Chapter 13 – Bonding in Diatomics

$$\hat{H}_{HF}\sigma_i(\vec{r}_i) = \varepsilon_i\sigma_i(\vec{r}_i)$$

Hartree-Fock equation

orbital energy

orbital

LCAO – MO method

$$\sigma_j = \sum_i c_{ij}\phi_i$$

atomic orbital

molecular orbitall

(1) choose atomic basis set $\{\phi_i\}$

(2) determine $\{c_{ij}\}$ variationally by minimizing E_{HF}

If $\sigma_1 = c_{11}\phi_1 + c_{21}\phi_2 \longrightarrow \sigma = c_1\phi_1 + c_2\phi_2$

$$\langle \varepsilon \rangle = \frac{\int \sigma_1^* \hat{H}_{HF} \sigma_1 d\tau}{\int \sigma_1^* \sigma_1 d\tau} = \frac{c_1^2 H_{11} + c_2^2 H_{22} + 2c_1 c_2 H_{12}}{c_1^2 + c_2^2 + 2c_1 c_2 S_{12}}$$

$\partial \langle \varepsilon \rangle / \partial c_1 = 0$ and $\partial \varepsilon / \partial c_2 = 0 \quad \Rightarrow$

$$(H_{11} - \varepsilon) c_1 + (H_{12} \varepsilon S_{12}) c_2 = 0$$
$$(H_{12} - \varepsilon S_{12}) c_1 + (H_{22} - \varepsilon) c_2 = 0$$

$$\begin{pmatrix} H_{11} - \varepsilon & H_{12} - \varepsilon S_{12} \\ H_{12} - \varepsilon S_{12} & H_{22} - \varepsilon \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \quad \text{or} \quad \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{pmatrix} 1 & S_{12} \\ S_{21} & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

H c = E S c

Nontrival solution $\Longrightarrow \begin{vmatrix} H_{11} - \varepsilon & H_{12} - \varepsilon S_{12} \\ H_{12} - \varepsilon S_{12} & H_{22} - \varepsilon \end{vmatrix} = 0$

$$\left(H_{11}-\varepsilon\right)\left(H_{22}-\varepsilon\right)-\left(H_{12}-\varepsilon S_{12}\right)^2=0$$

$$\varepsilon^2-\varepsilon\left(H_{11}+H_{22}\right)+H_{11}H_{22}-\left(H_{12}^2-2\varepsilon H_{12}S_{12}+\varepsilon^2 S_{12}^2\right)=0$$

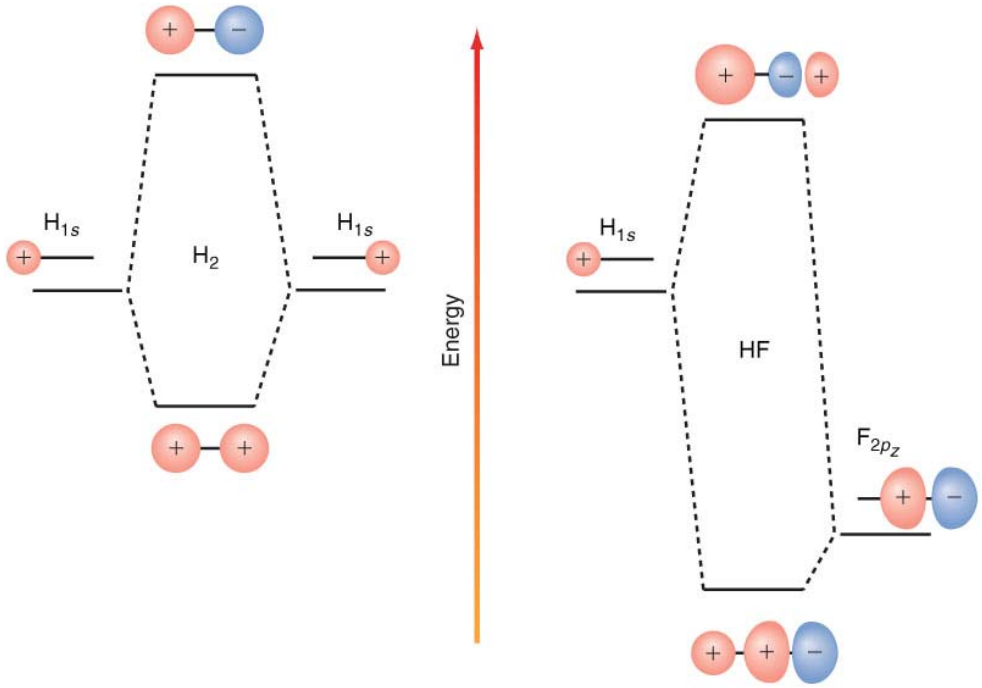
$$\varepsilon=\frac{H_{11}+H_{22}-2H_{12}S_{12}}{2\left(1-S_{12}^2\right)}\pm\frac{\sqrt{\left(H_{11}+H_{22}-2H_{12}S_{12}\right)^2+4\left(1-S_{12}^2\right)\left(H_{12}^2-H_{11}H_{22}\right)}}{2\left(1-S_{12}^2\right)}$$

For a homonuclear diatomic

$$H_{11}=H_{22}\quad\Rightarrow\quad\varepsilon_1=\frac{H_{11}+H_{12}}{1+S_{12}},\quad\varepsilon_2=\frac{H_{11}-H_{12}}{1-S_{12}}$$

General case with $S_{12}=0$

$$\varepsilon=\frac{H_{11}+H_{22}}{2}\pm\frac{1}{2}\sqrt{\left(H_{11}-H_{12}\right)^2+4H_{12}^2}$$

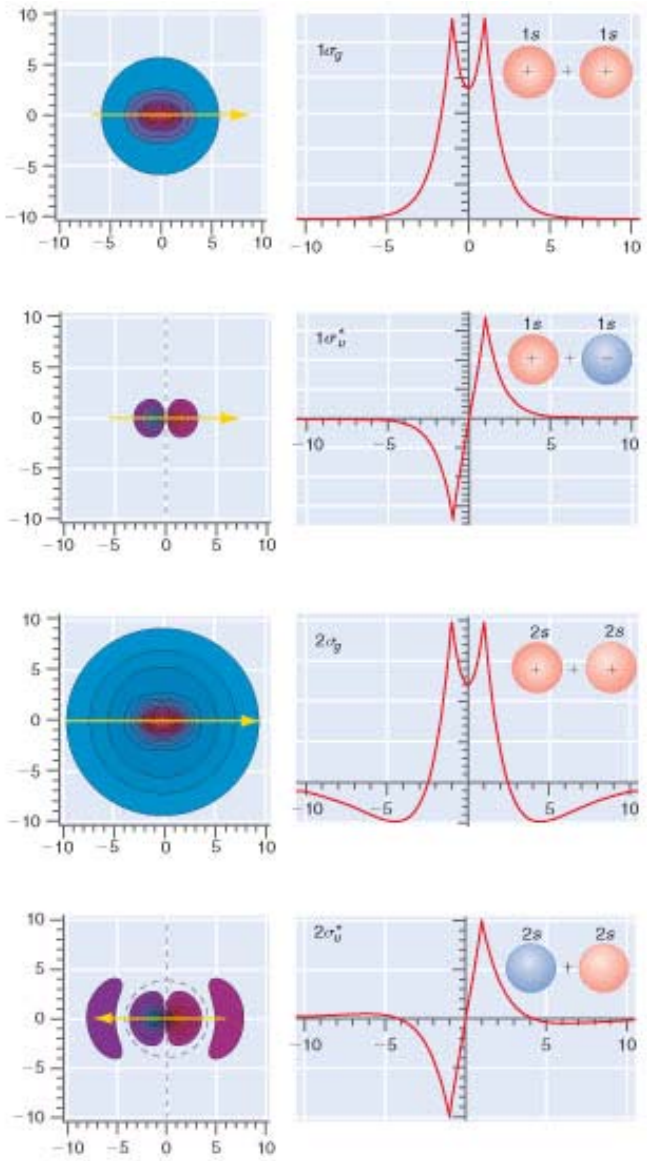


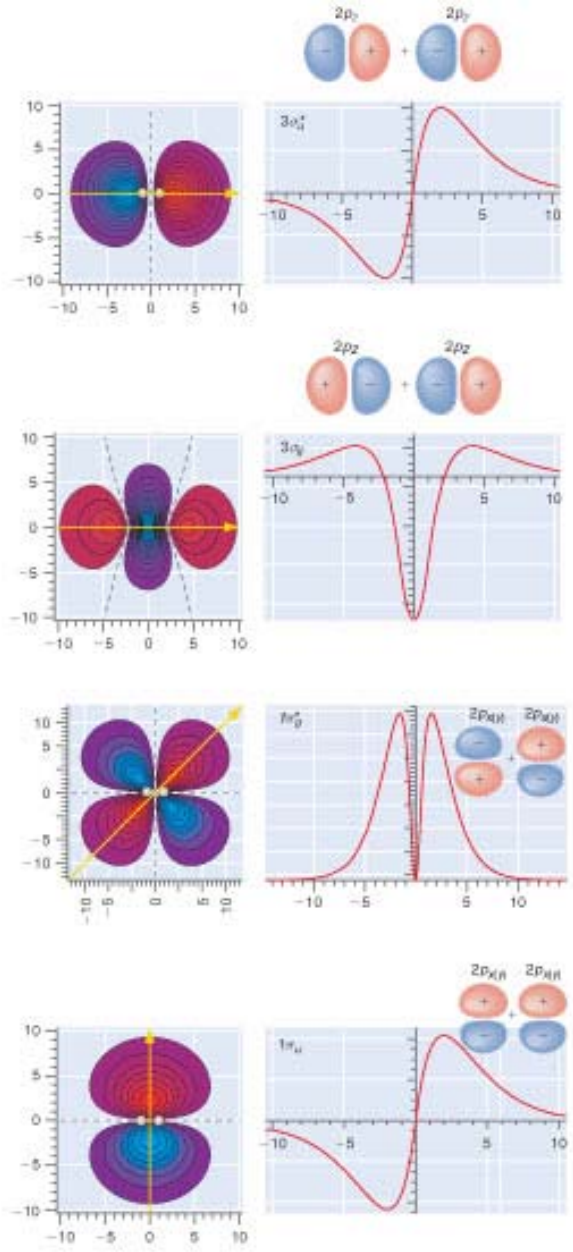
$$\varepsilon_+ \approx H_{11} + \frac{H_{12}^2}{H_{11} - H_{22}}$$

$$\varepsilon_- \approx H_{22} - \frac{H_{12}^2}{H_{11} - H_{22}}$$

If $\left|H_{11} - H_{22}\right| >> 2\left|H_{12}\right|$

Given ε_1 and ε_2, can solve for c_1
(actually, c_{11},c_{21}; c_{12}, c_{22})





$1s \rightarrow 1\sigma_g$

$1\sigma_u$

$2s \rightarrow 2\sigma_g$

$2\sigma_u$

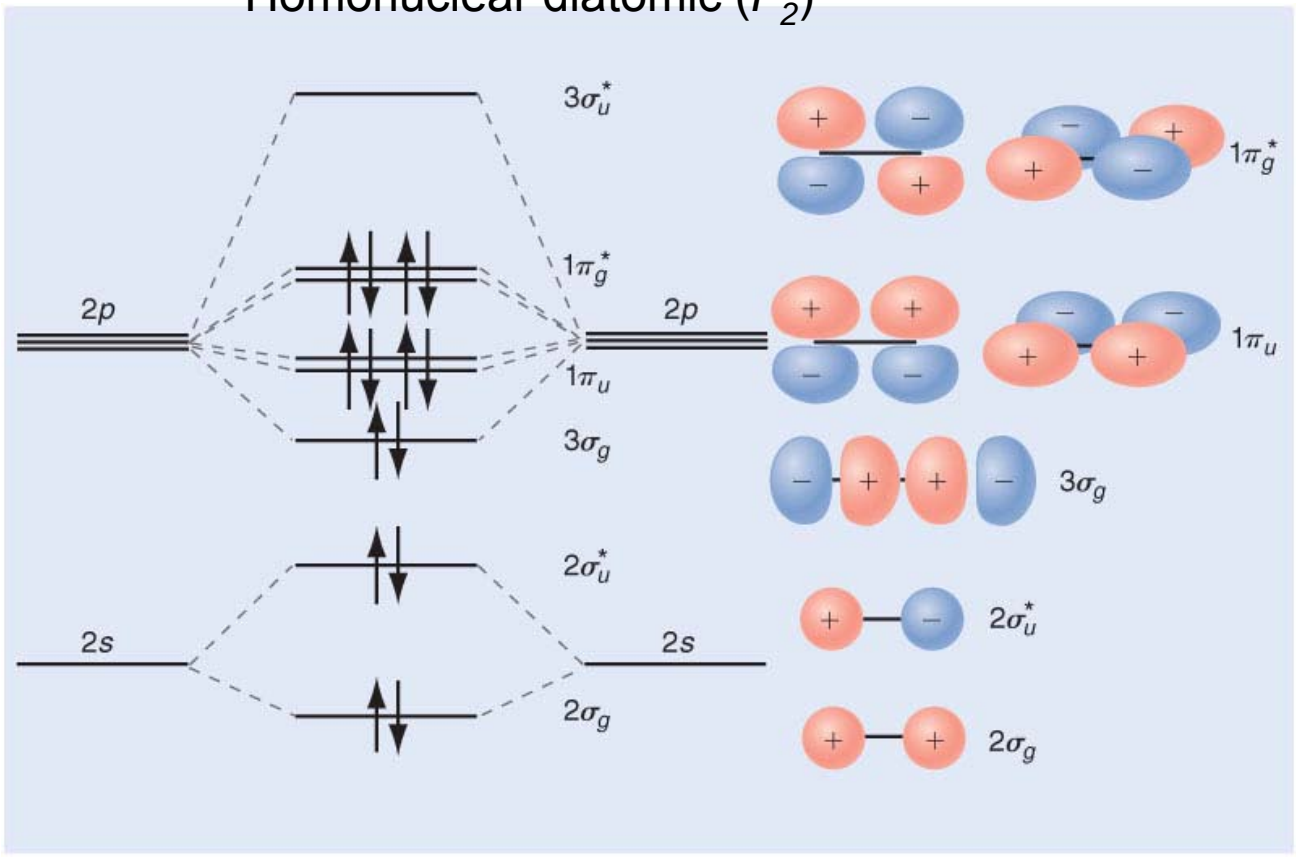
$2p_z \rightarrow 3\sigma_g$

$3\sigma_u$

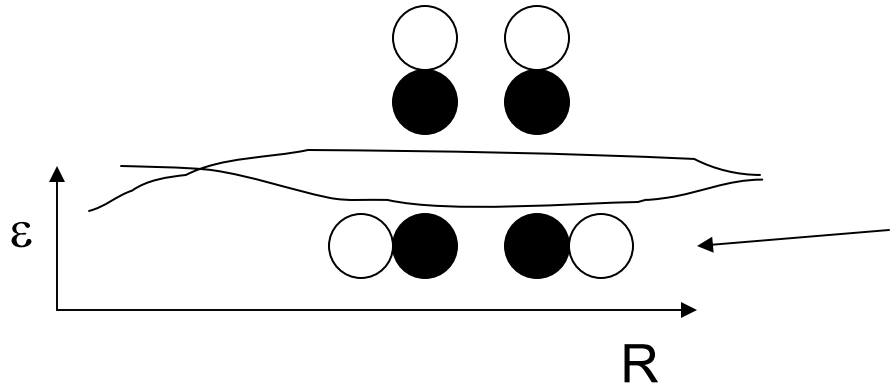
$2p_x \rightarrow 1\pi_{ux}, 1\pi_{uy}$

$2p_y \quad 1\pi_{gx}, 1\pi_{gy}$

Homonuclear diatomic (F_2)



Exact order of MO's derived from *2p* AO's depends on distance



σ_g favored at long R; π_u at short R

$Li_2 \quad ... \quad 2\sigma_g^2, \qquad BO = 1$

$Be_2 \quad ... \quad 2\sigma_g^2 2\sigma_u^2, \qquad BO = 0$

$B_2 \quad ... \quad 2\sigma_g^2 2\sigma_u^2 1\pi_u^2, \qquad BO = 1$

$C_2 \quad ... \quad 2\sigma_g^2 2\sigma_u^2 1\pi_u^4, \qquad BO = 2$

$N_2 \quad ... \quad 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2, \qquad BO = 3$

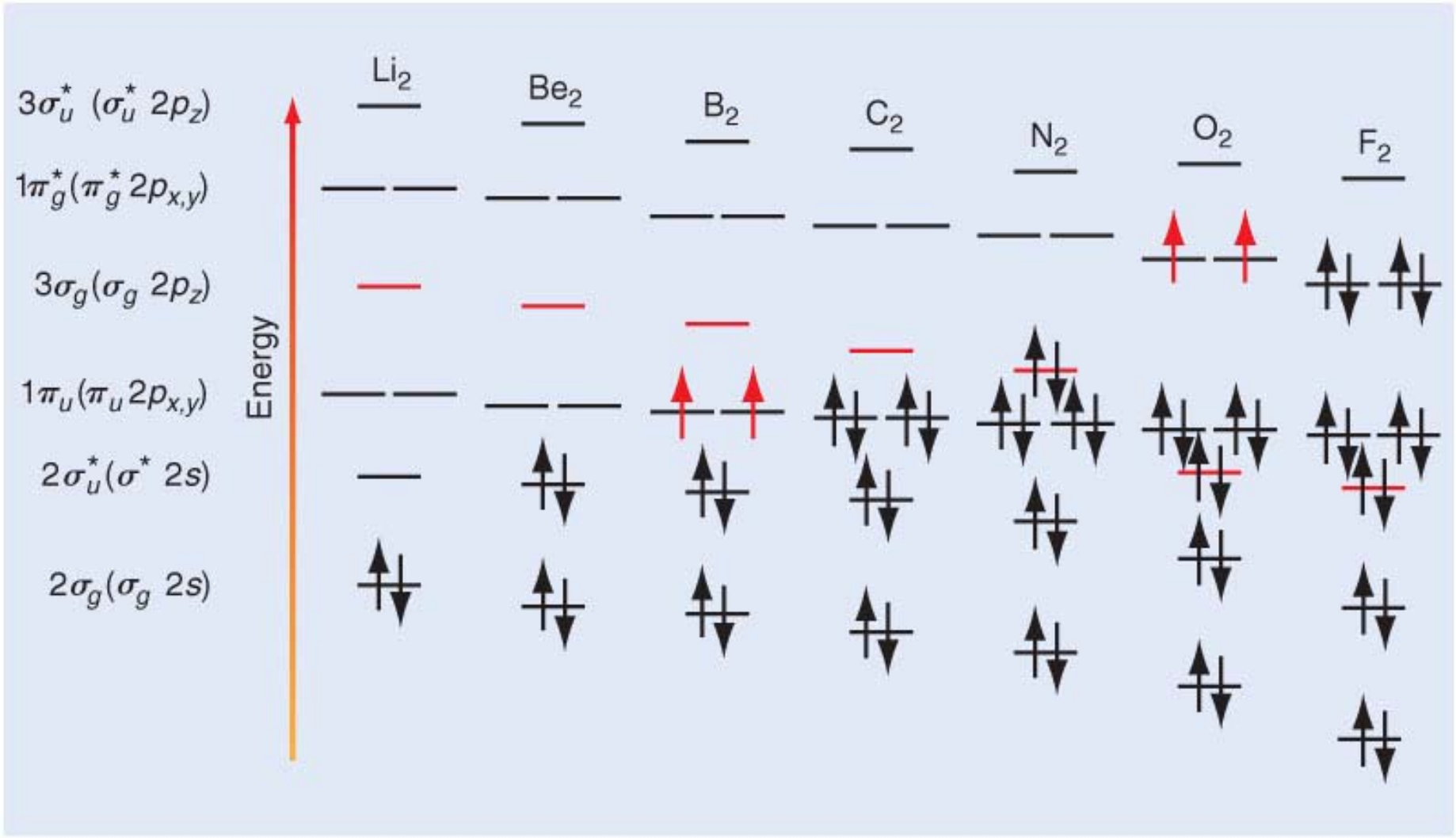
$O_2 \quad ... \quad 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2 1\pi_g^2, \qquad BO = 2$

$F_2 \quad ... \quad 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2 1\pi_g^4, \qquad BO = 1$

$Ne_2 \quad ... \quad 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2 1\pi_g^4 3\sigma_u^2, \qquad BO = 0$

Bond order =

$$\frac{\#\text{ bonding} - \#\text{ antibonding electron}}{2}$$



Li_2 $^1\sum_g$

Be_2 $^1\sum_g$

B_2 $^3\sum_g$ $\left(\text{also } ^1\sum_g, ^1\Delta_g\right)$

C_2 $^1\sum_g$

N_2 $^1\sum_g$

O_2 $^3\sum_g$ $\left(\text{also } ^1\sum_g, ^1\Delta_g\right)$

F_2 $^1\sum_g$

Ne_2 $^1\sum_g$

CO $\longrightarrow$ isoelectronic with N_2 $\Rightarrow$ $BO = 3$

"g", "u" symmetry not present

$\underbrace{1\sigma^2 2\sigma^2}_{1s}$ $\underbrace{3\sigma^2 4\sigma^2}_{2s}$ $\underbrace{5\sigma^2}_{2p_z}$ $\underbrace{1\pi^4}_{2p_x,\ 2p_y}$

$^1\sum$ ground state

C_2^- isoelectronic with N_2^+

Note B_2 expected to have several low-lying excited states

$$\begin{cases} 1\pi_u^2 \rightarrow {}^3\sum_g, {}^1\sum_g, {}^1\Delta_g \\ 3\sigma_g 1\pi_u \rightarrow {}^3\Pi_u, {}^1\Pi_u \\ 3\sigma_g^2 \rightarrow {}^1\sum_g \end{cases}$$

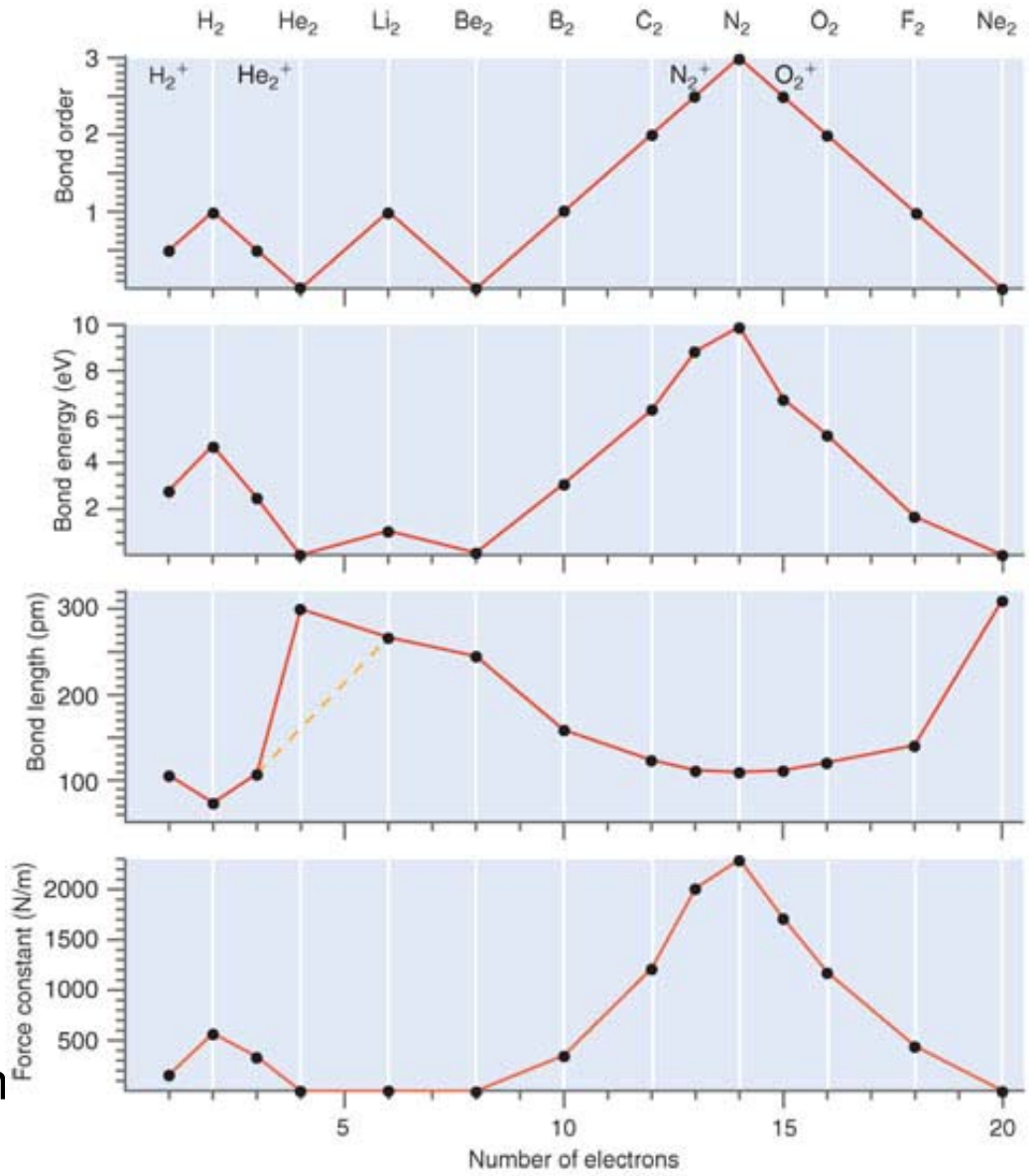


Table 13.11

Correlation between bond order and bond energy

high bond order $\Rightarrow$ strong bon
$\Rightarrow$ short R_e
$\Rightarrow$ large force constant

Homonuclear diatomics – *g, u* symmetry lost

$$CO \qquad \underbrace{1\sigma^2 2\sigma^2}_{1s} \; \underbrace{3\sigma^2 4\sigma^2}_{2s} \; \underbrace{5\sigma^2}_{2p_z} \; \underbrace{1\pi^4}_{2p_x, 2p_y}$$

$$HF \qquad 1\sigma^2 \; 2\sigma^2 \; 3\sigma^2 \; 1\pi^4$$

$$F_{1s} \quad F_{2s} \quad F_{2p_z} \quad F_{2p_x}, F_{2p_y}$$

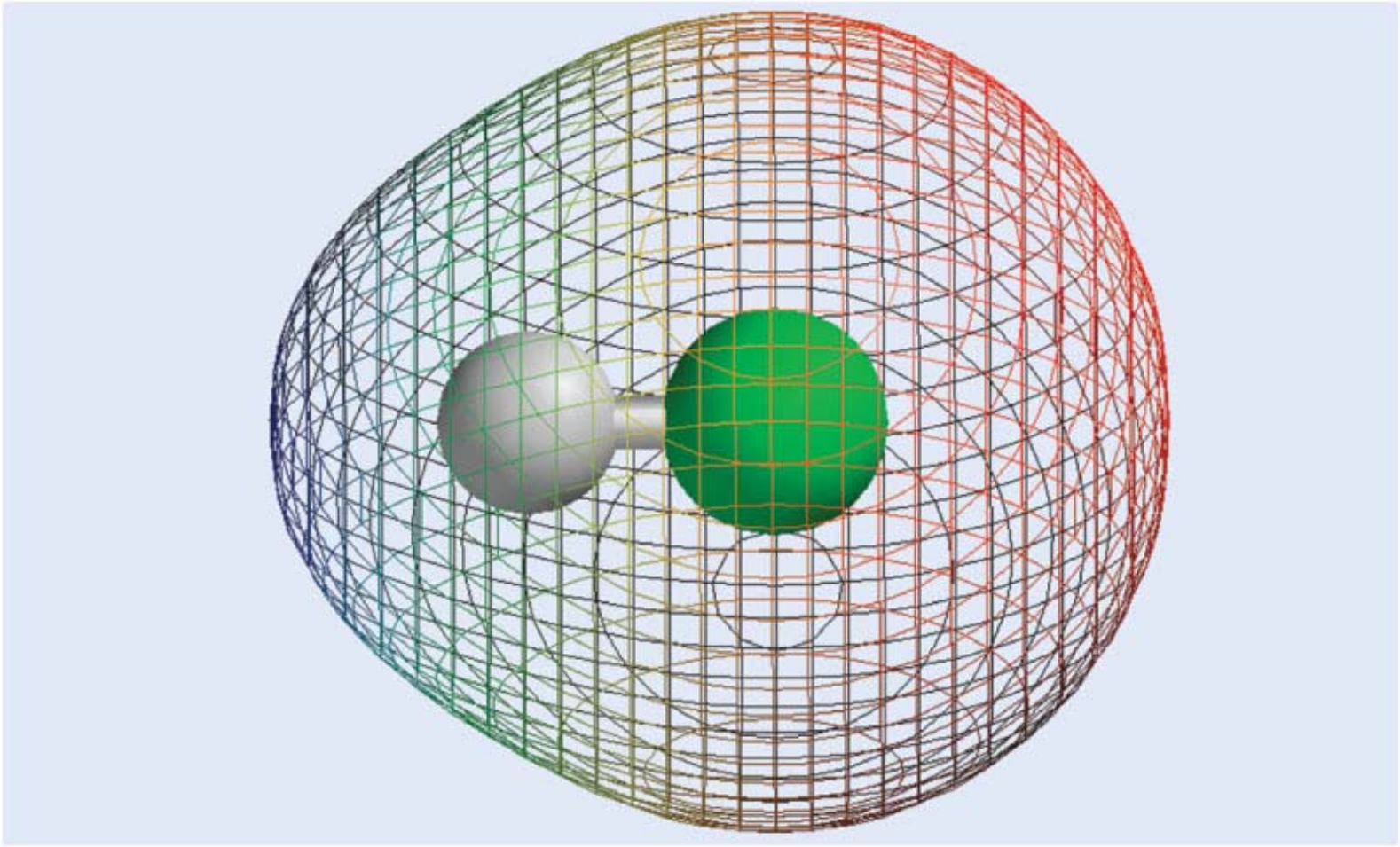
$$+ H_{1s}$$

lone pairs

Note numbering error in text

Electrostatic potential

$$\phi(x,y,z) = \underbrace{\sum_i \frac{q_i}{4\pi\varepsilon_0 r_i}}_{\text{nuclei}} \underbrace{- e\int \frac{\rho(x,y,z)}{4\pi\varepsilon_0 r_e} dxdydz}_{\text{electrons}}$$



Electrostatic potential: HF