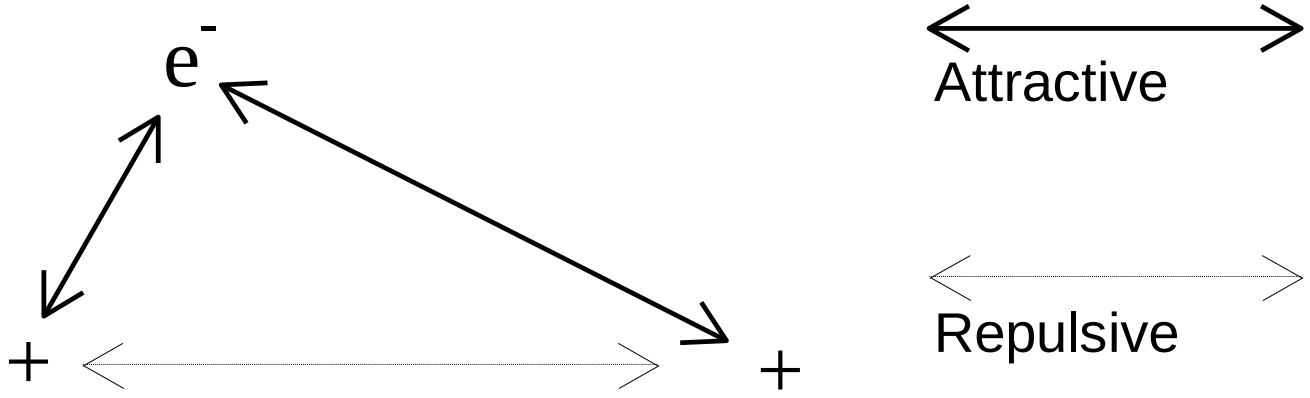
Chemistry 3830

Molecular Orbital Theory

Molecular Orbitals of H_2^+

One electron system:



Born-Oppenheimer approximation:

- Electrons are lighter and much (!) faster moving than nuclei.
- Electrons equilibrate fast when nuclei move.
- Nuclei are considered with a fixed distance from each other

Practically: a one-particle system.

Schrödinger's equation can be solved.

Approximate MO Theory

Linear Combination of Atomic Orbitals (LCAO) Method

$$\Psi = c_1\varphi_1 + c_2\varphi_2 + c_3\varphi_3 + \cdots . = \sum_{i=1}^{n} c_i\varphi_i$$

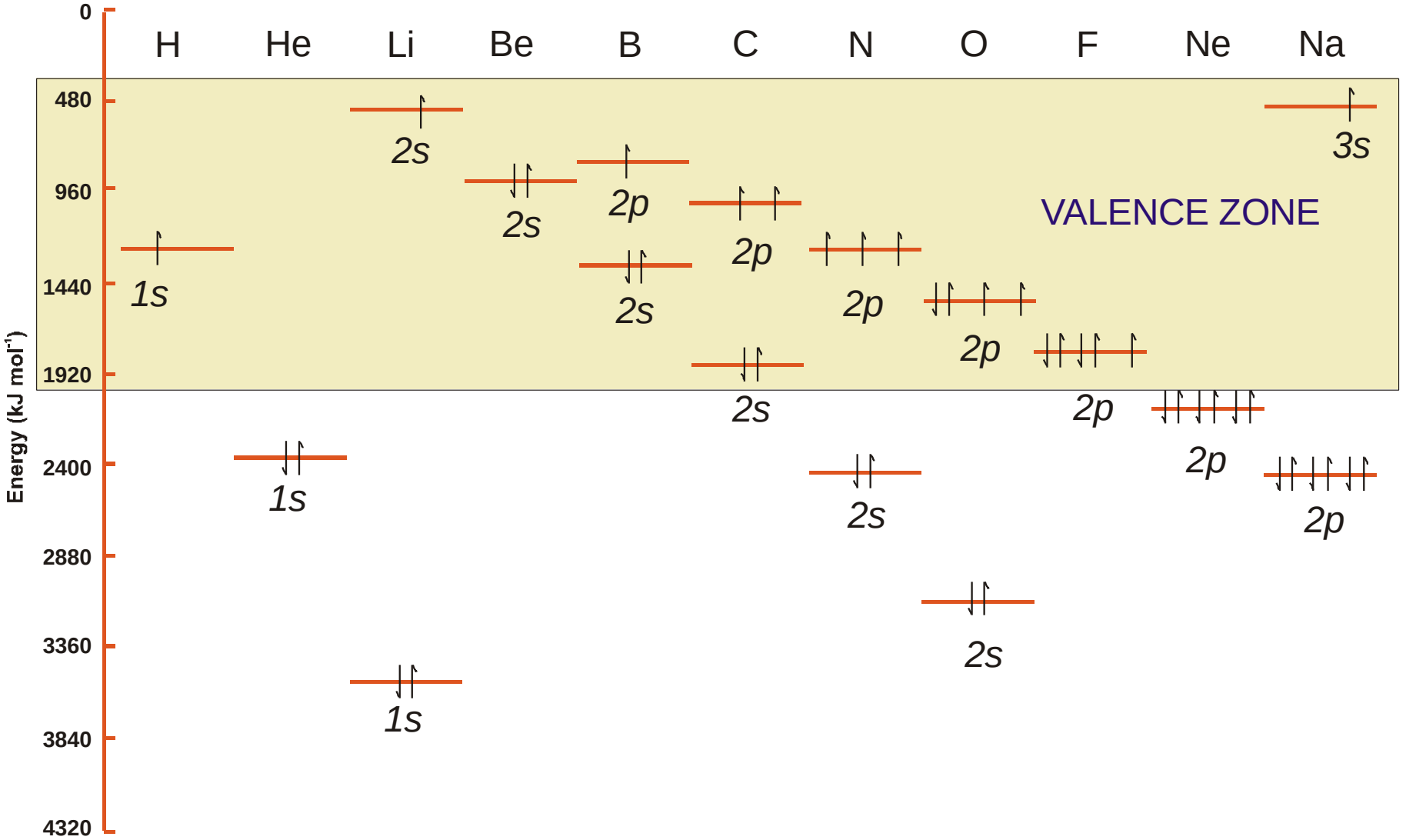
1. Symmetry:
    - Only AOs of the same/correct symmetry (symmetry species) can interact.

2. Relative Energies
    - Only AOs of similar energies will interact.

3. Spatial Extension/Overlap
    - AOs must overlap in order to interact.

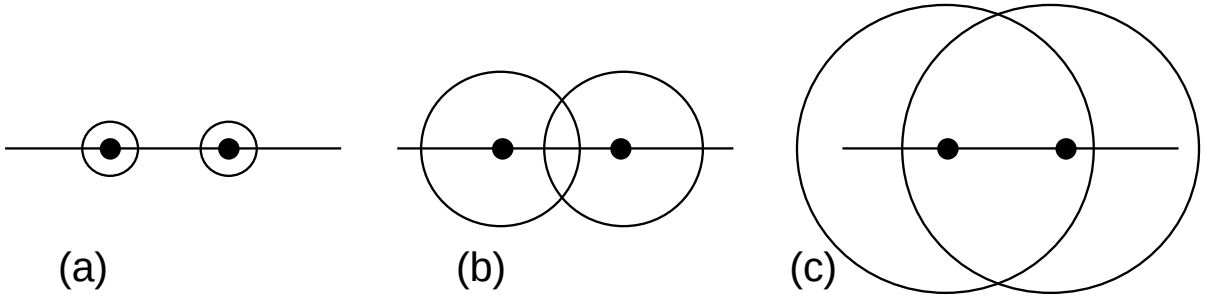
Valence AOs

- Valence AOs have the right property to interact to form MOs.



Overlap

- Core orbitals are too small to effectively overlap with each other.

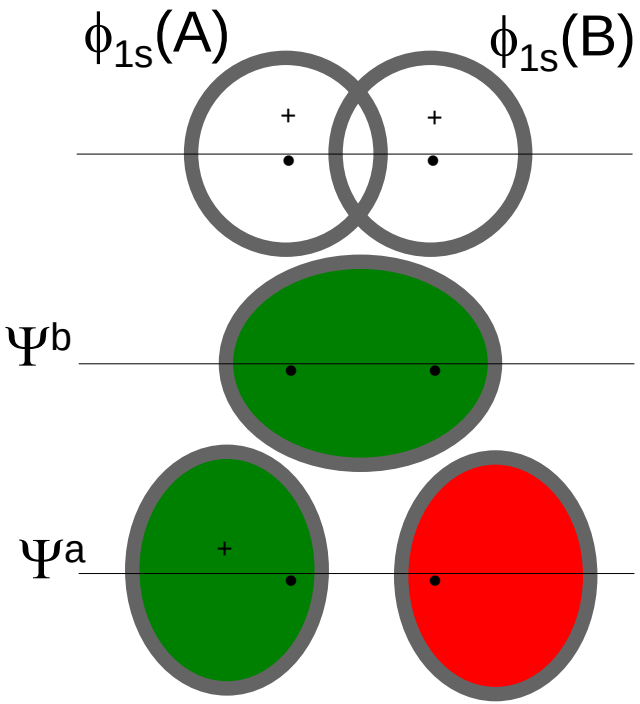


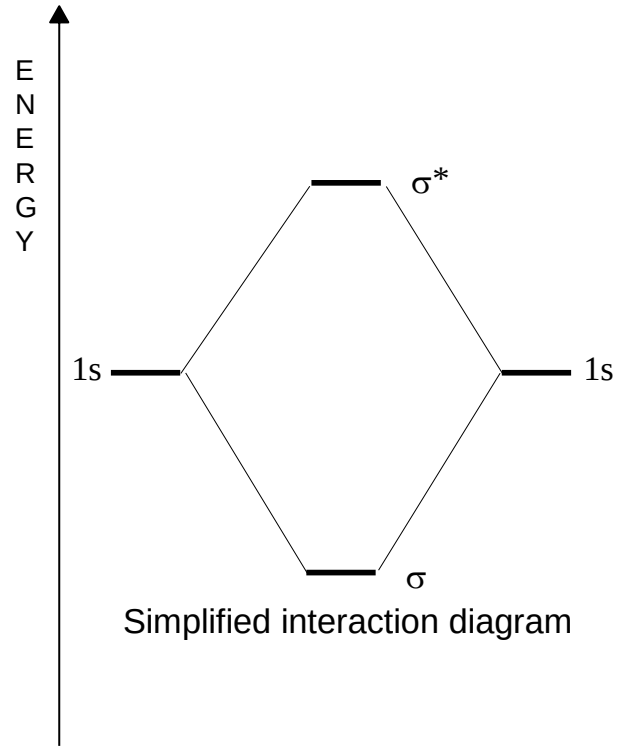
- Valence orbitals have the right size to effectively overlap with each other.

σ symmetric overlap:

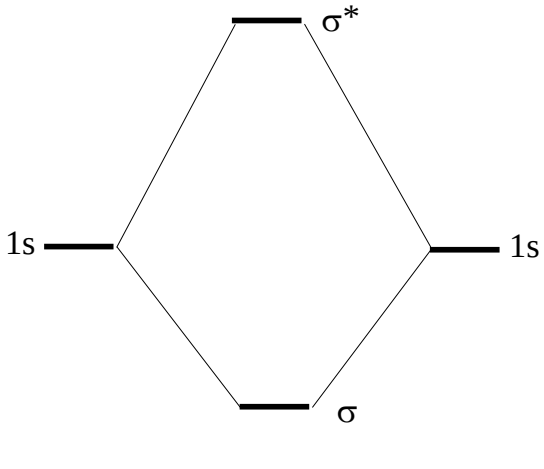
π symmetric overlap:

1st Row Diatomics



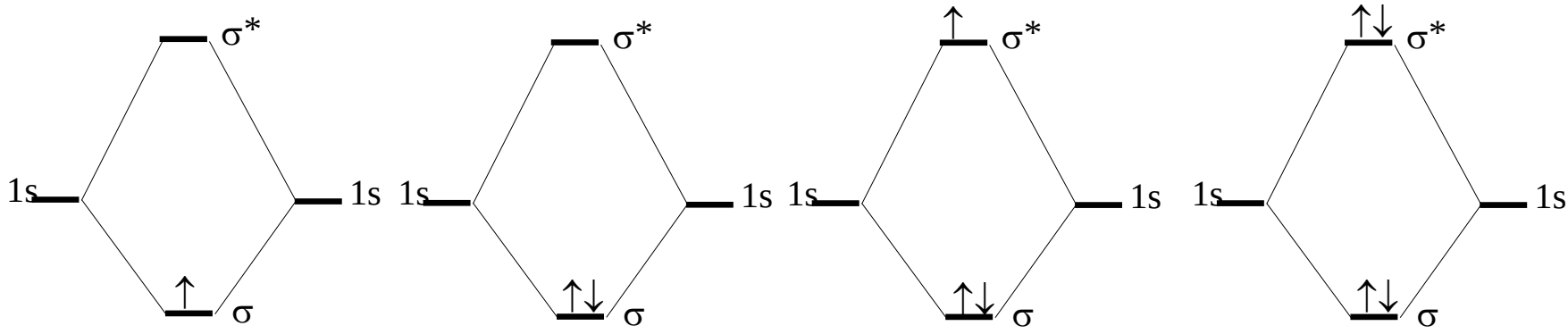


Simplified interaction diagram



Correct interaction diagram

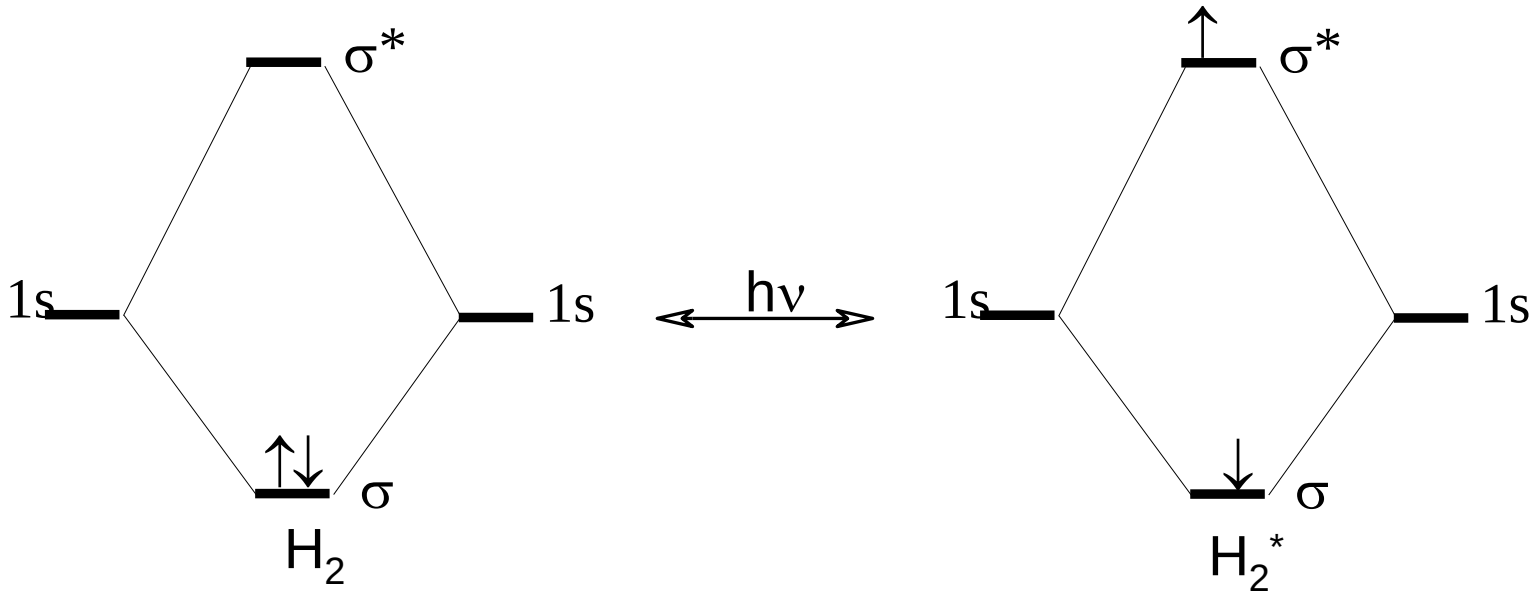
1st Row Diatomics

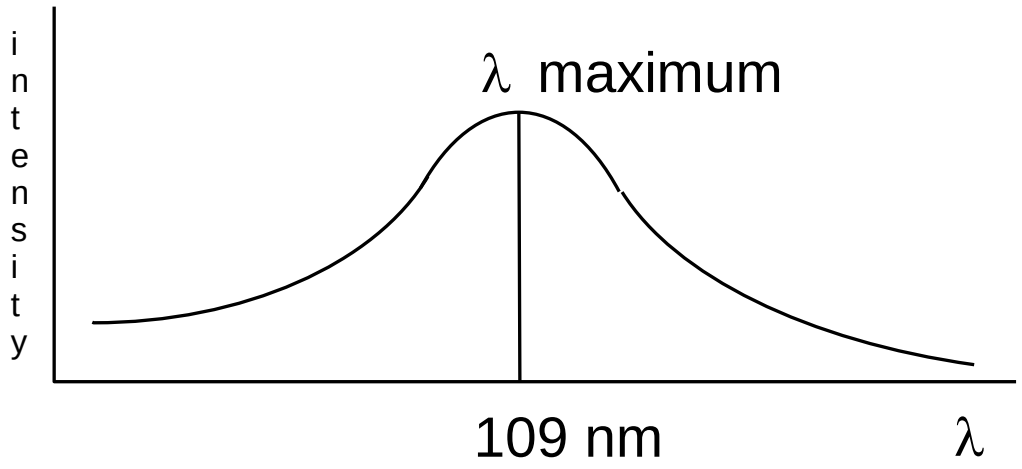


	H_2^+	H_2	He_2^+	He_2
B.D.E.	272 kJ mol^{-1}	452 kJ mol^{-1}	301 kJ mol^{-1}	0 kJ mol^{-1}
r_0	106 pm	76 pm		
Configuration	$(s)^1$	$(\sigma)^2$	$(\sigma)^2(\sigma^*)^1$	$(\sigma)^2(\sigma^*)^2$
Bond Order	0.5	1	0.5	0

bond order = ½ [# of electrons in bonding MO's – # of electrons in anti-bonding MO's]

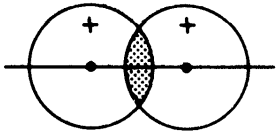
UV/Vis Spectroscopy



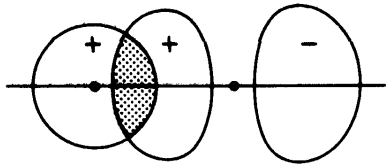


σ MOs

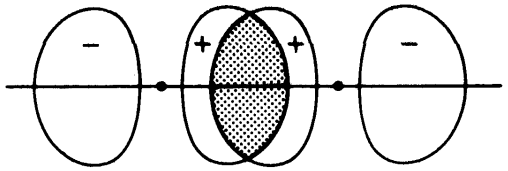
σ Bonds



s *s*

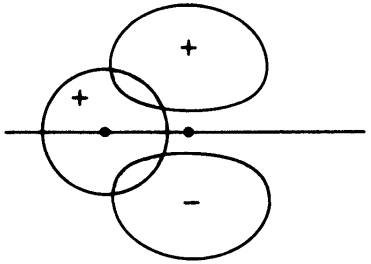


s p_z

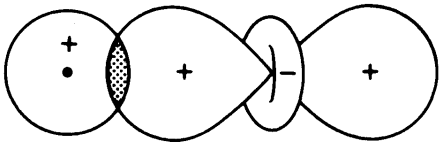


p_z p_z

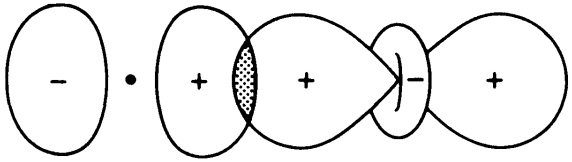
but not



s p_y or p_x



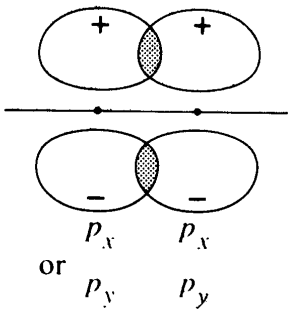
s d_z2



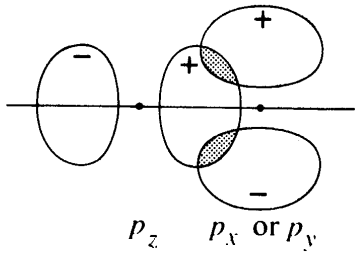
p_z d_z2

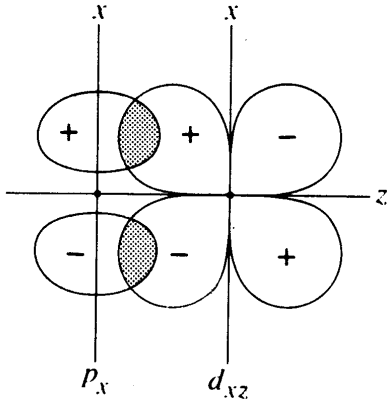
π and δ MOs

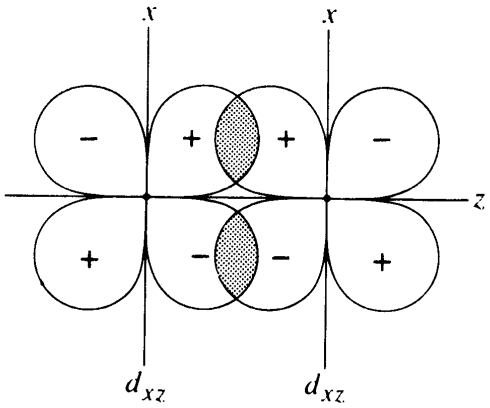
π Bonds



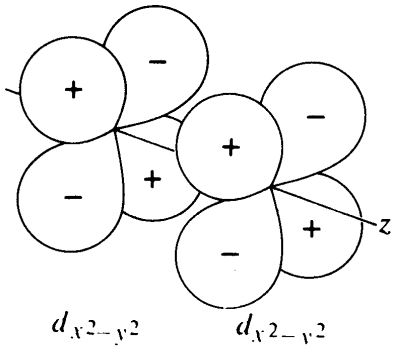
but not

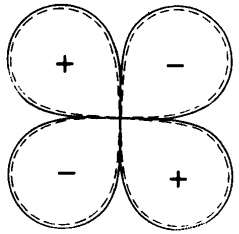






δ Bonds





looking down z axis, one atom behind the other

$d_{x^2-y^2}$ orbitals

(dotted line for more distant orbital)