第四章 双原子分子结构与性质

Chapter 4 Structures and Properties of diatomic molecules

第四章 双原子分子结构与性质 目录

Contents

§ 4.1 分子轨道理论与H_2^+结构

4.1.1 H_2^+的基态

4.1.2 分子轨道理论

§ 4.2 双原子分子结构与性质

4.2.1 同核双原子分子

4.2.2 异核双原子分子

两个或多个原子之所以能结合在一起形成稳定的分子，是因为原子间存在强烈的相互作用，即化学键。

化学键：离子键、共价键和金属键等

三大理论

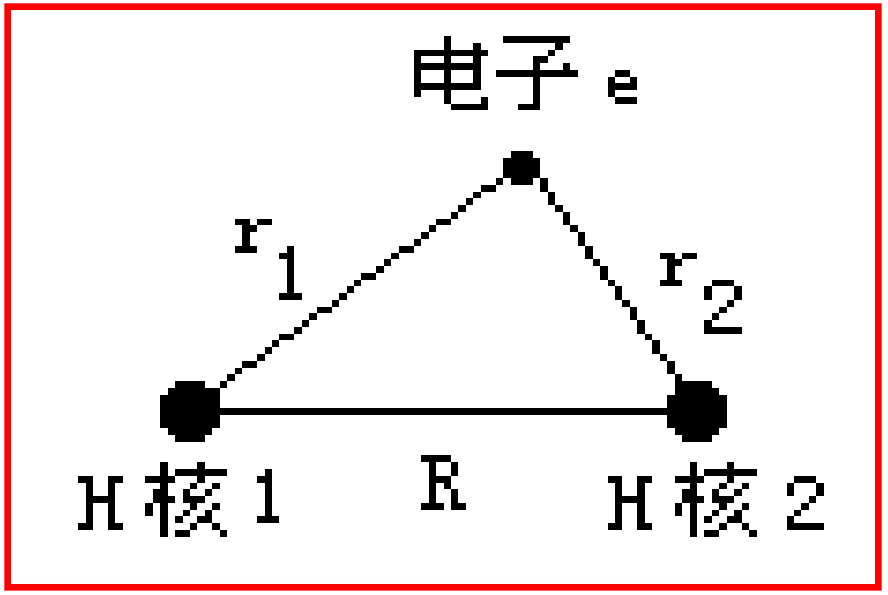
- 价键理论（VBT）：原子间局部作用
- 分子轨道理论(MOT)：电子在整个分子中运动
- 配位场理论（LFT）：配合物

§4.1 分子轨道理论与H_2^+结构

J. J. 汤姆逊，

阴极射线

单电子体系



4.1.1 H_2^+的基态

4.1.1.1 定核近似下的薛定谔方程

定核近似: 假设核不动，研究电子的运动。

原子单位制 a. u. (atomic unit)

单位长度：玻尔半径（0.529 Å）

单位质量：电子的质量（$9.1095*10^{-31}$ Kg）

单位电荷：电子的电荷（$1.60219*10^{-19}$ C）

单位能量：哈特里（Hartree）

在a.u中 $m_e = 1,\quad e = 1,\quad a_0 = 1,\quad \hbar = 1$?

$$a_0 = \frac{\varepsilon_0 h^2}{\pi m e^2} = \frac{4\pi \cdot \varepsilon_0 h^2}{4\pi \cdot \pi m e^2}$$

P6(1－17)

$$= \frac{4\pi\varepsilon_0}{m e^2} \frac{h^2}{4\pi^2}$$

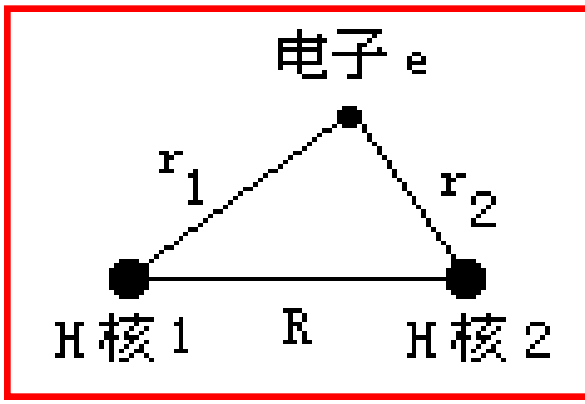
$$= \frac{4\pi\varepsilon_0}{m e^2} \hbar^2$$

H_2^+的Schrödinger方程

$$\left[-\frac{\hbar^2}{2m}\nabla^2-\frac{e^2}{4\pi\varepsilon_o r_1}-\frac{e^2}{4\pi\varepsilon_o r_2}+\frac{e^2}{4\pi\varepsilon_o R}\right]\Psi=E\Psi$$

原子单位制

$$\left[-\frac{1}{2}\nabla^2-\frac{1}{r_1}-\frac{1}{r_2}+\frac{1}{R}\right]\Psi=E\Psi$$



单电子体系： Schrödinger方程可精解，椭圆坐标系

近似求解

变分法

4.1.1.2 线性变分法简介

(1) 变分原理

体系： $\hat{H}$

$$\hat{H}\Psi_0 = E_0\Psi_0$$

试探波函数 Ψ ▪▪▪▪▪▶ Ψ_0 (真实波函数)

（Ψ 为一合格的波函数）

$$\overline{E} = \frac{\int \Psi^* \hat{H} \Psi \, d\tau}{\int \Psi^* \Psi \, d\tau} \geq E_0$$

$$\begin{cases} \Psi = \Psi_0 & \overline{E} = E_0 \\ \Psi \neq \Psi_0 & \overline{E} > E_0 \end{cases}$$

变分原理

当Ψ为体系真实的基态波函数时，上式出现等式“=”，否则为“>”。

例: 一维势箱中自由粒子基态波函数为

$$\Psi_1=\sqrt{\frac{2}{l}}\sin\frac{\pi x}{l}$$

$$\hat{H}=-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

将其代入上式，则有：

$$\overline{E}=\frac{\int\Psi^*\hat{H}\Psi d\tau}{\int\Psi^*\Psi d\tau}=\int\Psi^*\hat{H}\Psi d\tau$$

$$=\cdots=\frac{h^2}{8ml^2}(\text{即为基态能量})$$

若取 $\Psi = x(l-x)$ 作为波函数，

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

$$\int \Psi^* \hat{H}\, \Psi d\tau = \int_0^l x(l-x)\hat{H}\, x(l-x)\, dx$$

$$= \int_0^l x(l-x)\left(-\frac{\hbar^2}{2m}\right)\frac{d^2}{dx^2}[x(l-x)]dx$$

$$= -\frac{\hbar^2}{2m}\int_0^l x(l-x)(-2)\, dx = \frac{\hbar^2 a^3}{6m}$$

$$\int \Psi^* \Psi d\tau = \int_0^l x^2 (l-x)^2 dx = \frac{l^5}{30}$$

$$\overline{E} = \frac{\int_0^l \Psi^* \hat{H} \Psi dx}{\int_0^l \Psi^* \Psi dx} = \frac{\hbar^2 l^3}{6m} \div \frac{l^5}{30} = \frac{5h^2}{4\pi^2 m l^2}$$

$$= 0.12665 \frac{h^2}{ml^2} > 0.125 \frac{h^2}{ml^2}$$

$$\text{err} = 1.3\%$$

变分过程 ⟸ 不断试探的过程

试探函数 Ψ

$$\overline{E}=\frac{\int \Psi^{*}\hat{H}\Psi\, d\tau}{\int \Psi^{*}\Psi\, d\tau}$$

反复这一过程，$\overline{E}$ 越低越好

$$\left|\overline{E}_{(n+1)}-\overline{E}_{n}\right|<\varepsilon \quad \sim 10^{-5}\ eV$$

(2) 线性变分法

试探函数 $\Psi = c_1\phi_1 + c_2\phi_2 + \cdots + c_m\phi_m$

$$\bar{E} = \frac{\int \Psi^* \hat{H} \Psi d\tau}{\int \Psi^* \Psi d\tau} = \bar{E}(c_1, c_2, \cdots, c_m) \geq E_0$$

求极小值

$$\frac{\partial \bar{E}}{\partial c_1} = \frac{\partial \bar{E}}{\partial c_2} = \cdots = \frac{\partial \bar{E}}{\partial c_m} = 0$$

$$c_1^2 + c_2^2 + \cdots c_m^2 = 1$$

Ψ归一化

①$c_1, c_2, \ldots, c_m$的值，

⟹ Ψ

②最低 $\bar{E}$ ⟹ E_0

4.1.1.3 H_2^+的线性变分法的解

H原子轨道

试探函数 $\Psi = c_1\phi_1 + c_2\phi_2$

$$\overline{E} = \frac{\int \Psi^* \hat{H} \Psi d\tau}{\int \Psi^* \Psi d\tau} = \frac{\int (c_1\phi_1 + c_2\phi_2)\hat{H}(c_1\phi_1 + c_2\phi_2)d\tau}{\int (c_1\phi_1 + c_2\phi_2)(c_1\phi_1 + c_2\phi_2)d\tau}$$

$$= \frac{c_1^2 H_{11} + 2c_1c_2H_{12} + c_2^2 H_{22}}{c_1^2 + 2c_1c_2S_{12} + c_2^2}$$

$$H_{11}=\int\phi_1\hat{H}\phi_1\,d\tau=\int\phi_2\hat{H}\phi_2\,d\tau=H_{22}$$

库仑积分 ⟹ **H原子轨道能量**

$$H_{12}=\int\phi_1\hat{H}\phi_2\,d\tau=\int\phi_2\hat{H}\phi_1\,d\tau=H_{21}$$

交换积分 ⟹ **两个H原子轨道交盖引起的能量下降值(<0)**

$$S_{12}=\int\phi_1\phi_2\,d\tau=\int\phi_2\phi_1\,d\tau=S_{21}$$

重迭积分 ⟹ **两个H原子轨道交盖的程度**

$$\frac{\partial \overline{E}}{\partial c_1} = \frac{\partial \overline{E}}{\partial c_2} = 0$$

$$\Psi = c_1\phi_1 + c_2\phi_2$$

$$\begin{cases} c_1(H_{11} - E) + c_2(H_{12} - ES_{12}) = 0 \\ c_1(H_{12} - ES_{12}) + c_2(H_{22} - E) = 0 \end{cases}$$

久期方程

非零解 (即C_1和C_2不能同时为零)

$$\begin{vmatrix} H_{11} - E & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - E \end{vmatrix} = 0$$

久期行列式

则：

$$E_1 = \frac{H_{11} + H_{12}}{1 + S_{12}} \qquad E_2 = \frac{H_{11} - H_{12}}{1 - S_{12}}$$

$$\begin{cases} c_1(H_{11} - E) + c_2(H_{12} - ES_{12}) = 0 \\ c_1(H_{12} - ES_{12}) + c_2(H_{22} - E) = 0 \end{cases}$$

久期方程

$$c_1^2 + c_2^2 = 1$$

归一化

$$c_1 = c_2 = \frac{1}{\sqrt{2 + 2S_{12}}} \qquad c_1 = -c_2 = \frac{1}{\sqrt{2 - 2S_{12}}}$$

$$\Psi = c_1\phi_1 + c_2\phi_2$$

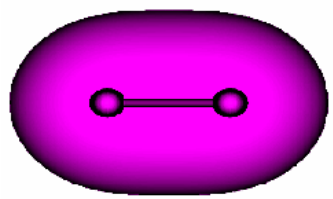
H_2^+体系 → 线性变分法 → MO及其能级

$$E_1 = \frac{H_{11} + H_{12}}{1 + S_{12}} \qquad E_2 = \frac{H_{11} - H_{12}}{1 - S_{12}}$$

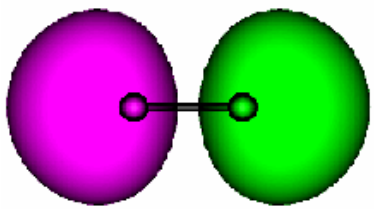
$$\Psi_1 = \frac{1}{\sqrt{2 + 2S_{12}}}(\phi_1 + \phi_2) \qquad \Psi_2 = \frac{1}{\sqrt{2 - 2S_{12}}}(\phi_1 - \phi_2)$$

4.1.1.4 解的讨论：

(1)MO波函数



Ψ_1没有节面



Ψ_2有1个节面

(2)MO能级

设$S_{12}\approx 0$

H原子轨道能量

$$E_1=\frac{H_{11}+H_{12}}{1+S_{12}}\cong H_{11}+H_{12}<H_{11}$$

Ψ_1：成键分子轨道

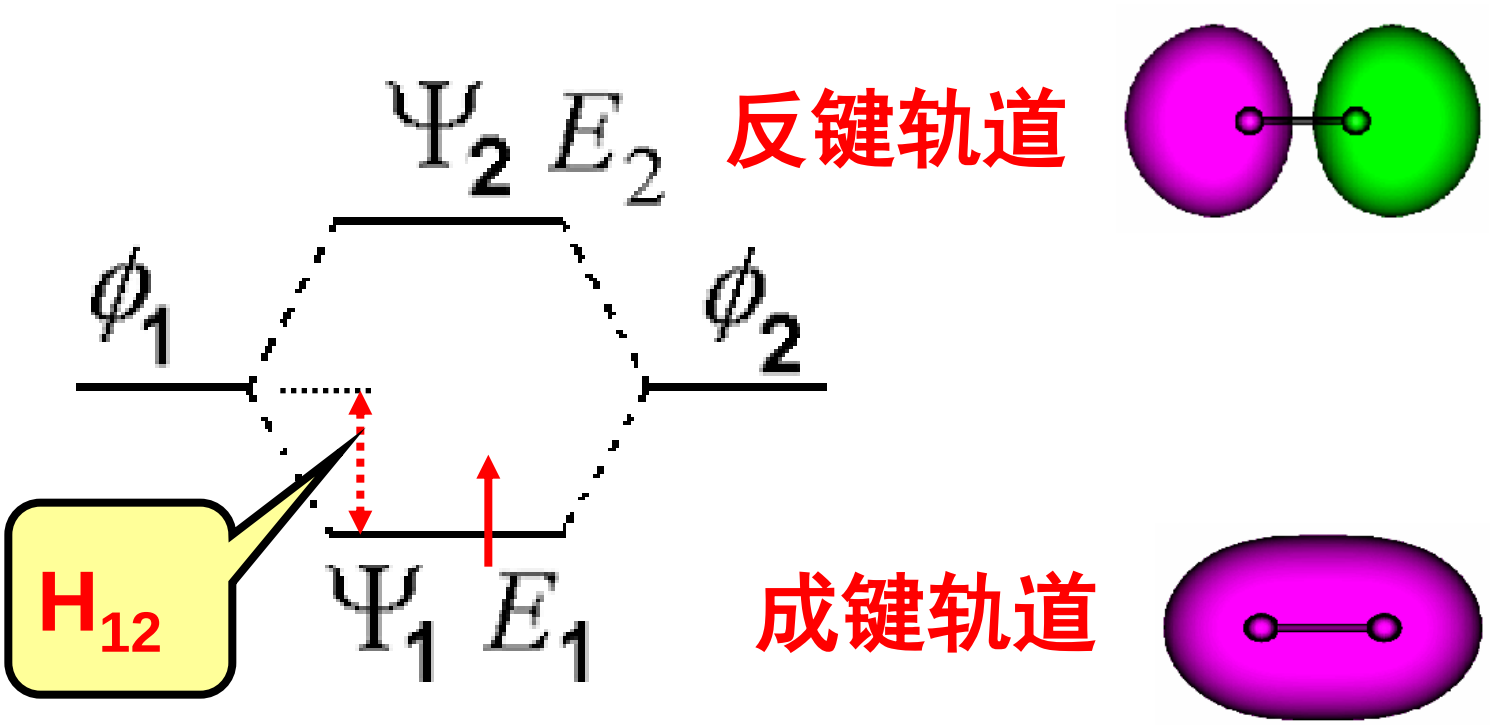
$$E_2=\frac{H_{11}-H_{12}}{1-S_{12}}\cong H_{11}-H_{12}>H_{11}$$

Ψ_2:反键分子轨道

交换积分$H_{12}<0$

两个H原子轨道交盖引起的能量下降值

(3)轨道作用图



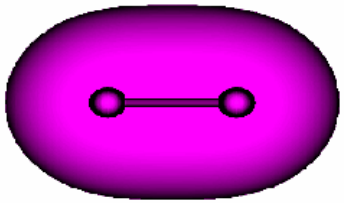
H_2^+的电子组态为$(\psi_1)^1$。

(4) 共价键的本质—离域效应

$$H + H^{+} \longrightarrow H_2^{+}$$

电子在H原子的1s轨道 → 电子绕1个核运动

电子在H_2^+的ψ_1轨道 → 绕2个核运动 → 运动范围扩大 → 离域效应



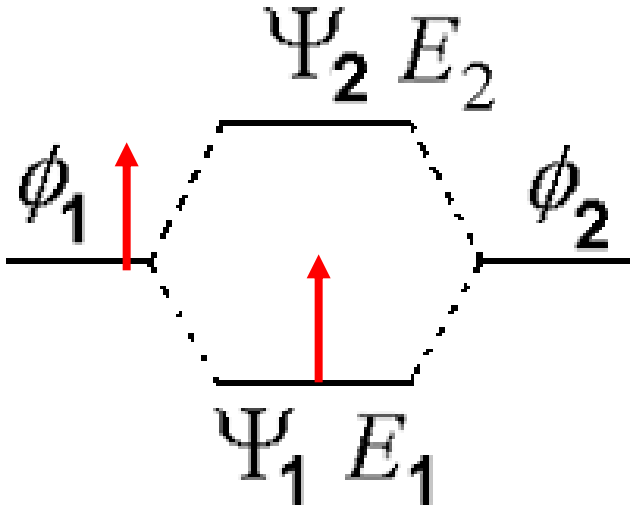
离域效应

(1)电子运动范围扩大. “共有财产”

在整个分子内运动.

(2)电子的能量↓，有利分子稳定。

共价键成因中最基本的因素



H_2^+

(5) MO能级与核间距

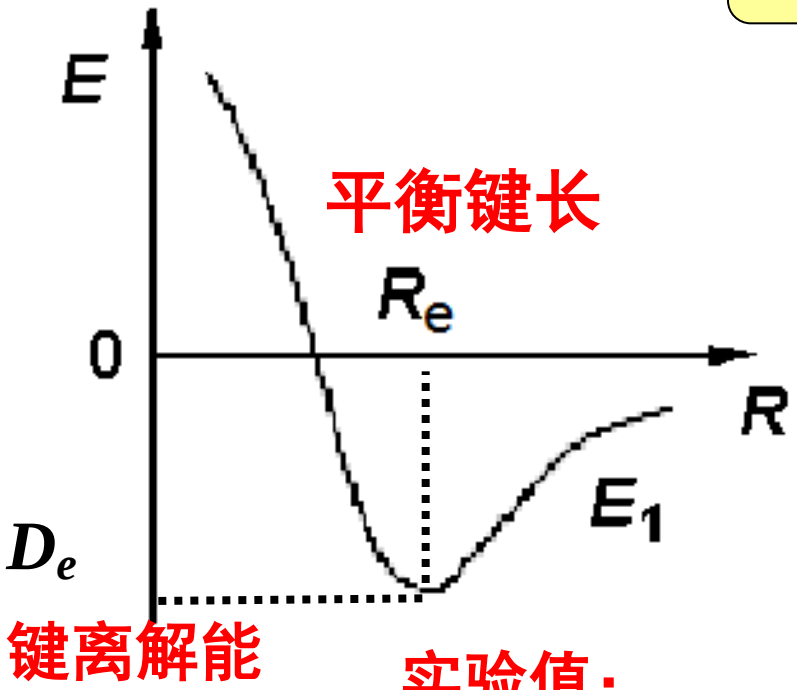
$$E_1 = \frac{H_{11} + H_{12}}{1 + S_{12}}$$

H_{12}:交换积分

H_{12}:重迭积分

两个H原子轨道交盖的程度

与原子间距有关



简单采用LCAO-MO，得到
R_e=132 pm, D_e=170.8 kJ/mol

进一步考虑收缩及极化效应，则
R_e=105.8 pm, D_e=268.8 kJ/mol

实验值：
R_e=106 pm, D_e=269 kJ/mol

4.1.2 分子轨道理论

强调 | 电子在整个分子内中运动， “共有财产”

4.1.2.1 分子中的单电子波函数—MO

分子中电子的运动状态 —分子轨道MO

分子轨道理论核心思想:

原子轨道线性组合为分子轨道

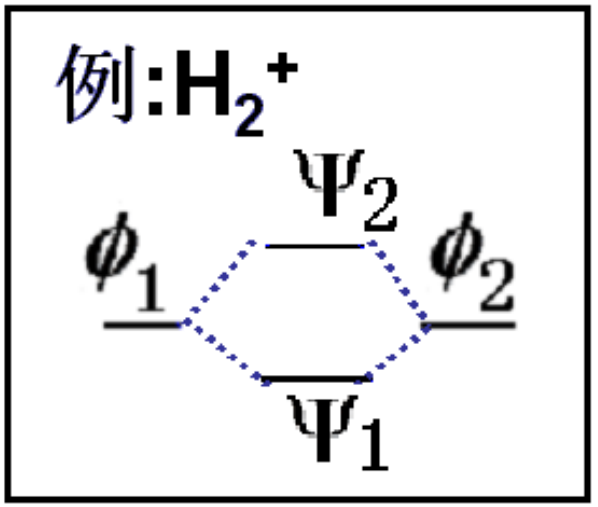
—LCAO-MO

$$\Psi_i = c_{i1}\phi_1 + c_{i2}\phi_2 + \cdots + c_{im}\phi_m$$

MO ϕ_i : AO

(1)数目保守性：

*m*个AO ⟹ *m* 个 MO



(2)AO在MO中的贡献

—|系数|^2

例: H_2^+ $\Psi_1 = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)$

ϕ_1和ϕ_2在Ψ_1的贡献各为 1/2

(3) LCAO-MO的基本原则

①能量相近

例:HF分子

H: E_{1s}=-13.6ev

F: E_{1s}=-696.3ev

E_{2s}=-401ev

E_{2p}=-18.6ev

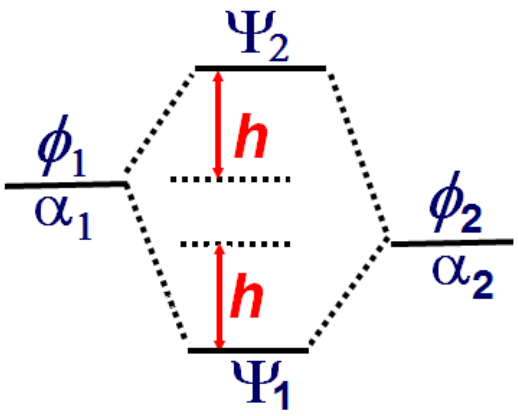
相近

一般来说, 价轨道间能量相近.

轨道作用图

Ψ_1含较多ϕ_2成份

Ψ_2含较多ϕ_1成份



$$c_{12}^2 > c_{11}^2$$
$$c_{21}^2 > c_{22}^2$$

h=0 没有形成MO

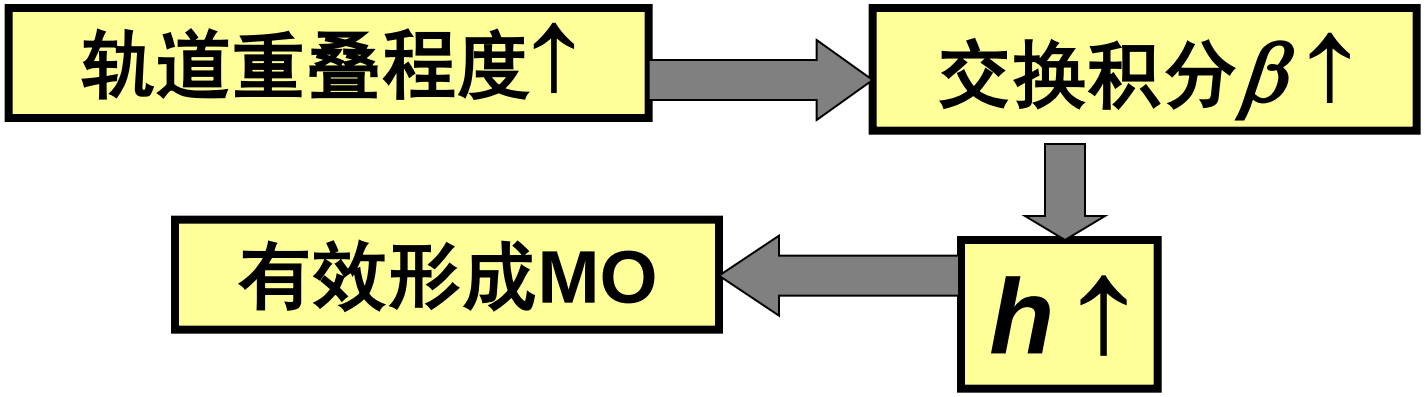
$h^{\uparrow}$ 形成MO越有效

$$\Psi_1 = c_{11}\phi_1 + c_{12}\phi_2$$
$$\Psi_2 = c_{21}\phi_1 + c_{22}\phi_2$$

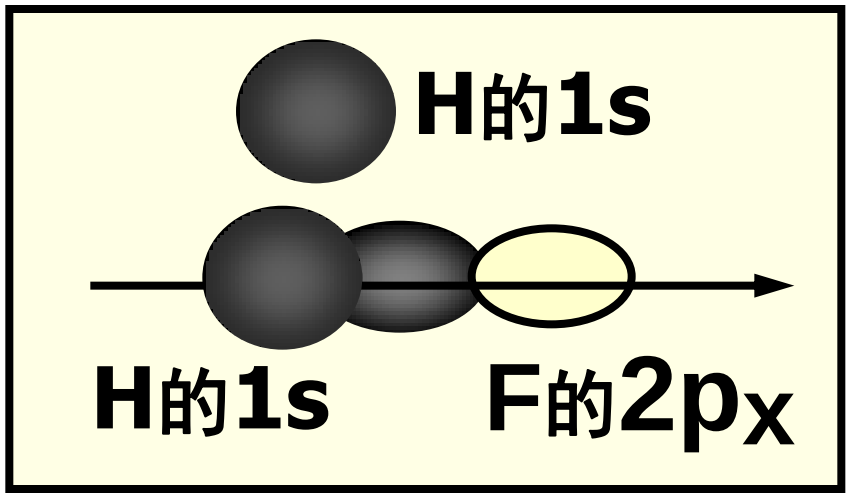
$$h = \frac{1}{2}\left[\sqrt{(\alpha_1-\alpha_2)^2+4\beta^2}-(\alpha_1-\alpha_2)\right]$$

$\alpha_1=\alpha_2$ 时，h取最大值$=|\beta|$ ⇒ Φ_1和Φ_2交换积分

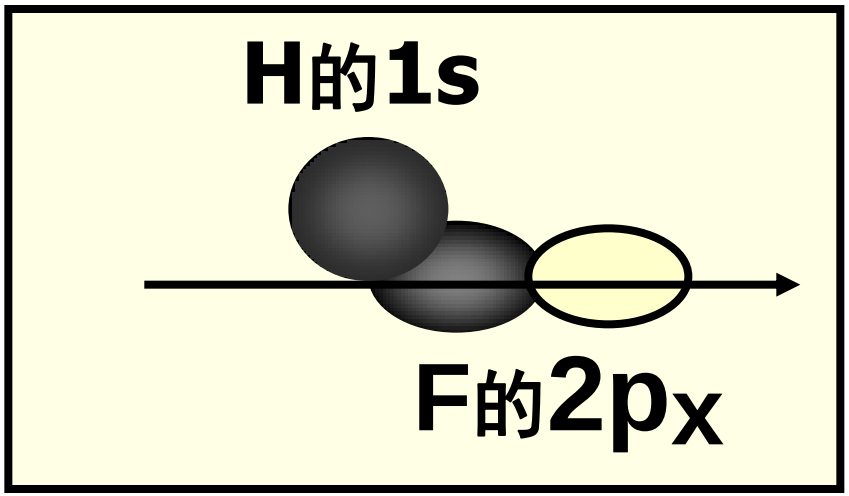
②最大重叠原则



例: HF分子



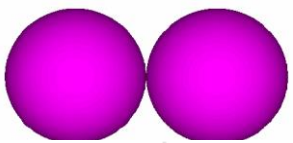
最大重叠



重叠不好

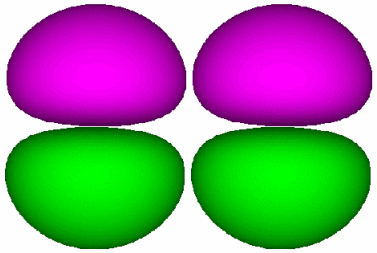
③对称性匹配

s s

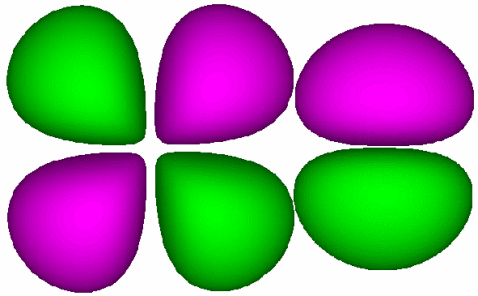


$$\Psi_1 = \frac{1}{\sqrt{2}}(\phi_{1s}^{a} + \phi_{1s}^{b})$$

p_x p_x

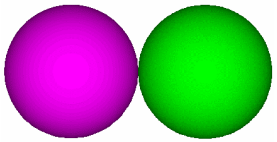


d_{xz} p_x

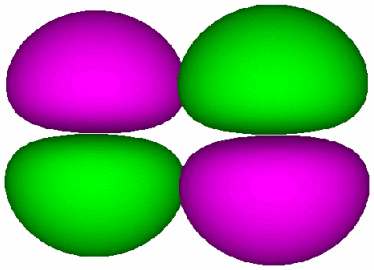


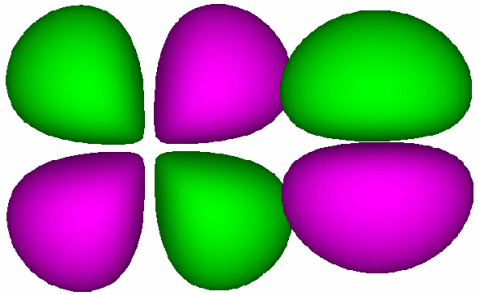
同号重叠，对称匹配，组成成键轨道

差别

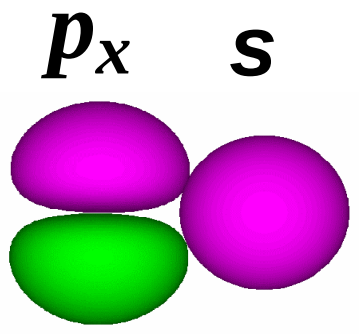


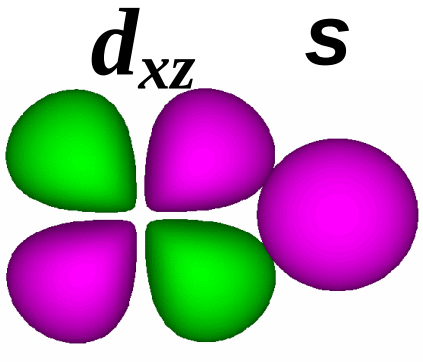
$$\Psi_2 = \frac{1}{\sqrt{2}}(\phi_{1s}^{a} - \phi_{1s}^{b})$$

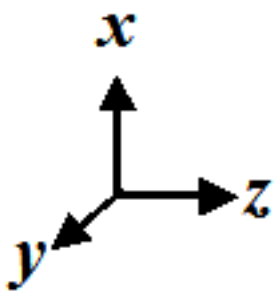


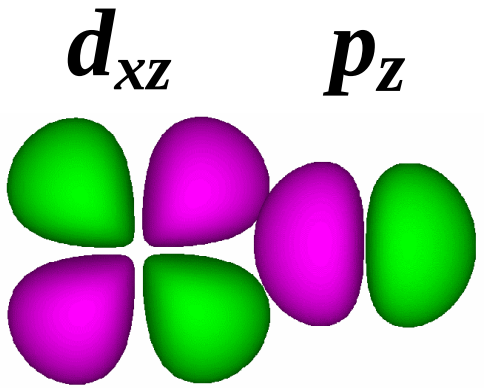


异号重叠，对称匹配，组成反键轨道









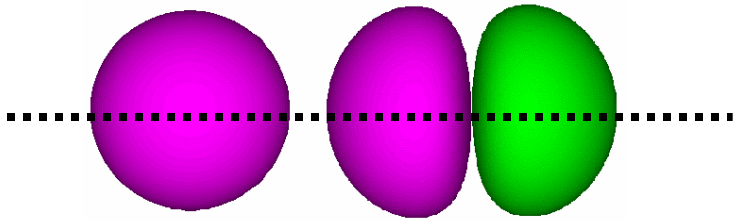
同、异号重叠完全抵消，对称不匹配，不能组成任何分子轨道。

4.1.1.2 MO的类型、符号和能级顺序

(1)分子轨道的类型

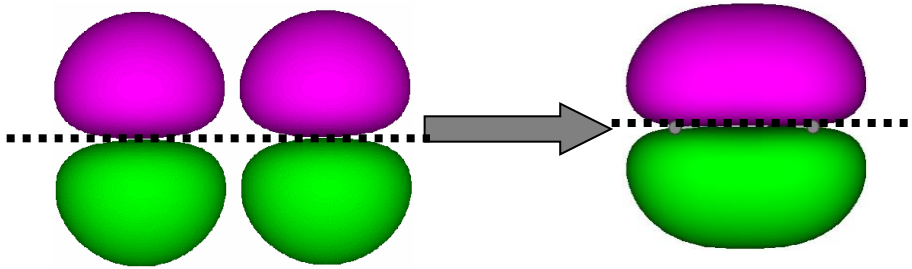
σ型MO－电子云沿键轴呈圆柱型对称.

头顶头



π型MO－电子云相对于键轴有一个节面

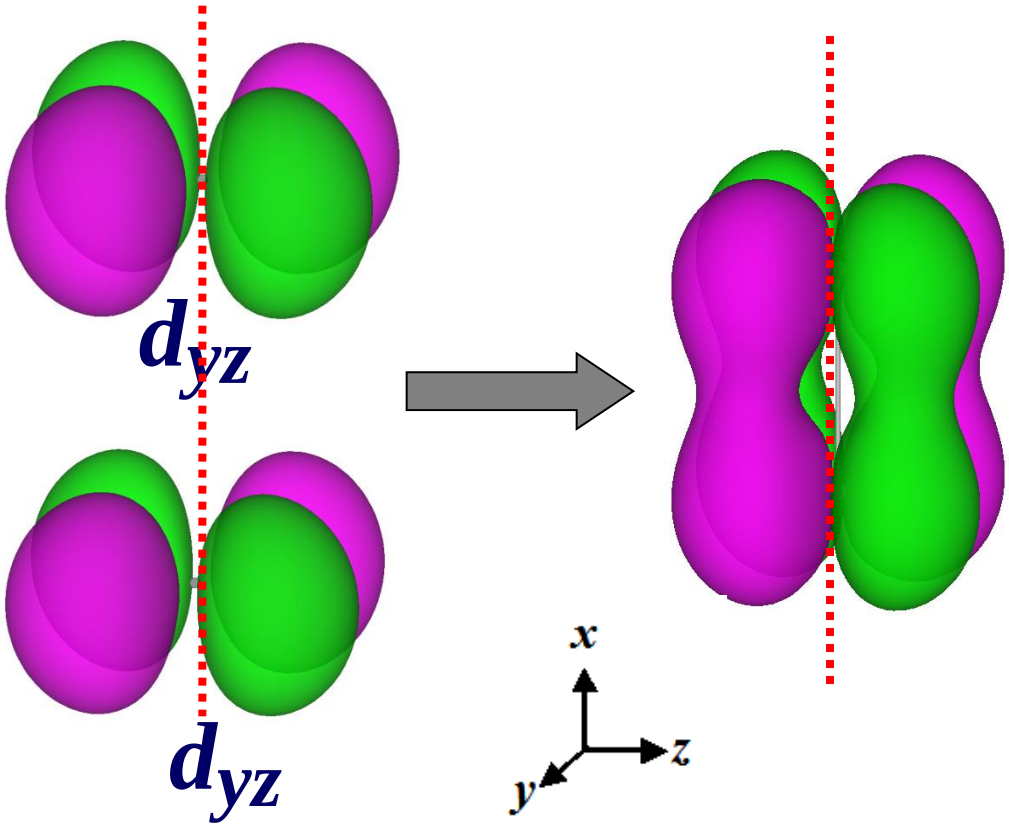
肩并肩



δ型MO—电子云相对于键轴有二个节面

面贴面

例：d_{yz}和d_{yz}轨道沿 X轴。

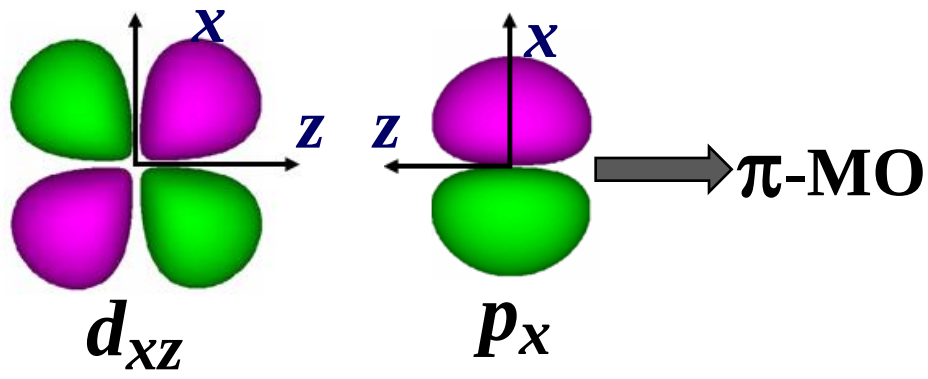


节面1—XZ

节面2—XY

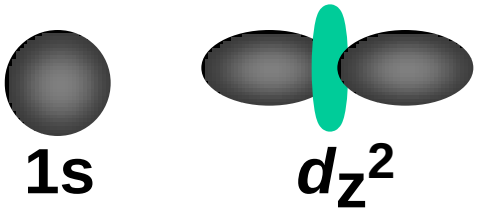
绘制AB双原子分子的轨道作用图时，要采用左/右手坐标系，并将键轴对着画。

例：以z轴作为键轴，
A、B原子各提供
d_{xz}轨道与p_x轨道



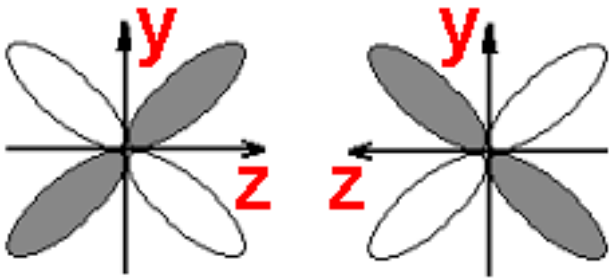
例：z为键轴

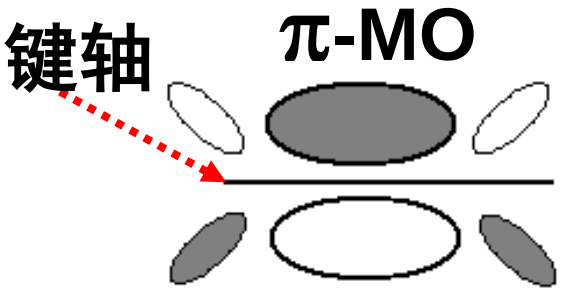
(1) s, d_{z^2}



σ-MO

(2) d_{yz},d_{yz}

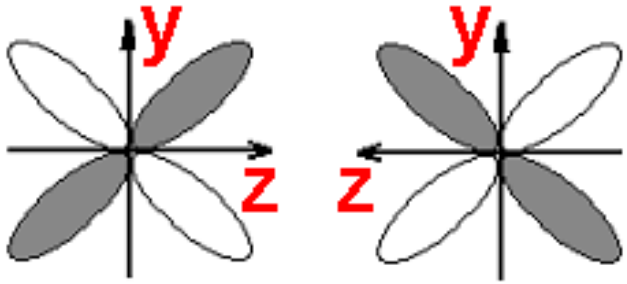




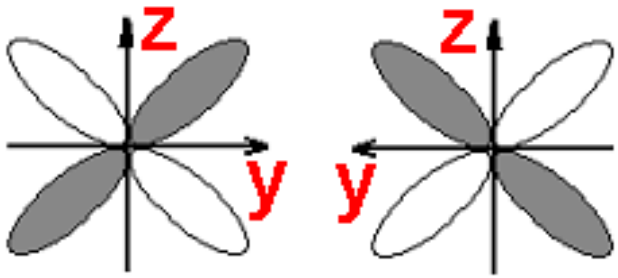
注意：轨道作用的方向

例：d_{yz}, d_{yz}

沿 z 轴靠近，π-MO

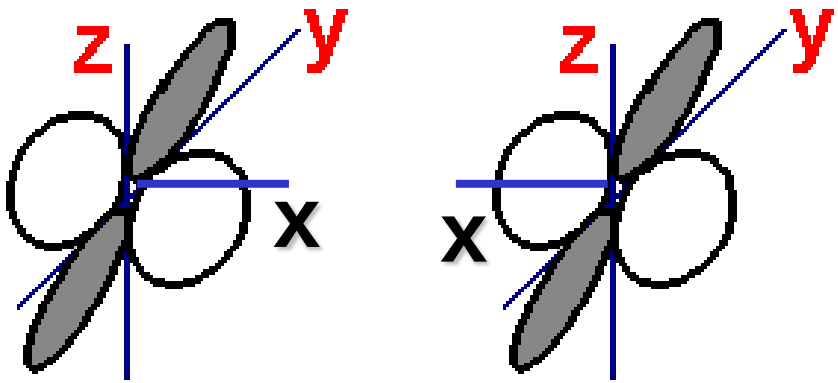


沿 y 轴靠近，π-MO

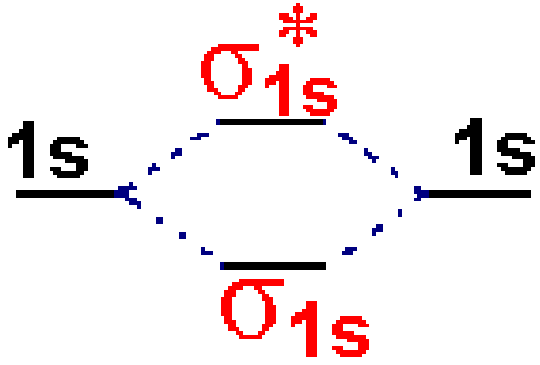


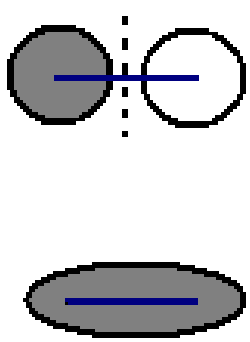
沿 x 轴靠近

δ-MO



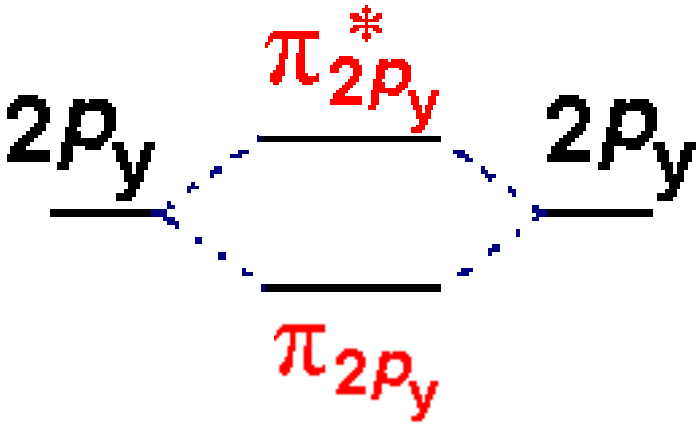
(2)分子轨道的符号 ← 分离原子符号

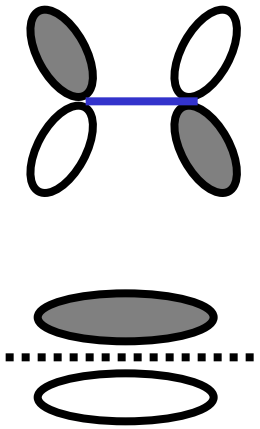




σ*1s

σ1s



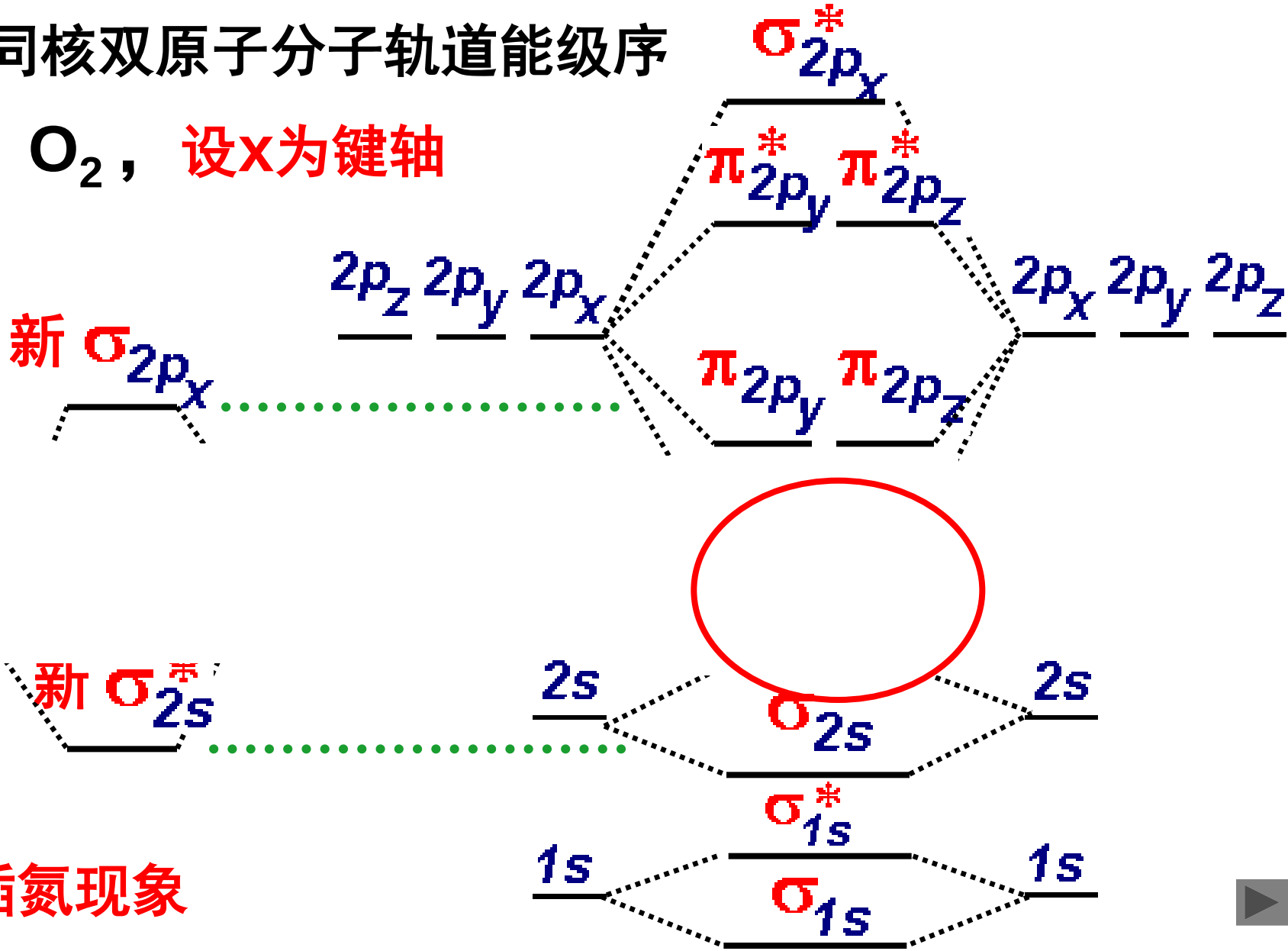


π*2py

π2py

(3)同核双原子分子轨道能级序

例：O_2，设x为键轴



插氮现象

Notes：

(a)对于O, F等形成的同核双原子分子或离子，

MO能级序为：$\sigma_{1s} < \sigma_{1s}^{*} < \sigma_{2s} < \sigma_{2s}^{*}$

$< \sigma_{2p_x} < \pi_{2p_y}\ \pi_{2p_z} < \pi_{2p_y}^{*}\ \pi_{2p_z}^{*} < \sigma_{2p_x}^{*}$

(b)对于Li, Be, C, N形成的同核双原子分子或离子，有“插氮现象”，MO能级序为$\sigma_{1s} < \sigma_{1s}^{*} < \sigma_{2s} < \sigma_{2s}^{*}$

$< \pi_{2p_y}\ \pi_{2p_z} < \sigma_{2p_x} < \pi_{2p_y}^{*}\ \pi_{2p_z}^{*} < \sigma_{2p_x}^{*}$

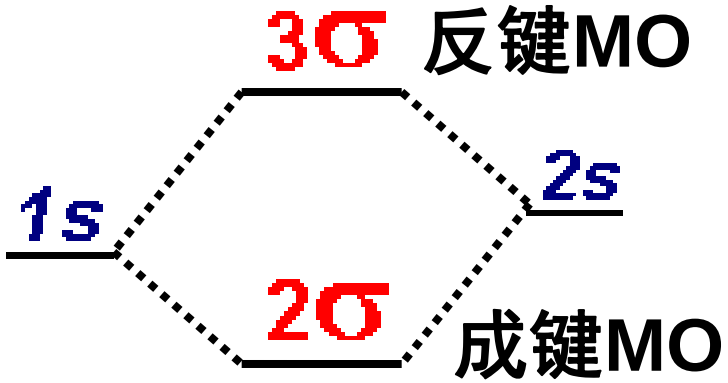
(4)异核双原子分子轨道能级序

1σ，2σ，3σ …依次表示能量递增的σ-MO

1π，2π，3π … 依次表示能量递增的π-MO

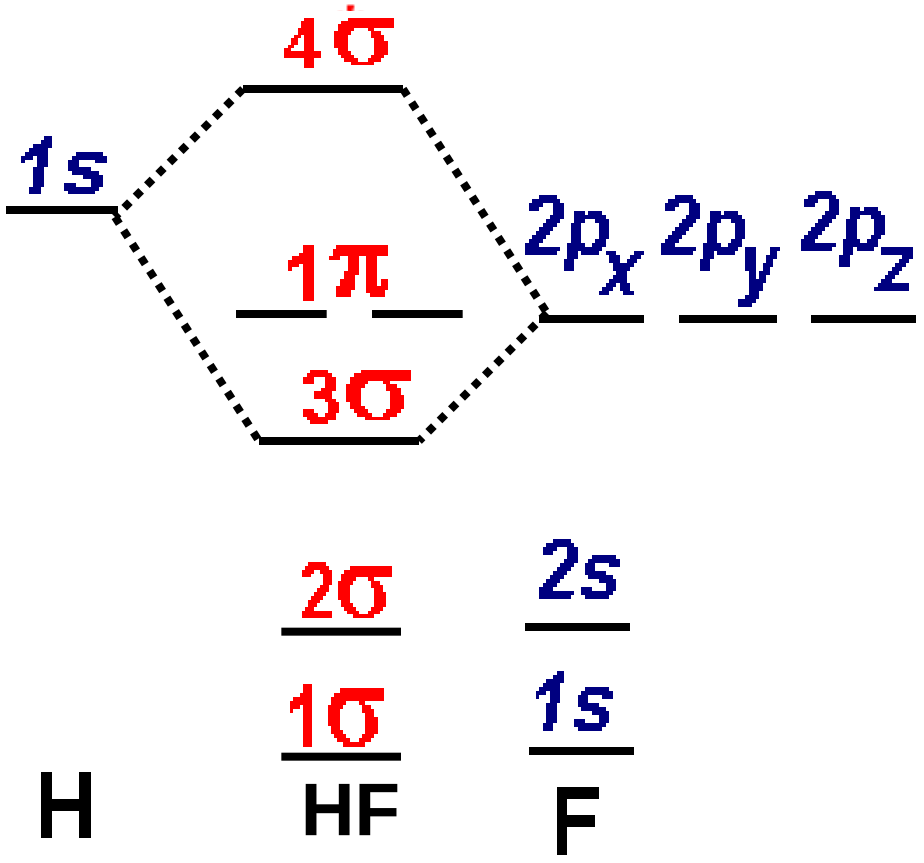
1δ，2δ，3δ… 依次表示能量递增的δ-MO

例1：LiH分子



$$(1\sigma)^2(2\sigma)^2$$

例2：HF分子



$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^4$$

先 后

4.1.2.3 电子填充（构造）原则

——能量最低原则，保里原理， 洪特规则

例1：O_2：

16e

$$(\sigma_{1s})^2(\sigma_{1s}^*)^2\ (\sigma_{2s})^2(\sigma_{2s}^*)^2\ (\sigma_{2p_x})^2$$
$$(\pi_{2p_y})^2(\pi_{2p_z})^2\ (\pi_{2p_y}^*)^1(\pi_{2p_z}^*)^1$$

例2：N_2：

14e

插氮现象

$$(\sigma_{1s})^2(\sigma_{1s}^*)^2\ (\sigma_{2s})^2(\sigma_{2s}^*)^2$$
$$(\pi_{2p_y})^2(\pi_{2p_z})^2\ (\sigma_{2p_x})^2$$

例3：LiH分子

例4：HF分子

§4.2 双原子分子结构与性质

1. 组态、键级

组态： 电子排布的方式，例如：H_2，$(\sigma_{1s})^2$

$$\text{键级} = \frac{1}{2}\left(\sum \text{成键电子数} - \sum \text{反键电子数}\right)$$

↓

化学键的强度 ⟷ 分子的稳定性

4.2.1 同核双原子分子

例1：H_2^+，1e　　组态：$(\sigma_{1s})^1$

键级$=\frac{1}{2}(1-0)=0.5$　　单电子σ键

H_2，2e　　组态：$(\sigma_{1s})^2$

键级$=\frac{1}{2}(2-0)=1$　　双电子σ键

例2：He_2^+，3e 组态：$(\sigma_{1s})^2(\sigma_{1s}^*)^1$

键级$=\frac{1}{2}(2-1)=0.5$ 三电子σ键

✗ He_2，4e 组态：$(\sigma_{1s})^2(\sigma_{1s}^*)^2$

键级$=\frac{1}{2}(2-2)=0$ 分子不存在

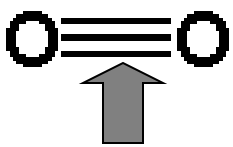
例3：O_2 16e

$$(\sigma_{1s})^2(\sigma_{1s}^*)^2\ (\sigma_{2s})^2(\sigma_{2s}^*)^2\ (\sigma_{2p_x})^2$$

$$(\pi_{2p_y})^2(\pi_{2p_z})^2\ (\pi_{2p_y}^*)^1(\pi_{2p_z}^*)^1$$

顺磁性

键级 $= \frac{1}{2}(10-6) = 2$



一个双电子 σ 键, 两个三电子 π 键

O_2^+ 15e

$$(\sigma_{1s})^2(\sigma_{1s}^*)^2\ (\sigma_{2s})^2(\sigma_{2s}^*)^2\ (\sigma_{2p_x})^2$$

$$(\pi_{2p_y})^2(\pi_{2p_z})^2\ (\pi_{2p_y}^*)^1$$ 顺磁性

键级= $\frac{1}{2}(10-5)=2.5$ ⟸ O_2^+比O_2稳定。

$[O{=}{=}O]^+$

一个双电子σ键,一个双电子π键,一个三电子π键

例4：N_2 14e

$$(\sigma_{1s})^2(\sigma_{1s}^*)^2\ (\sigma_{2s})^2(\sigma_{2s}^*)^2$$

$$(\pi_{2p_y})^2(\pi_{2p_z})^2(\sigma_{2p_x})^2$$ 抗磁性

$$\text{键级}=\frac{1}{2}(10-4)=3$$

$$N\equiv N$$

一个双电子 σ 键，两个双电子 π 键

例5：F_2 18e

$$(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_x})^2$$

$$(\pi_{2p_y})^2(\pi_{2p_z})^2(\pi_{2p_y}^*)^2(\pi_{2p_z}^*)^2$$ 抗磁性

$$\text{键级}=\frac{1}{2}(10-8)=1$$

F——F 双电子 σ 键

4.2.2 异核双原子分子

例1：LiH分子, 4e

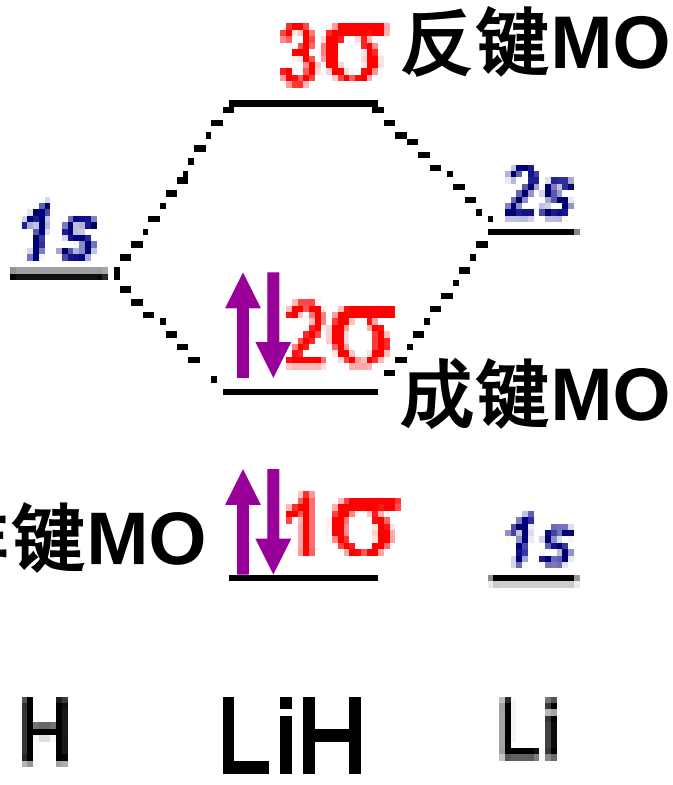
$$(1\sigma)^2(2\sigma)^2$$

抗磁性

键级= $\frac{1}{2}(2-0)=1$

双电子 σ 键

Li —H



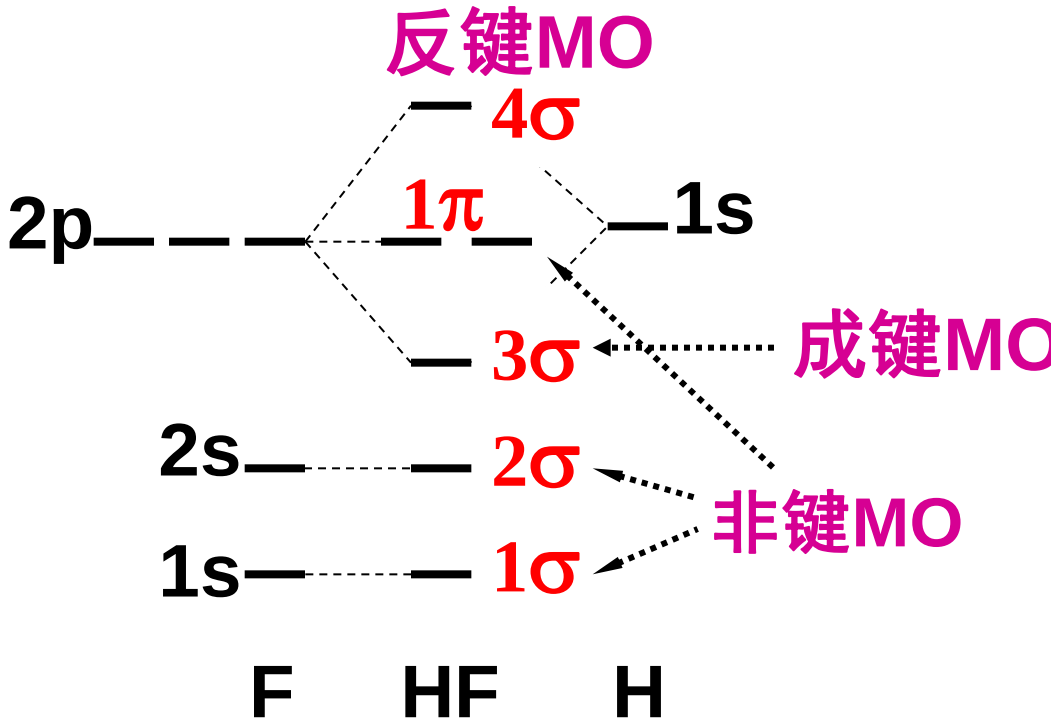
例2: HF分子,10e

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^4$$

抗磁性

键级= $\frac{1}{2}(2-0)=1$

H — F
双电子 σ 键



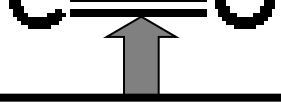
例3：CO分子, 14e 等电子体 N_2 非极性键

N_2: $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p_y})^2(\pi_{2p_z})^2(\sigma_{2p_x})^2$

CO: $(1\sigma)^2\ (2\sigma)^2\ (3\sigma)^2\ (4\sigma)^2\ (1\pi)^4\ (5\sigma)^2$

键级 $= \frac{1}{2}(10-4) = 3$

叁键 极性键



一个双电子σ键, 两个双电子 π 键

Notes: 等电子体的电子组态不一定相同。

① N_2 、CO、CN^-电子组态类似。

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2$$

键级=3　　叁键

② O_2^+ 和NO是等电子体，电子组态不同。

无插氮现象　　有插氮现象