Applied Statistical Mechanics
Lecture Note - 4

Quantum Mechanics – Molecular Structure

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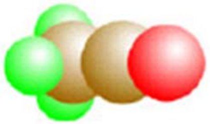


Subjects

- Structure of Complex Atoms - Continued
- Molecular Structure

Structure of Complex Atoms
- Continued

The Spectra of Complex Atoms

- The spectra of atoms rapidly become very complicated as the number of electrons increases.
- Spectra of an atom : The atom undergoes transition with a change of energy; ΔE = hν
    - Gives information about the energies of electron
    - However, the actual energy levels are not given solely by the energies of orbitals
    - Electron-Electron interactions

Measuring Ionization Energy (H atoms)

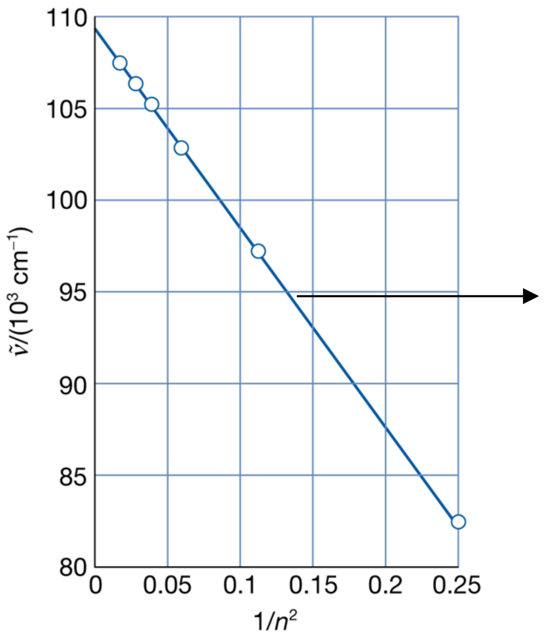
- The plot of wave numbers vs. $1/n^2$ gives the ionization energy for hydrogen atoms

$$\Delta E = E - E_{lower} = h\nu$$

$$\bar{\nu} = \frac{\nu}{c} = -\frac{R_H}{n^2} - \frac{E_{lower}}{hc}$$

$$I = E_{lower}$$

$$\bar{\nu} = \frac{I}{hc} - \frac{R_H}{n^2}$$



Slope = I

Quantum defects and ionization energies

- Energy levels of many-electron atoms do not vary as $1/n^2$
- The outermost electron
    - ☐ Experience slightly more charge than 1e
    - ☐ Other Z-1 atoms cancel the charge slightly lower than 1
    - ☐ Quantum Defect (δ): empirical quantity

$$E = -\frac{hcR_H}{n^2}$$

$$E = -\frac{hcR}{(n-\delta)^2}$$

$$\bar{\nu} = \frac{I}{hc} - \frac{R}{n^2} \longrightarrow$$

Rydberg state

Pauli exclusion principle and the spins

- Palui exclusion principle
  - “ No more than two electrons may occupy any given orbital and, if two occupy one orbital, then their spin must be paired “
  - “ When label of any two identical fermions are exchanged, the total wavefunction changes sign. When the label of any two identical bosons are exchanged, the total wavefunction retain its sign “

Pauli exclusion principle and the spins

- Two electrons (fermions) occupy an orbital Ψ then ;

$$\Psi(1,2) = -\Psi(2,1)$$

- Total Wave function = (orbital wave function)*(spin wave function)

$$\psi(1)\psi(2)$$

four possibility

$$\alpha(1)\alpha(2) \qquad \boxed{\alpha(1)\beta(2) \quad \alpha(2)\beta(1)} \qquad \beta(1)\beta(2)$$

We cannot tell which one is α and β

$$\sigma_+(1,2) = (1/2^{1/2})\{\alpha(1)\beta(2) + \beta(1)\alpha(2)\}$$

$$\sigma_-(1,2) = (1/2^{1/2})\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}$$

Normalized Linear Combination of two spin wave functions

$$\psi(1)\psi(2)\alpha(1)\alpha(2)$$

$$\psi(1)\psi(2)\sigma_+(1,2)$$

$$\psi(1)\psi(2)\sigma_-(1,2)$$

$$\psi(1)\psi(2)\beta(1)\beta(2)$$

Pauli exclusion principle and the spins

Requirement : $\Psi(1,2) = -\Psi(2,1)$

$$\begin{aligned}
&\psi(1)\psi(2)\alpha(1)\alpha(2) && \Psi(1,2) = \Psi(2,1) \\
&\psi(1)\psi(2)\sigma_{+}(1,2) && \Psi(1,2) = \Psi(2,1) \\
&\psi(1)\psi(2)\sigma_{-}(1,2) \quad \longrightarrow && \Psi(1,2) = -\Psi(2,1) \\
&\psi(1)\psi(2)\beta(1)\beta(2) && \Psi(1,2) = \Psi(2,1)
\end{aligned}$$

$$\sigma_{+}(1,2) = (1/2^{1/2})\{\alpha(1)\beta(2) + \beta(1)\alpha(2)\} = \sigma_{+}(2,1)$$

$$\sigma_{-}(1,2) = (1/2^{1/2})\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\} = -\sigma_{-}(2,1)$$

$\boxed{\psi(1)\psi(2)\sigma_{-}(1,2)}$ → **Only one acceptable**

Singlet and Triplet State

- Excited State of He atom
  - $1s^2 \rightarrow 1s^1\ 2s^1$
  - The two electrons need not to be paired
  - Singlet : paired spin arrangement ↑↓

    $$\sigma_-(1,2) = (1/2^{1/2})\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}$$

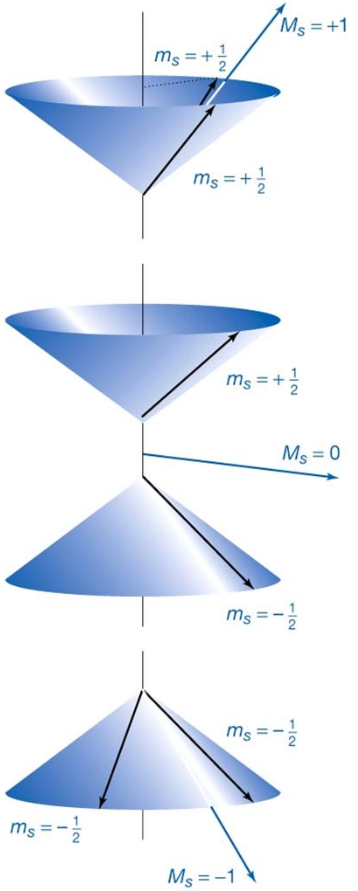
  - Triplet : parallel spin arrangement ↑↑

    $$\alpha(1)\alpha(2)$$

    $$\sigma_+(1,2) = (1/2^{1/2})\{\alpha(1)\beta(2) + \beta(1)\alpha(2)\}$$

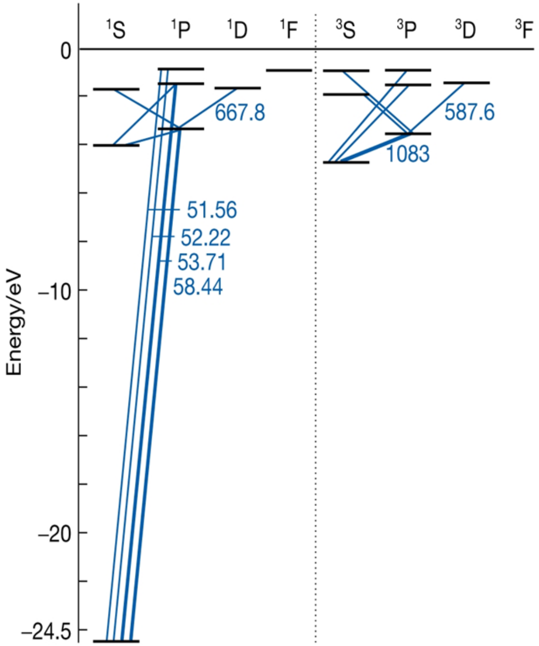
    $$\beta(1)\beta(2)$$

  - Hund’s principle : *triplet states generally lie lower than triplet state*



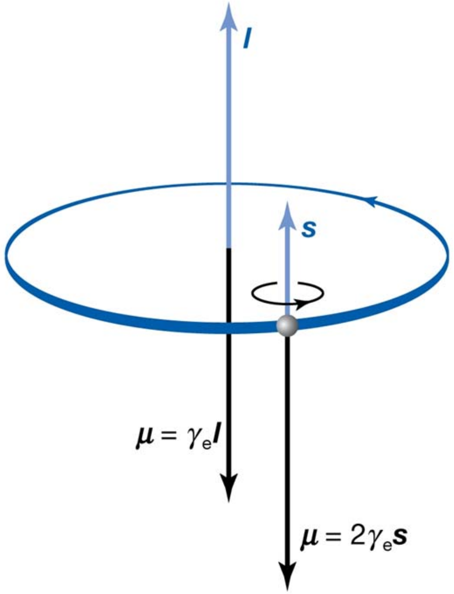
Spectrum of atomic Helium

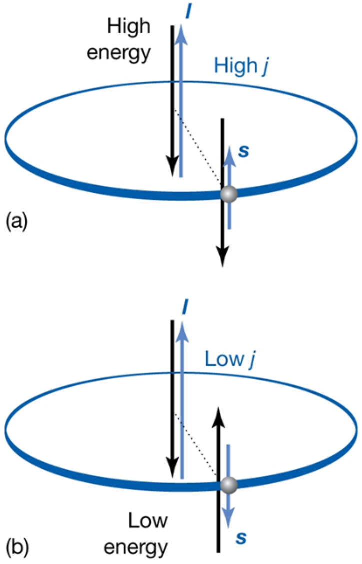
- Spectrum of He atom is more complicated than H atom
  - Only one electron is excited
    - Excitation of two electrons require more energy than ionization energy
  - No transitions take place between singlet and triplet states
    - Behave like two species



Spin-Orbit Coupling

- Electron spins has a further implication for energies of atoms when *l > 0* (finite orbital angular momentum)
- (spin magnetic momentum) + (magnetic moment doe to orbital angular momentum) → spin-orbit coupling





Parallel → high angular momentum

$$j = l + \frac{1}{2}$$

Opposed → low angular momentum

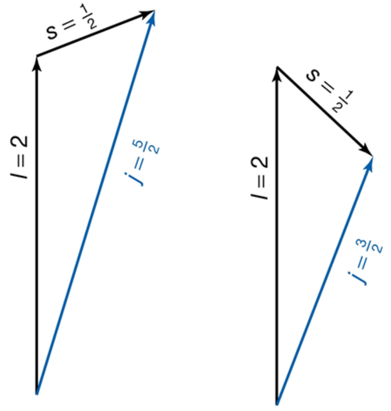
$$j = l - \frac{1}{2}$$

Spin-orbit coupling

- When *l=2*

$$j = l + \frac{1}{2} = \frac{5}{2}$$

$$j = l - \frac{1}{2} = \frac{3}{2}$$

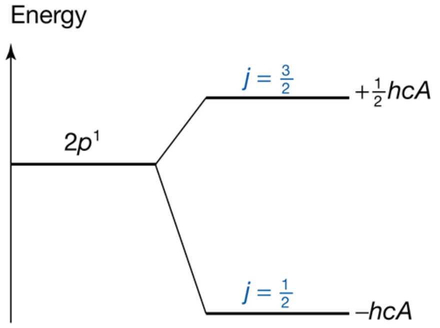


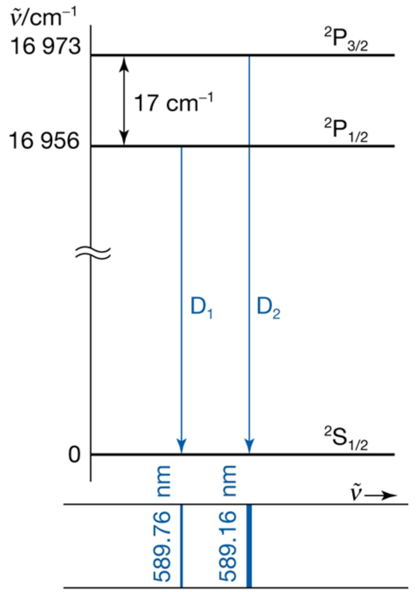
- Spin-Orbit Coupling constant (*A*)
  - ☐ Dependence of spin-orbit interaction on the value of j

$$E_{l,j,s} = \frac{1}{2} hcA(j(j+1) - l(l+1) - s(s+1))$$

Spin-Orbit Coupling

- Spin-orbit coupling depends on the nuclear charge
  - The greater the nucleus charge → the stronger spin-orbit coupling
  - Very small in H , very large in Pb
- Fine structure
  - Two spectral lines are observed
  - The structure in a spectrum due to spin-orbit coupling
  - Ex) Na (street light)





Term symbols and selection rules

- Skip…

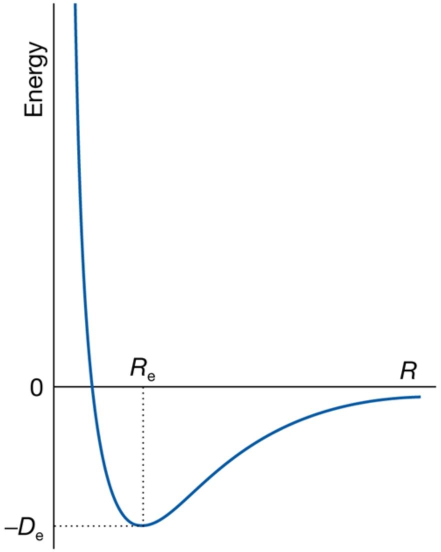
Molecular Structure

Topics

- Valence-Bond Theory
- Molecular Orbital Theory

Born-Oppenheimer approximation

- Assumption
  - The nuclei is fixed at arbitrary location
  - H2 molecule
    - Nuclei move about 1 pm
    - Electrons move about 1000 pm
- Use
  - different separation
  - → solve Schrodinger equation
  - → Energy of molecules vary with bond length
  - Equilibrium bond length (***R**$_e$*)
  - Bond Dissociation energy (***D**$_e$*)



→ **Structure Prediction, Property Estimation**

Valence-Bond Theory

- Consider H_2 molecule
  - If electron 1 is on atom A and electron 2 is on atom B

$$\psi = \psi_{H1S_A}(r_1)\psi_{H1S_A}(r_1)$$

↓ Simple notation

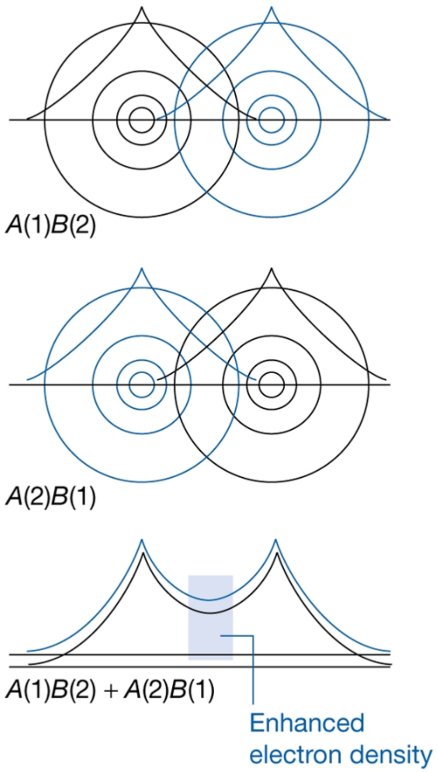
$$\psi = A(1)B(2) \qquad \psi = A(2)B(1)$$

↓ Linear combination of wave functions

$$\psi = A(1)B(2) \pm A(2)B(1)$$

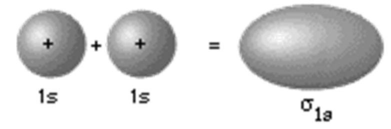
↓ Lower energy

$$\psi = A(1)B(2) + A(2)B(1)$$

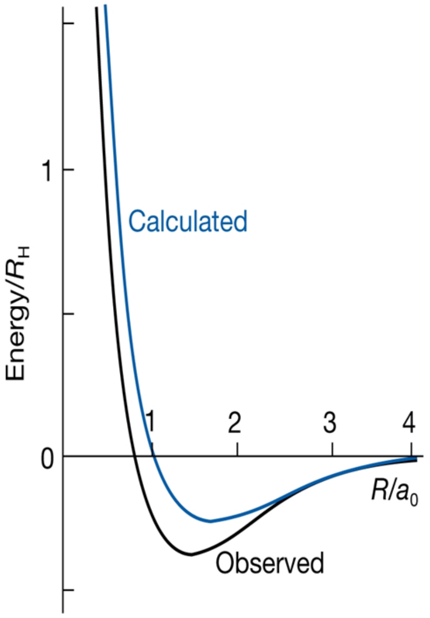


σ - bond

- *Cylindrical symmetry* around internuclear axis
- Rambles s-orbital : called sigma-bond
- Zero angular momentum around internuclear axis



- Molecular potential energy
- Spin : spin paring
  - According to Pauli principle spin must be paired



π-bond

- Essence of valence-bond theory
  - ☐ Pairing of the electrons
  - ☐ Accumulation of electron density in the internulear region
- N2 atom $2s_2 2p_x^1 2p_y^1 2p_z^1$

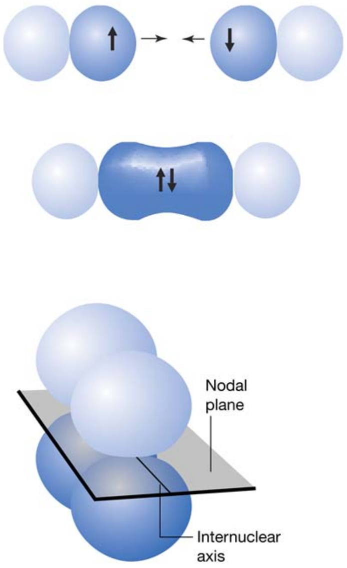
$p_z^1 \longrightarrow$ **σ–bond**

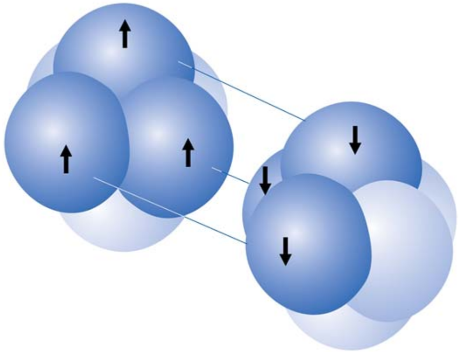
$p_x^1 \longrightarrow$

$p_y^1 \longrightarrow$

Cannot form σ-bond
not symmetrical
around internuclear axis

$\longrightarrow$ **π–bond**

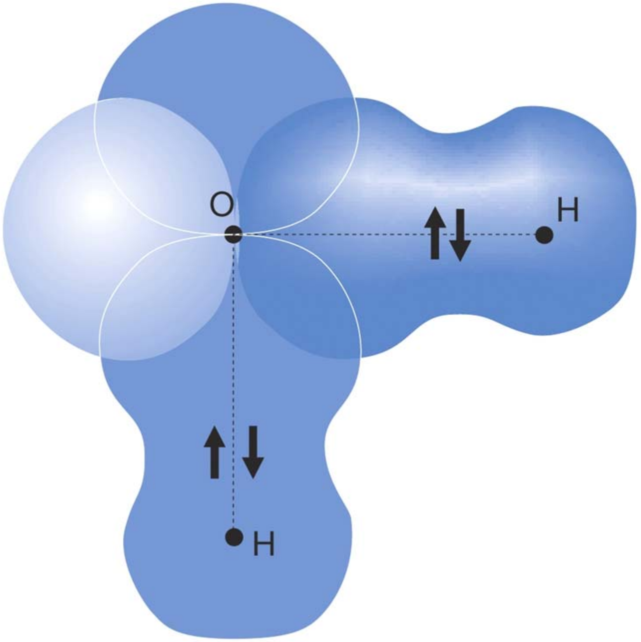




Water molecule

$2s_2 2p_x^2 2p_y^1 2p_z^1$ **Two σ–bonds**

Bond angle : 90 degree
→ Experimental 104.5 degree !

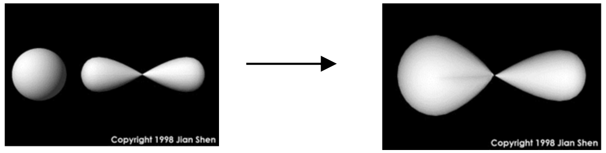


Promotion

- CH_4 molecule $2s_2 2p_x^1 2p_y^1$
  - cannot be explained by valence-bond theory
  - only two electrons can form bonds
- Promotion
  - Excitation of electrons to higher energy
  - If bonds are formed (lower energy) , excitation is worthwhile
  - 4 σ-bonds $2s_1 2p_x^1 2p_y^1 2p_z^1$

Hybridization

- Description of methane is still incomplete
  - Three s-bond (H1s – C2p)
    + one s-bond (H1s – C2s)
  - Cannot explain symmetrical feature of methane molecules
- Hybrid orbital
  - Interference between C2s + C2p orbital
  - Forming sp^3 hybrid orbital

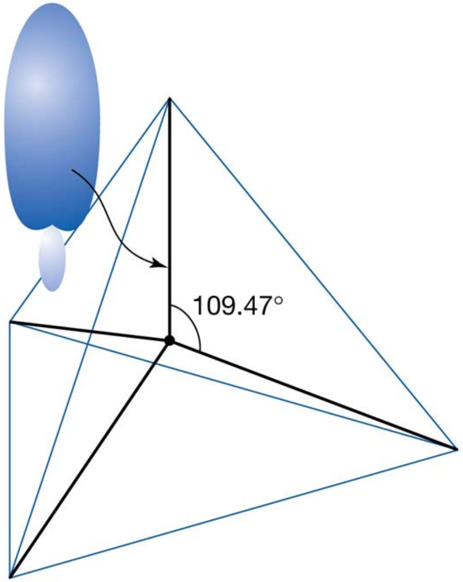


$$h_1 = s + p_x + p_y + p_z$$

$$h_2 = s - p_x - p_y + p_z$$

$$h_3 = s - p_x + p_y - p_z$$

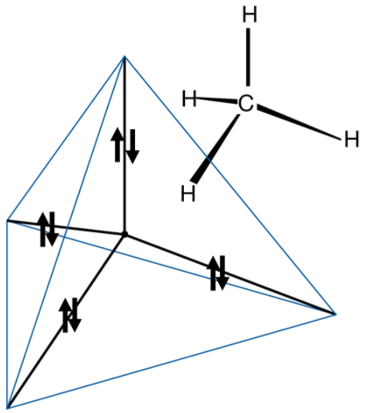
$$h_4 = s + p_x - p_y - p_z$$

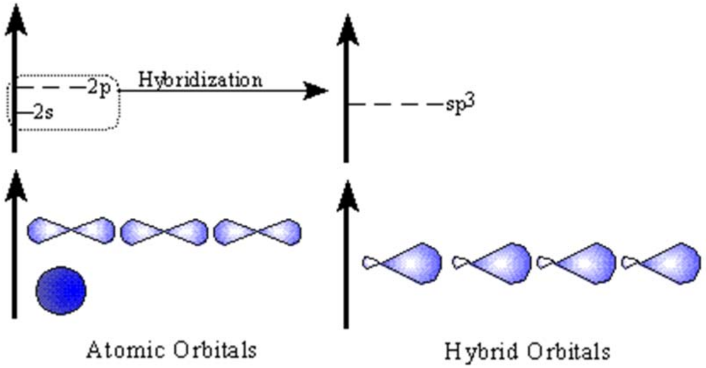


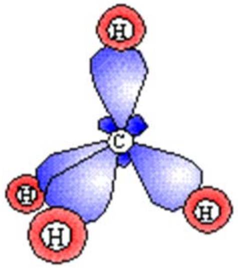
Hybridization

- Formation of σ-bond in methane

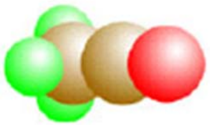
$$\psi = h_1(1)A(2) + h_1(2)A(1)$$







sp^2 hybridization : ethylene



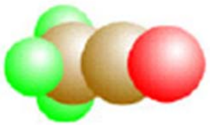
- sp^2 hybridization

$$h_1 = s + 2^{1/2} p_x$$

$$h_2 = s + (\frac{3}{2})^{1/2} p_x - (\frac{3}{2})^{1/2} p_y$$

$$h_3 = s - (\frac{3}{2})^{1/2} p_x - (\frac{3}{2})^{1/2} p_y$$

sp hybridization : acetylene

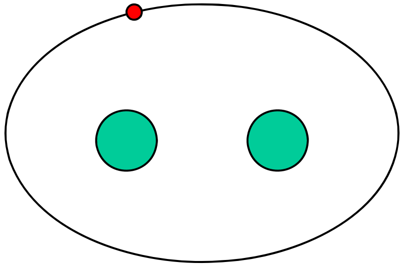


- sp hybridization

$$h_1 = s + p_z$$
$$h_2 = s - p_z$$

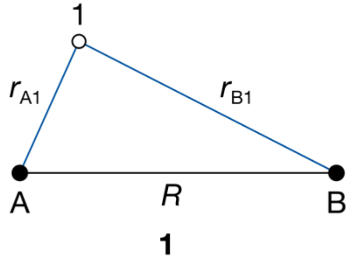
Molecular Orbital Theory

- Molecular Orbital (MO) Theory
  - Electrons should be treated as spreading throughout the entire molecule
  - The theory has been fully developed than VB theory
- Approach :
  - Simplest molecule (H_2^+ ion) → complex molecules



The hydrogen molecule-ion

- Hamiltonian of single electron in H_2^+



$$H = -\frac{\hbar}{2m_e}\nabla_1^2 + V \qquad V = -\frac{e^2}{4\pi\varepsilon_0}\left(\boxed{\frac{1}{r_{A1}} + \frac{1}{r_{B1}}}\boxed{-\frac{1}{R}}\right)$$

Attractions between electron and nuclei **Repulsion between the nuclei**

- Solution : one-electron wavefunction

  ➔ Molecular Orbital (MO)

- The solution is very complicated function
- This solution cannot be extended to polyatomic molecules

Linear Combination of Atomic Orbitals (LCAO-MO)

- If an electron can be found in an atomic orbital belonging to atom A and also in an atomic orbital belonging to atom b, then overall wavefuntion is superposition of two atomic orbital :

$$\psi_{\pm} = N(A \pm B) \longrightarrow$$

Linear Combination of Atomic Orbitals (LCO-MO)

$$A = \psi_{H1S_A} = \frac{e^{-r_A/a_0}}{\left(\pi a_0^3\right)^{1/2}}$$

$$B = \psi_{H1S_B} = \frac{e^{-r_B/a_0}}{\left(\pi a_0^3\right)^{1/2}}$$

- N : Normalization factor
- Called a **σ-orbital**

Normalization

$$\psi_{\pm} = N(A \pm B)$$

$$A = \psi_{H1S_A} = \frac{e^{-r_A/a_0}}{\left(\pi a_0^3\right)^{1/2}}$$

$$B = \psi_{H1S_B} = \frac{e^{-r_B/a_0}}{\left(\pi a_0^3\right)^{1/2}}$$

ψ_+

$$\int \psi^* \psi d\tau = 1$$

$$\int \psi^* \psi d\tau = N^2 \left\{ \int A^2 d\tau + \int B^2 d\tau + 2\int ABd\tau \right\} = N^2(1+1+2S)$$

$$S = \int ABd\tau \approx 0.59$$

$$N = 0.56$$

ψ_-

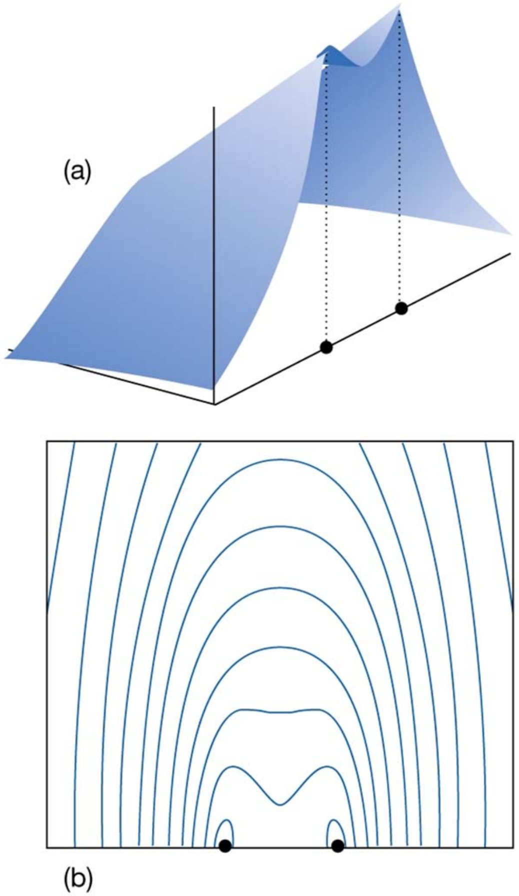
$$\int \psi^* \psi d\tau = 1$$

$$\int \psi^* \psi d\tau = N^2 \left\{ \int A^2 d\tau + \int B^2 d\tau - 2\int ABd\tau \right\} = N^2(1+1-2S)$$

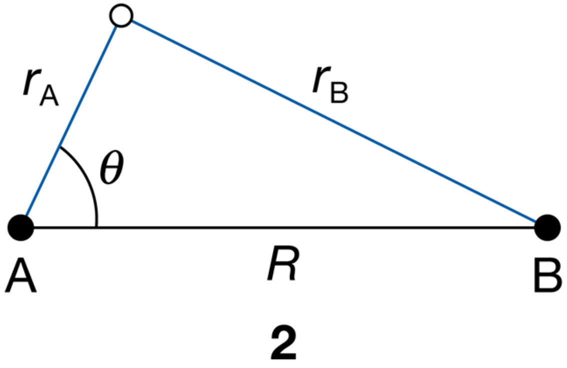
$$S = \int ABd\tau \approx 0.59$$

$$N = 1.10$$

LCAO-MO



Amplitude of the bonding orbital in hydrogen molecule-ion



r $_A$ **and** ***r*** $_B$ **are not independent**

$$r_B = \left\{ r_A^2 + R^2 - 2r_A R\cos\theta \right\}^{1/2}$$

Bonding Orbital

$$\psi_+^2 = N^2(\boxed{A^2} + \boxed{B^2} + \boxed{2AB})$$

An extra contribution to the density (Overlap density)

Probability density if the electron were confined to the atomic orbital B

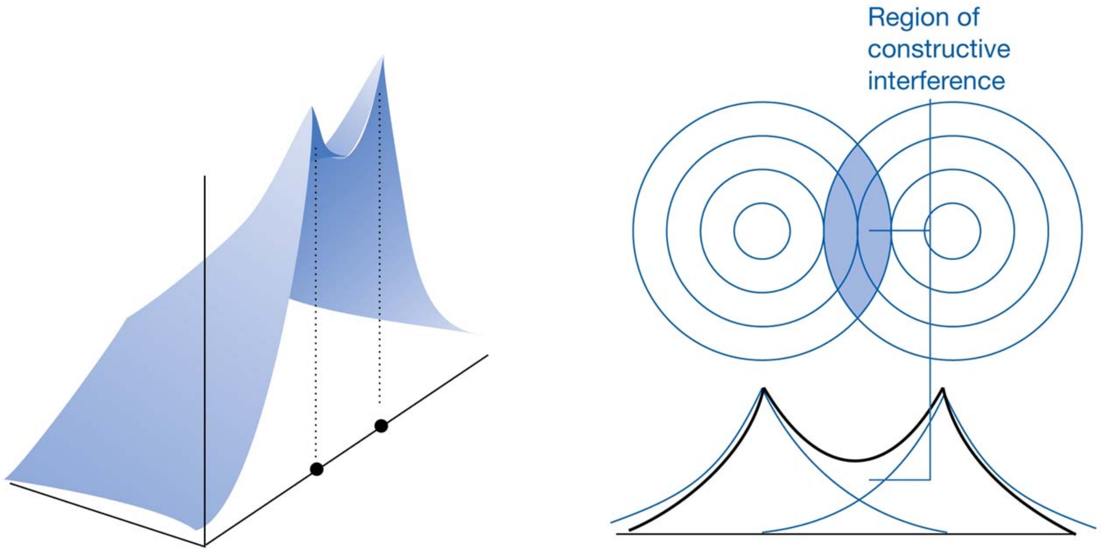
Probability density if the electron were confined to the atomic orbital A

- Overlap density → Crucial term
- Electrons accumulates in the region where atomic orbital overlap and interfere ***constructively***.

Bonding Orbital

- The accumulation of electron density between the nuclei put the electron in a position where it interacts strongly with both nuclei

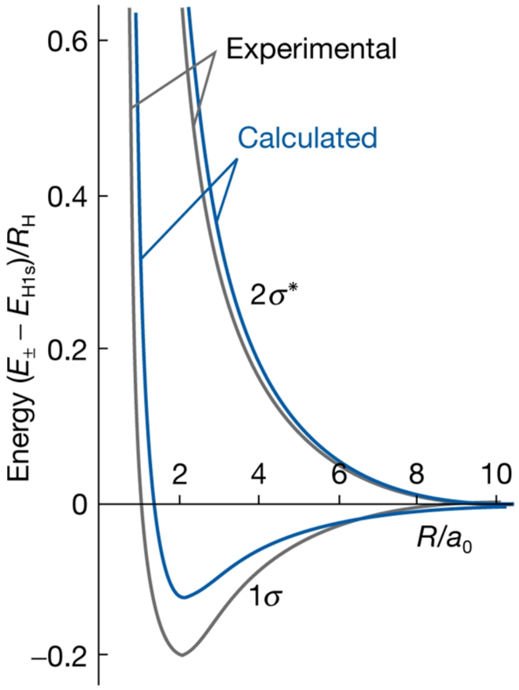
  → the energy of the molecule is lower than that of separate atoms



Bonding Orbital

- Bonding orbital
- called 1σ *orbital*
- σ *electron*

- The energy of 1σ orbital decreases as R decreases
- However at small separation, repulsion becomes large
- There is a minimum in potential energy curve
    - *Re = 130 pm (exp. 106 pm)*
    - *De = 1.77 eV (exp. 2.6 eV)*

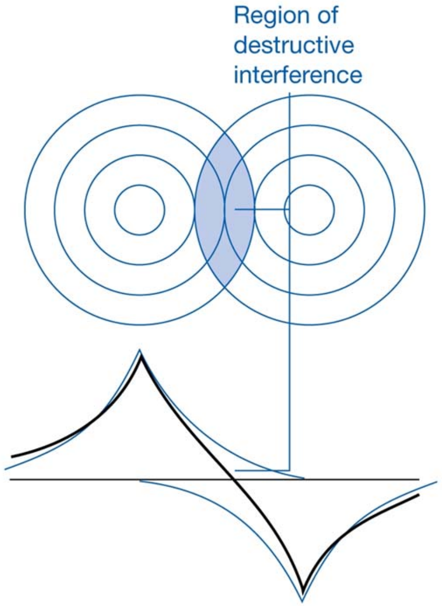


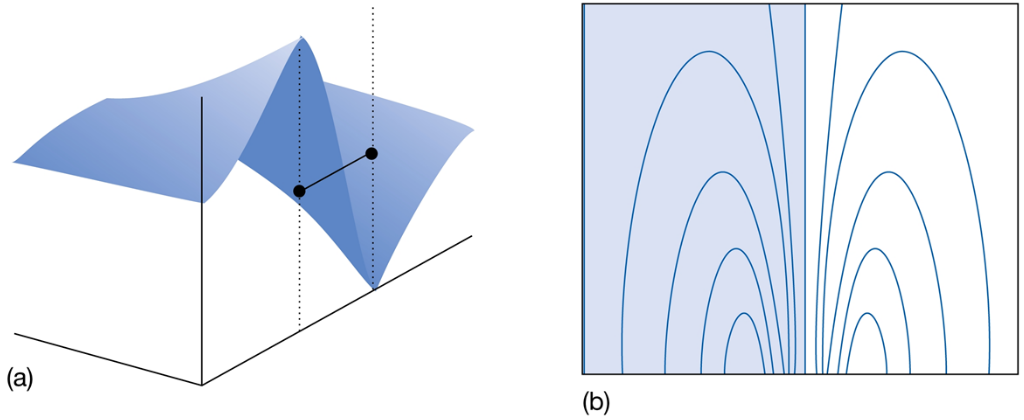
Antibonding Orbital

- Linear combination ψ_- corresponds to a higher energy

$$\psi_-^2 = N^2(A^2 + B^2 - 2AB)$$

- Reduction in probability density between the nuclei (-2AB term)
- Called 2σ orbital (often labeled $2\sigma^*$)



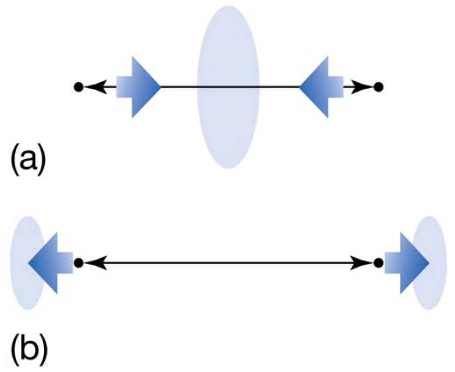


←

Amplitude of antibonding orbital

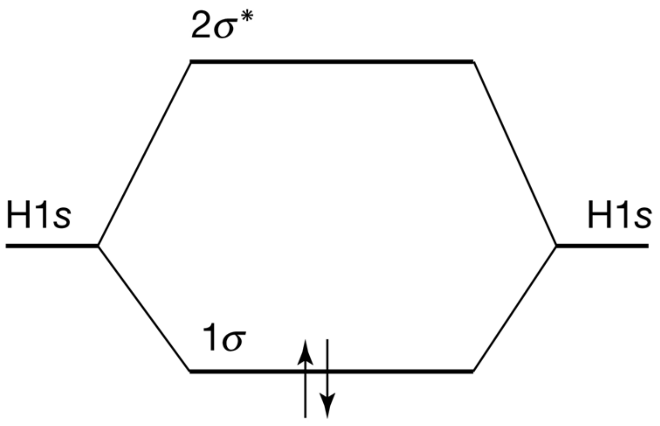
Antibonding orbital

- The electron is excluded from internuclear region → destabilizing



- The antibonding orbital is more antibonding than the bonding orbital is bonding

$$\left|E_- - E_{H1s}\right| > \left|E_+ - E_{H1s}\right|$$

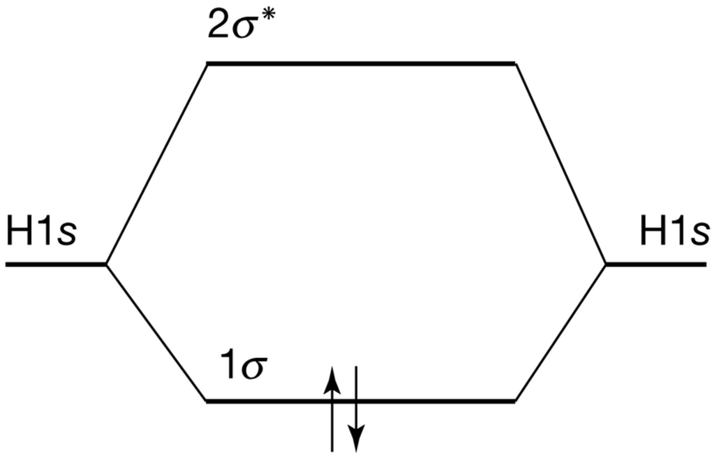


Molecular orbital energy diagram

The Structure of Diatomic Molecules

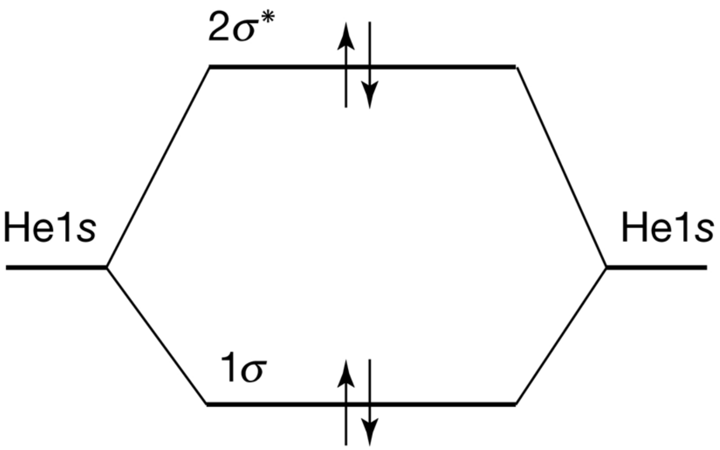
- Target : Many-electron diatomic molecules
- Similar procedure
  - Use H_2^+ molecular orbital as the prototype
  - Electrons supplied by the atoms are then accommodated in the orbitals to achieve lowest overall energy
  - Pauli’s principle + Hund’s maximum multiplicity rule

Hydrogen and He molecules



Hydrogen (H_2)

- Two electrons enter 1σ orbital
- Lower energy state than 2 H atoms



Helium (He)

- The shape is generally the same as H
- Two electrons enter 1σ orbital
- The next two electrons can enter 2σ* orbital
- Antibond is slightly higher energy than bonding
- He_2 is unstable than the individual atoms

Bond order

- A measure of the net bonding in a diatomic molecule
  - n : number of electrons in bonding orbital
  - n* : number of electrons in antibonding orbital

$$b = \frac{1}{2}(n - n^{*})$$

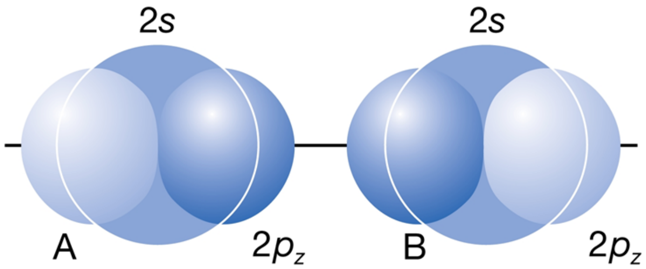
- Characteristics
  - The greater the bond order, the shorter the bond
  - The greater the bond order, the greater the bond strength

Period 2 diatomic molecules - σ orbital

- Elementary treatments : only the orbitals of valence shell are used to form molecular orbital
  - ☐ Valence orbitals in period 2 : *2s* and *2p*
- σ-orbital : *2s* and $2p_z$ orbital (cylindrical symmetry)

$$\psi = c_{A2s}\psi_{A2s} + c_{B2s}\psi_{B2s} + c_{A2p_z}\psi_{A2p_z} + c_{B2p_z}\psi_{B2p_z}$$

  - ☐ From an appropriate choice of *c* we can form four molecular orbital



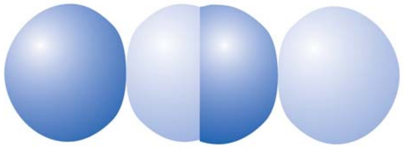
Period 2 diatomic molecules - σ orbital

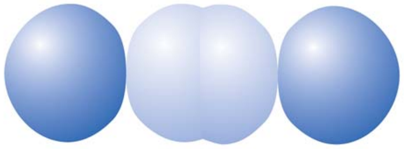
- Because 2s and 2p orbitals have distinctly two different energies, they may be treated separately.

$$\psi = c_{A2s}\psi_{A2s} \pm c_{B2s}\psi_{B2s}$$

$$\psi = c_{A2p_z}\psi_{A2p_z} + c_{B2p_z}\psi_{B2p_z}$$

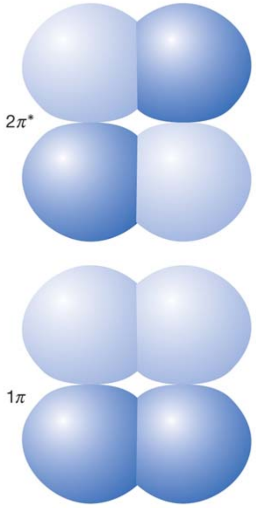
- Similar treatment can be used
  - □ *2s* orbitals → 1σ and 2σ*
  - □ $2p_z$ orbitals → 3σ and 4σ*

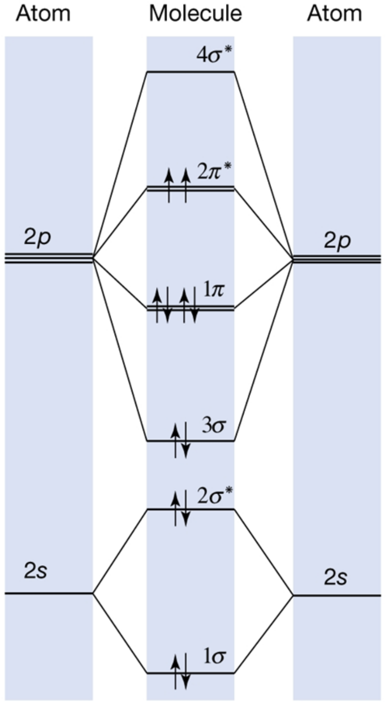

4σ*


3σ

Period 2 diatomic molecules - π orbital

- $2p_x$, $2p_z$ → perpendicular to intermolecular axis
  - Overlap may be constructive or distructive
  - Bonding or antibonding π orbital
  - Two π_x orbitals + Two π_y orbitals



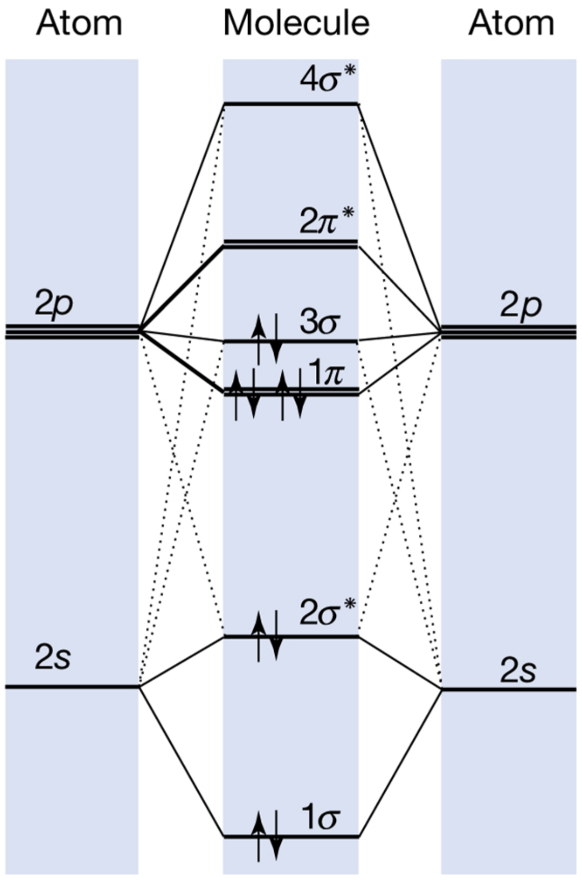


Period 2 diatomic molecules - π orbital

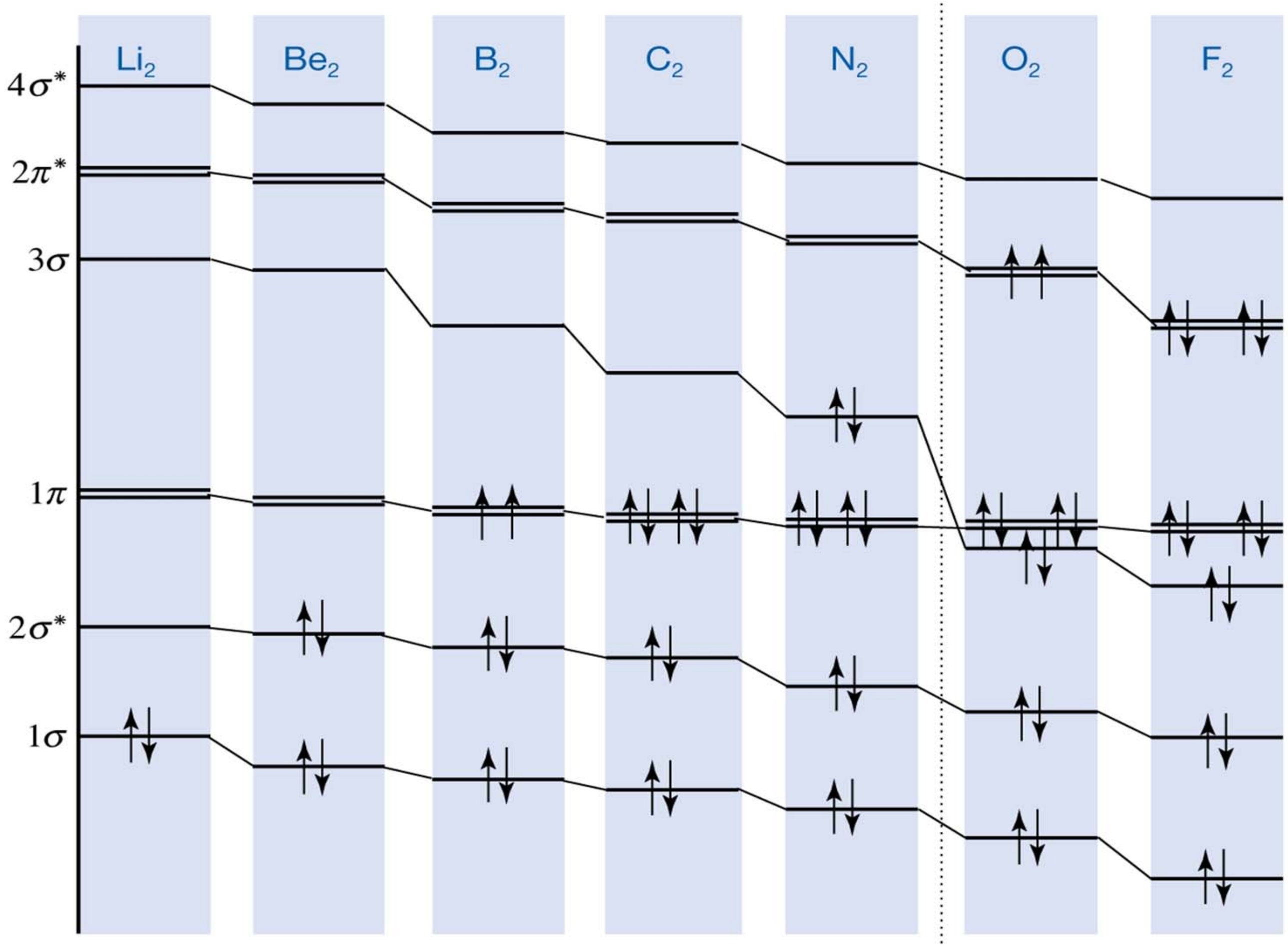
- The previous diagram is based on the assumption that 2s and 2pz orbitals contribute to completely different sets

→ In fact, all four atomic orbitals contribute joinlty to the four σ-orbital

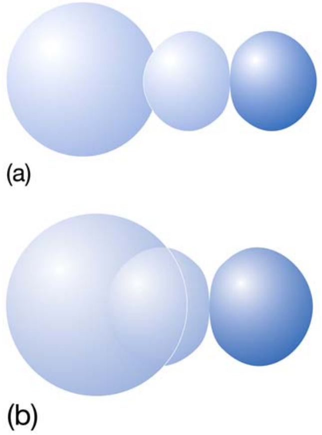
- The order and magnitude of energies change :



The variation of orbital energies of period 2 homonuclear diatomics



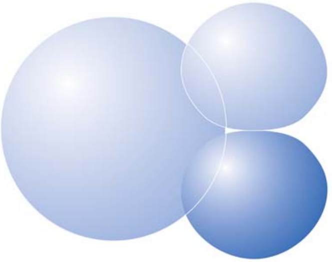
The overlap integral

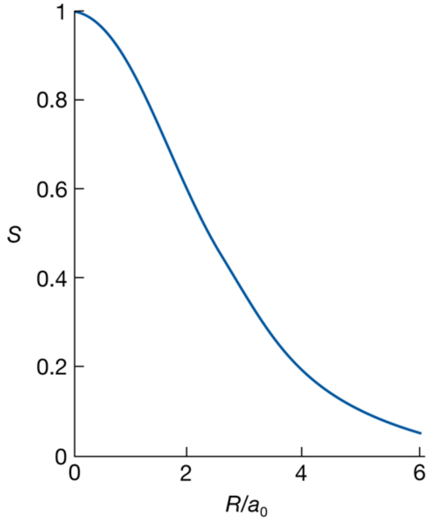


- The extent to which two atomic orbitals on different atom overlaps : the overlap integral

$$S = \int \psi_A^* \psi_B d\tau$$

  - ψ_A is small and ψ_B is large → S is small
  - ψ_A is large and ψ_B is small → S is small
  - ψ_A and ψ_B are simultaneously large → S is large
    - *1s* with same nucleus → S=1
    - $2s + 2p_x$ → S = 0





Structure of homonuclear diatomic molecule

- Nitrogen

  $1\sigma^2\ 2\sigma^{*2}\ 1\pi^4\ 3\sigma^2$

  $b = 0.5*(2+4+2-2) = 3$

  Lewis Structure : N ≡ N :

- Oxygen

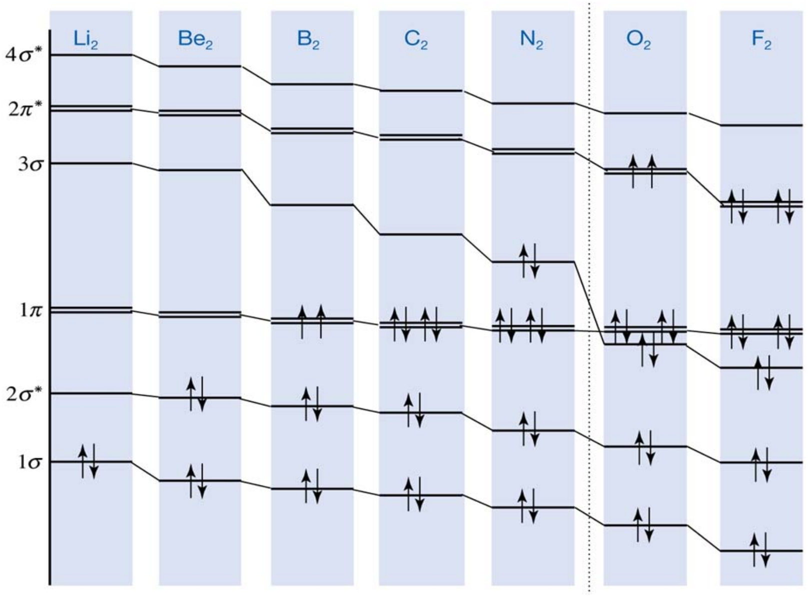
  $1\sigma^2\ 2\sigma^{*2}\ 3\sigma^2\ 1\pi^4\ 2\pi^{2*}$

  $b = 0.5*(2+2+4-2-2) = 2$

  last two electrons occupy different orbital : π_x and π_y (parallel spin)

→ angular momentum (s=1)

→ Paramagnetic



Quiz

- What is spin-orbit coupling ?
- What is the difference between sigma and pi bond ?
- Explain symmetrical structure of methane molecule.

$$2s_2 2p_x^1 2p_y^1$$