Moléculas Poliatômicas

$$\widehat{H}\Psi = E\Psi$$

$$\hat{H} = -\frac{\hbar^2}{2}\sum_{\alpha} \frac{1}{m_\alpha}\nabla_\alpha^2 - \frac{\hbar^2}{2m_e}\sum_{i} \nabla_i^2 + \sum_{\alpha}\sum_{\beta>\alpha}\frac{Z_\alpha Z_\beta e^2}{4\pi\varepsilon_0 r_{\alpha\beta}} - \sum_{\alpha}\sum_{i} \frac{Z_\alpha e^2}{4\pi\varepsilon_0 r_{i\alpha}} + \sum_{j}\sum_{i>j}\frac{e^2}{4\pi\varepsilon_0 r_{ij}}$$

núcleos α, β

elétrons i, j

coordenadas dos elétrons

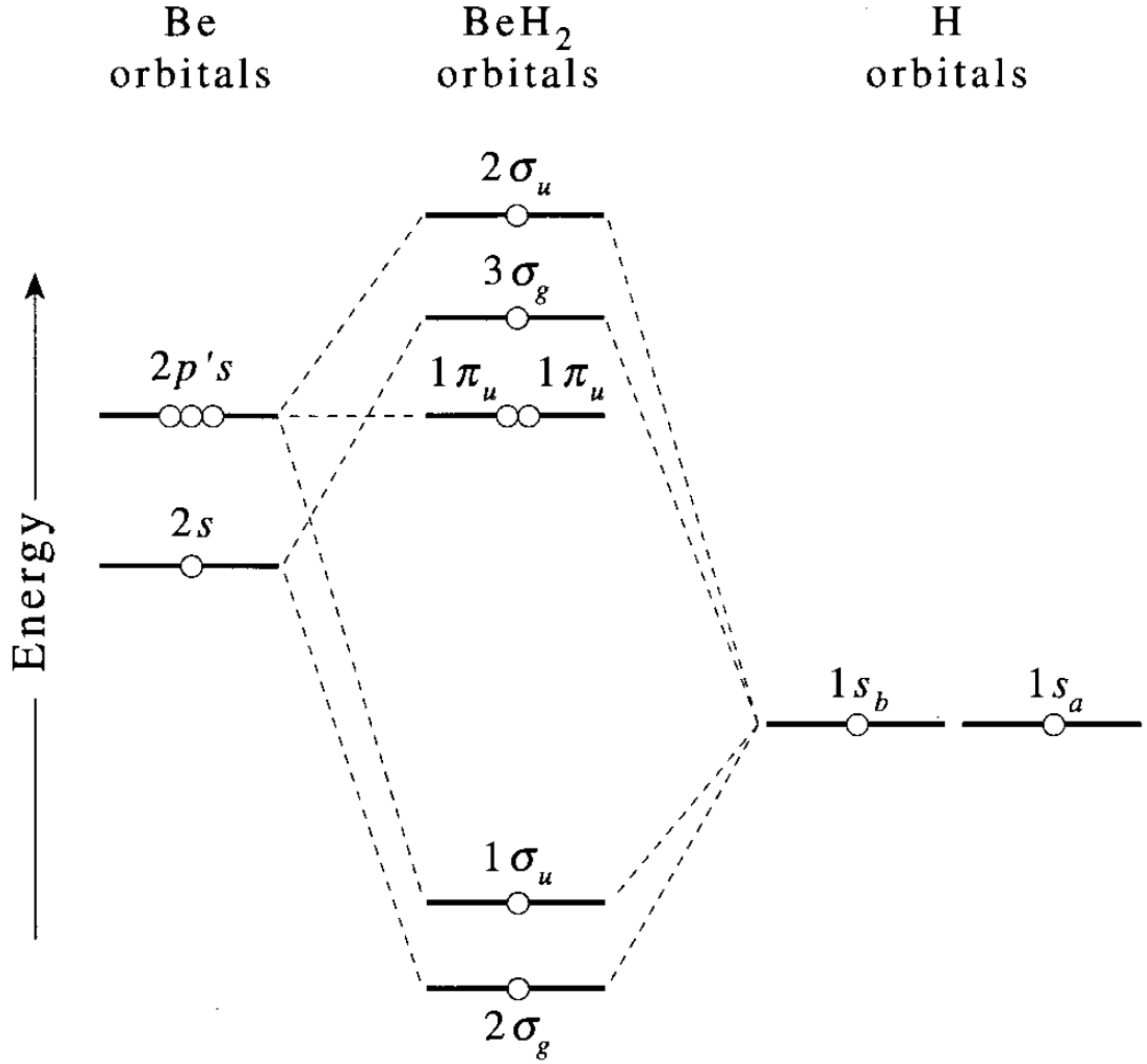
aproximação de Born-Oppenheimer → eq. de Schrödinger eletrônica → $\psi_{\mathrm{el}}\left(q_i; q_\alpha\right)$

depende parametricamente da configuração nuclear

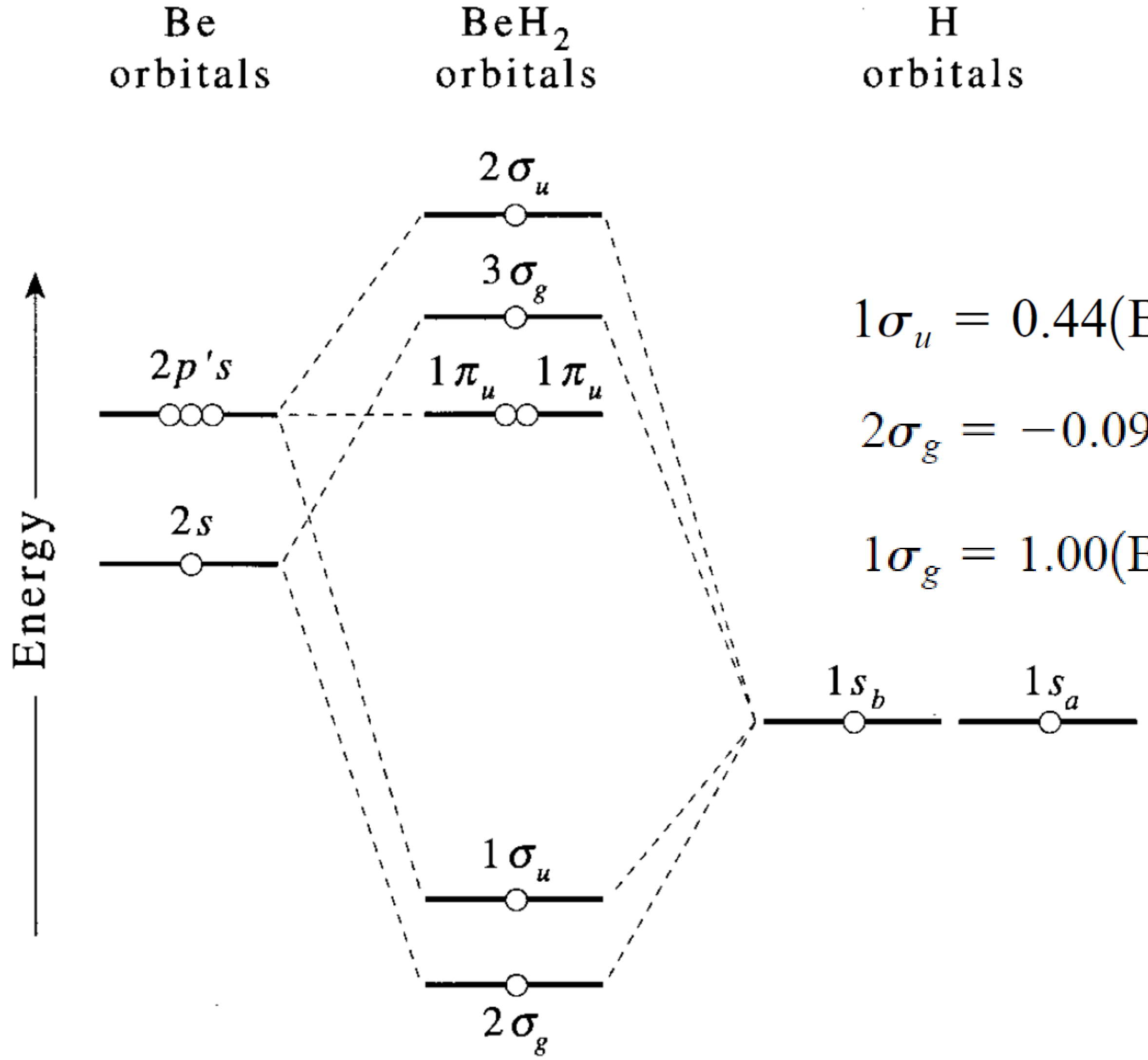
$$\psi = c_1 1s_{\mathrm{H_a}} + c_2 1s_{\mathrm{H_b}} + c_3 2s_{\mathrm{A}} + c_4 2p_{x\mathrm{A}} + c_5 2p_{y\mathrm{A}} + c_6 2p_{z\mathrm{A}}$$

$\mathbf{BeH_2}$

$(1\sigma_g)^2(2\sigma_g)^2(1\sigma_u)^2$



BeH_2 $(1\sigma_g)^2(2\sigma_g)^2(1\sigma_u)^2$

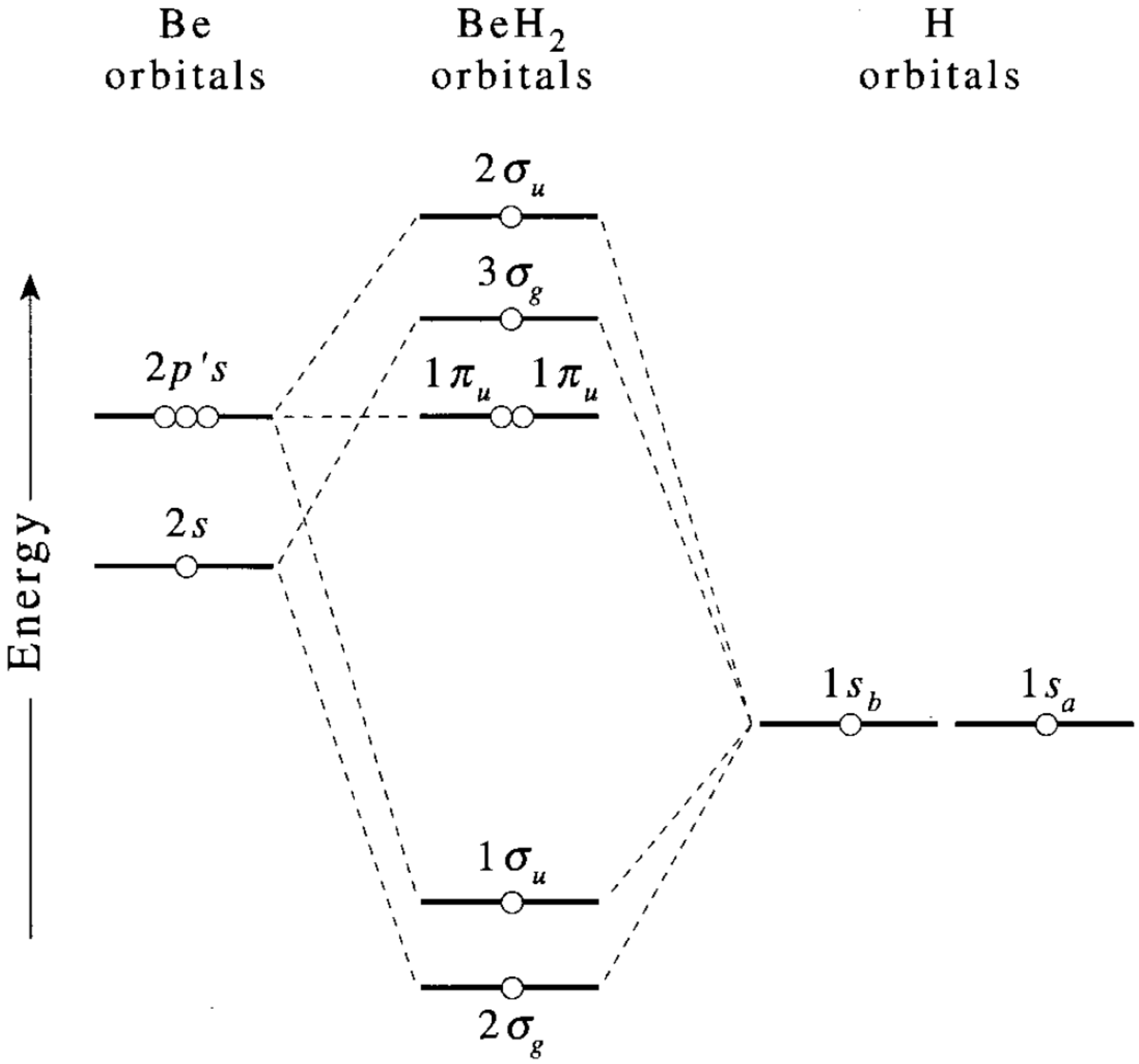


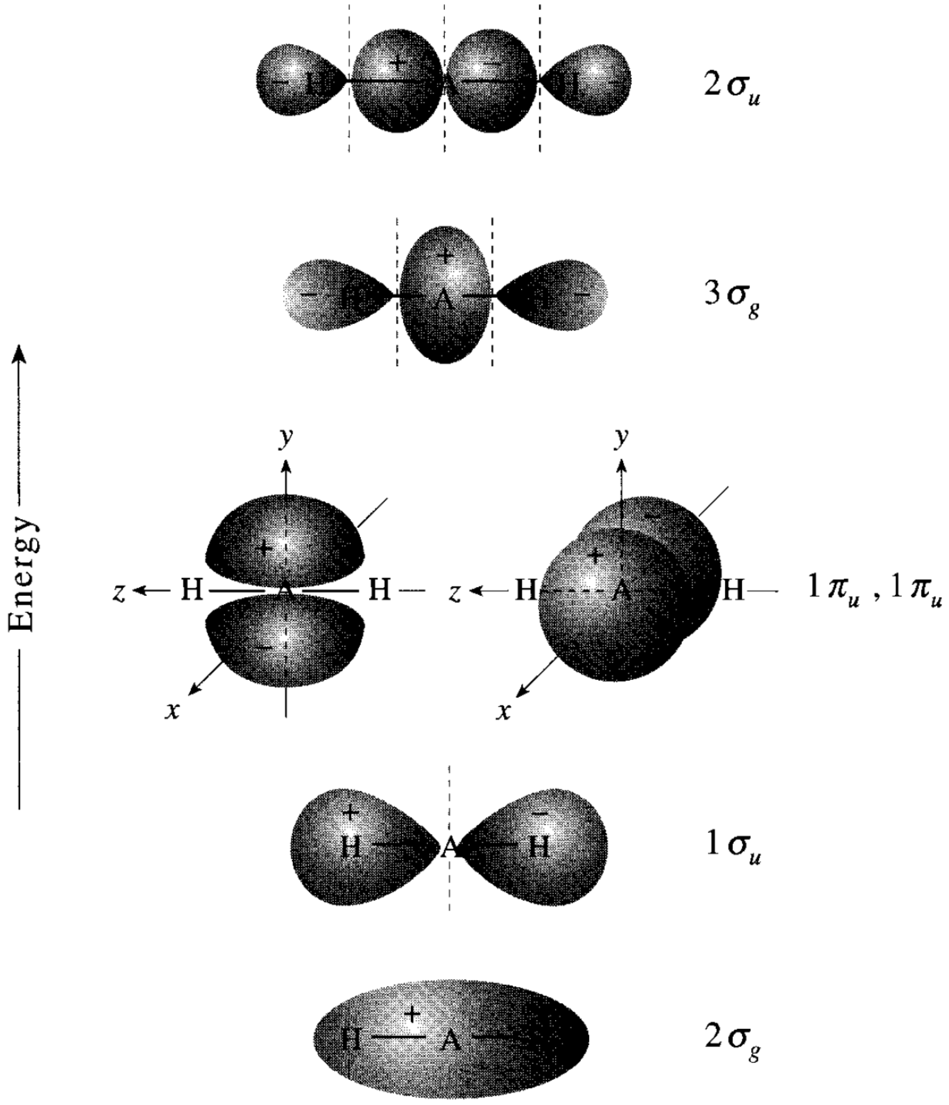
$$1\sigma_u = 0.44(\text{Be}2p_z) + 0.44(\text{H}_\text{A}1s - \text{H}_\text{B}1s)$$

$$2\sigma_g = -0.09(\text{Be}1s) + 0.40(\text{Be}2s) + 0.45(\text{H}_\text{A}1s + \text{H}_\text{B}1s)$$

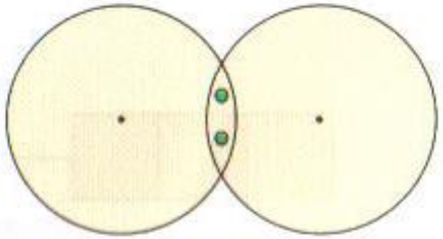
$$1\sigma_g = 1.00(\text{Be}1s) + 0.016(\text{Be}2s) - 0.002(\text{H}_\text{A}1s + \text{H}_\text{B}1s)$$

I. N. Levine, *Quantum Chemistry*, Prentice Hall, 5^a ed., 2000, cap. 19.6.


Be orbitals
BeH$_2$ orbitals
H orbitals
Energy
$2\sigma_u$
$3\sigma_g$
$2p's$
$1\pi_u$ $1\pi_u$
$2s$
$1s_b$
$1s_a$
$1\sigma_u$
$2\sigma_g$


$2\sigma_u$
$3\sigma_g$
Energy
y
z
x
H
A
+
−
$1\pi_u$, $1\pi_u$
$1\sigma_u$
$2\sigma_g$

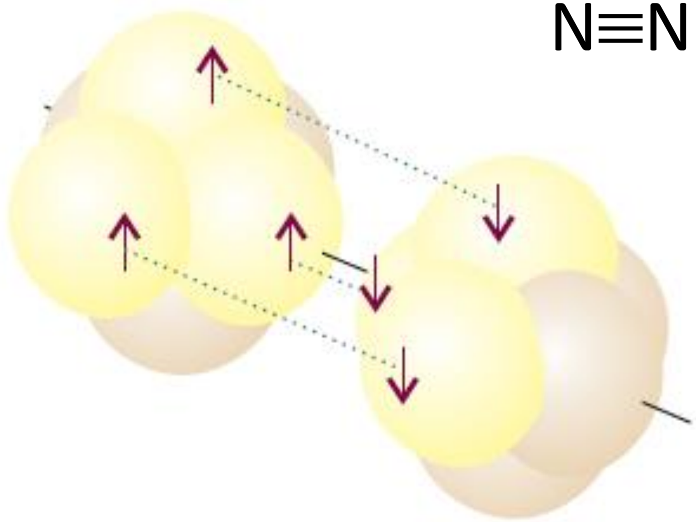
Teoria da Ligação de Valência



Par de elétrons compartilhado

Estruturas de Lewis (1916)

N≡N



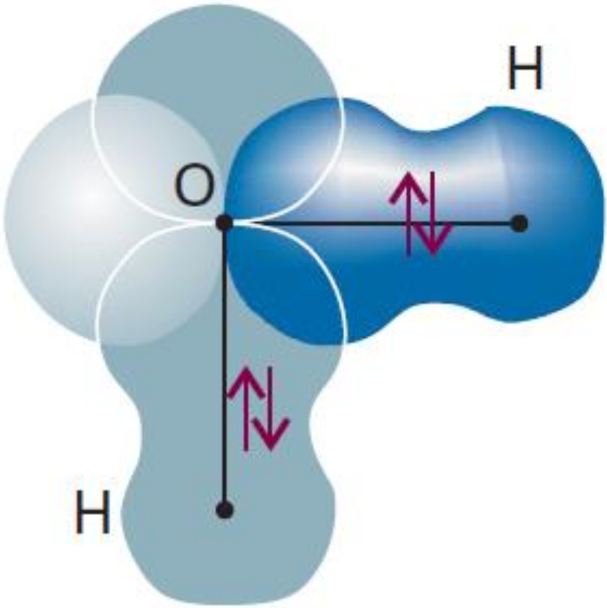
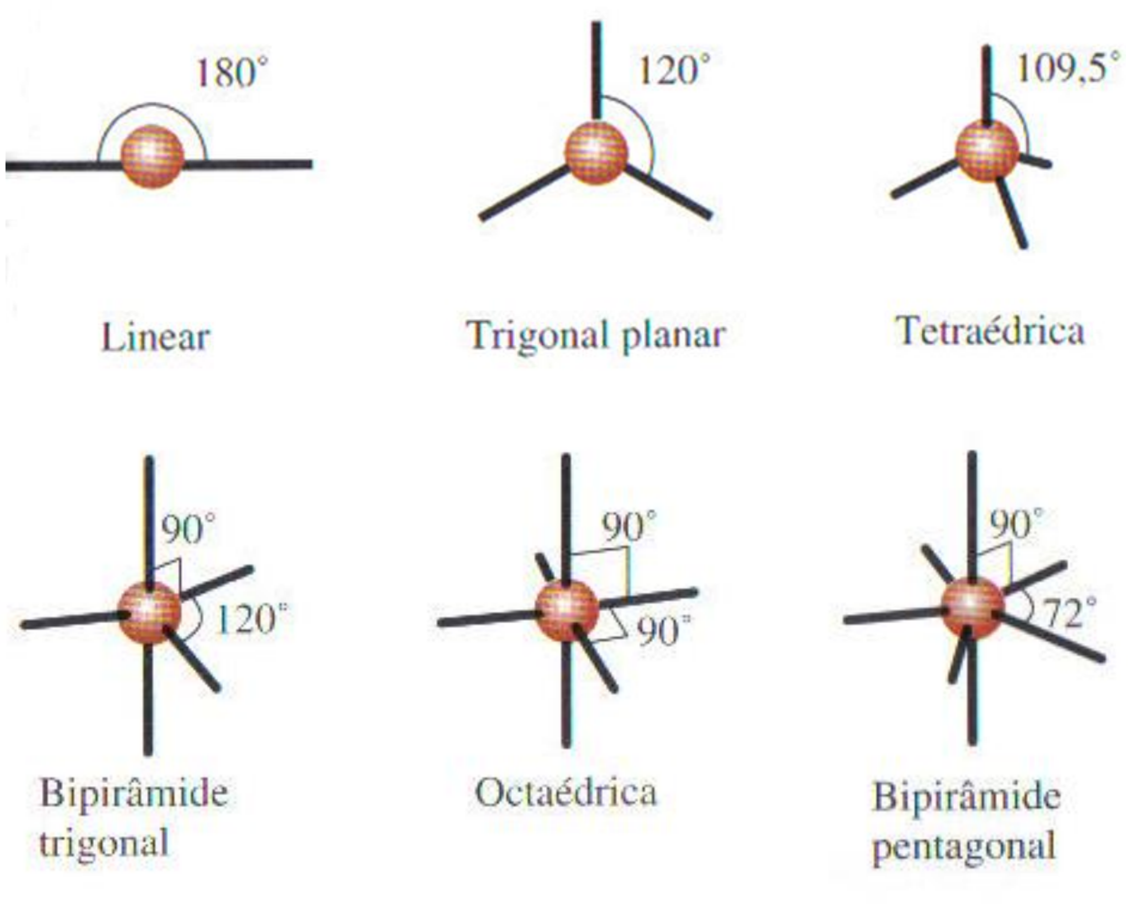
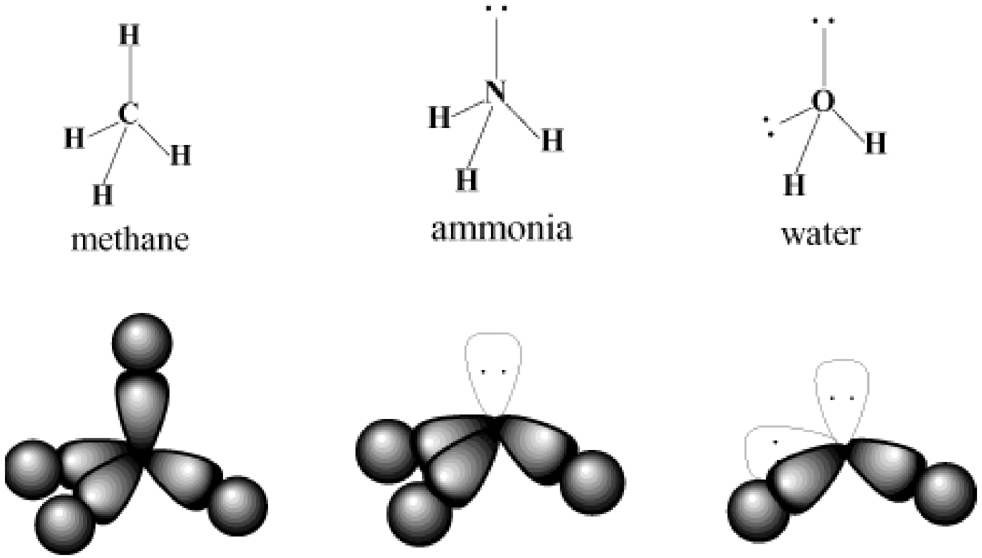


Fig. 11.6 A first approximation to the valence-bond description of bonding in an H_2O molecule. Each σ bond arises from the overlap of an H1*s* orbital with one of the O2*p* orbitals. This model suggests that the bond angle should be 90°, which is significantly different from the experimental value.

Estruturas moleculares básicas

Teoria VSEPR (*valence shell electron pair repulsion*)





Hibridização de Orbitais

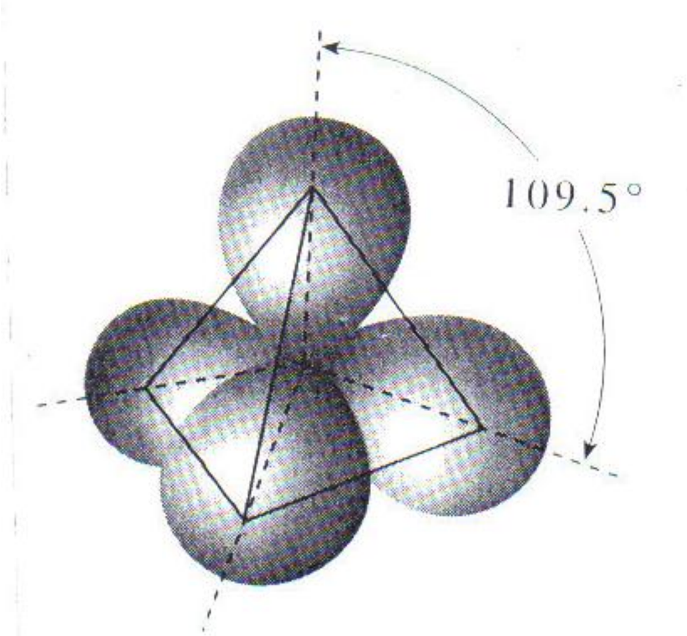
sp^3

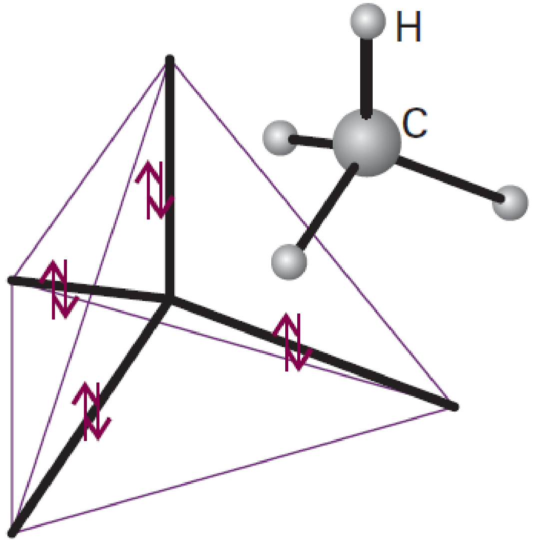
$$\psi_1 = \frac{1}{2}(2s + 2p_x + 2p_y + 2p_z)$$

$$\psi_2 = \frac{1}{2}(2s - 2p_x - 2p_y + 2p_z)$$

$$\psi_3 = \frac{1}{2}(2s + 2p_x - 2p_y - 2p_z)$$

$$\psi_4 = \frac{1}{2}(2s - 2p_x + 2p_y - 2p_z)$$



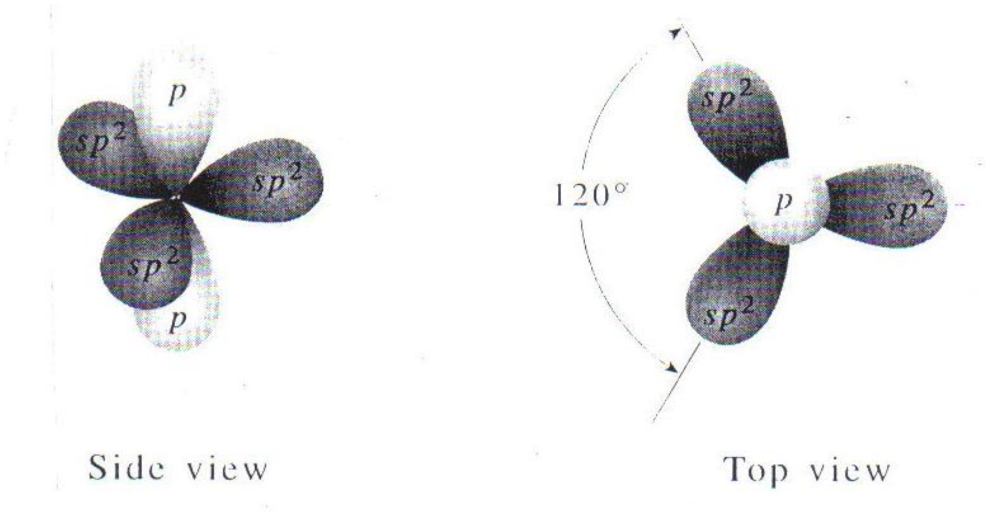


sp^2

$$\psi_1 = \frac{1}{\sqrt{3}}2s + \sqrt{\frac{2}{3}}2p_z$$

$$\psi_2 = \frac{1}{\sqrt{3}}2s - \frac{1}{\sqrt{6}}2p_z + \frac{1}{\sqrt{2}}2p_x$$

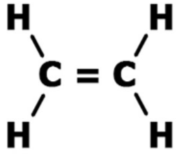
$$\psi_3 = \frac{1}{\sqrt{3}}2s - \frac{1}{\sqrt{6}}2p_z - \frac{1}{\sqrt{2}}2p_x$$

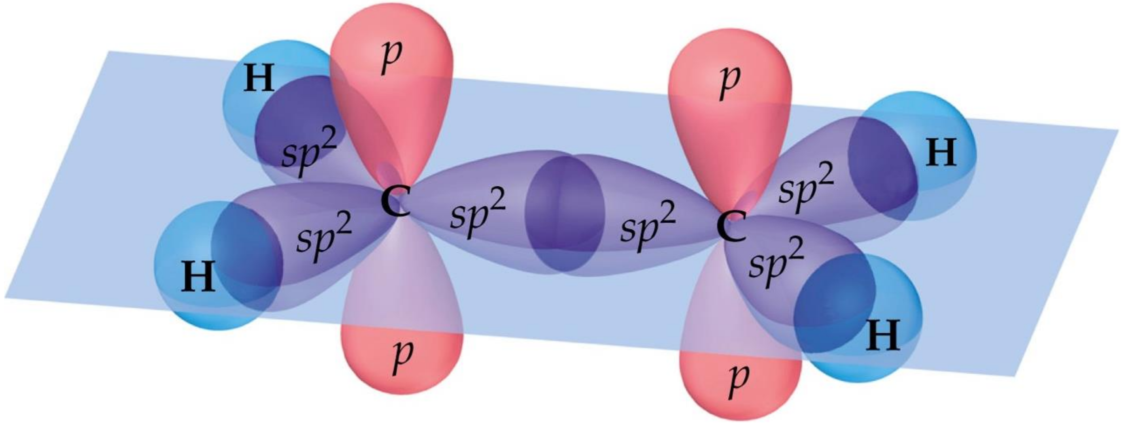


Side view

Top view

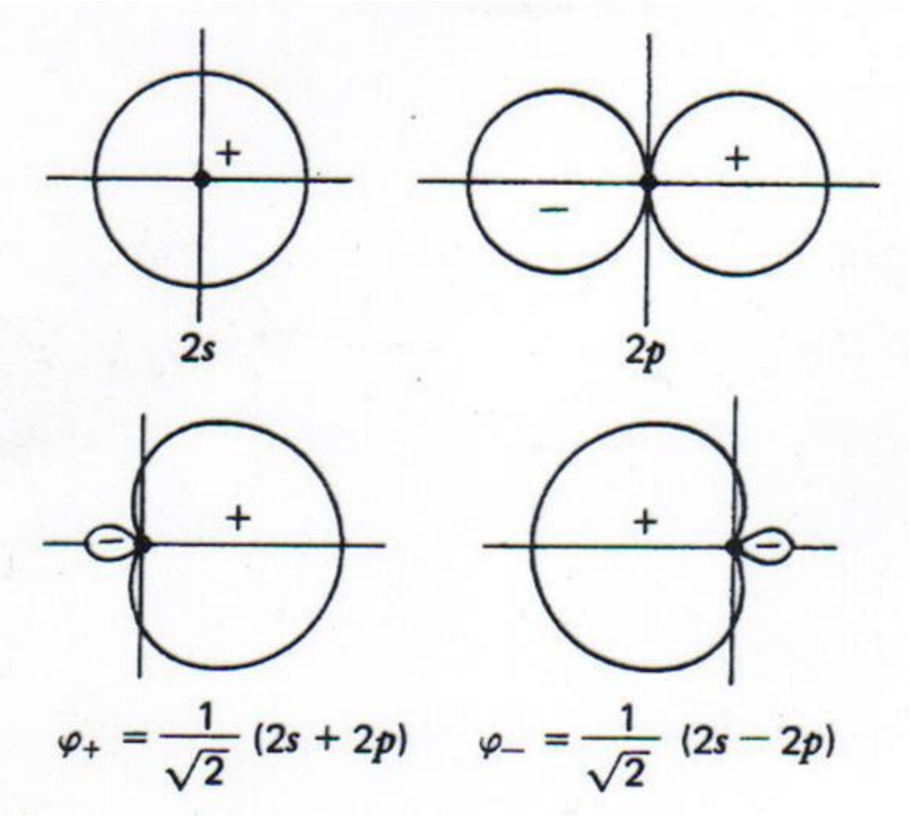
Eteno

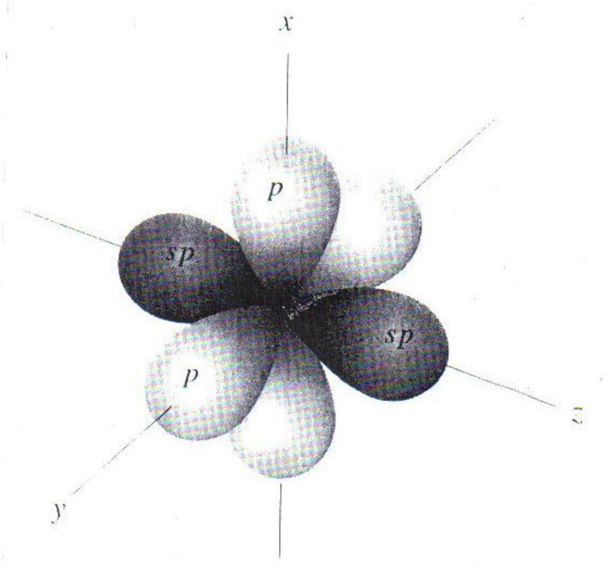




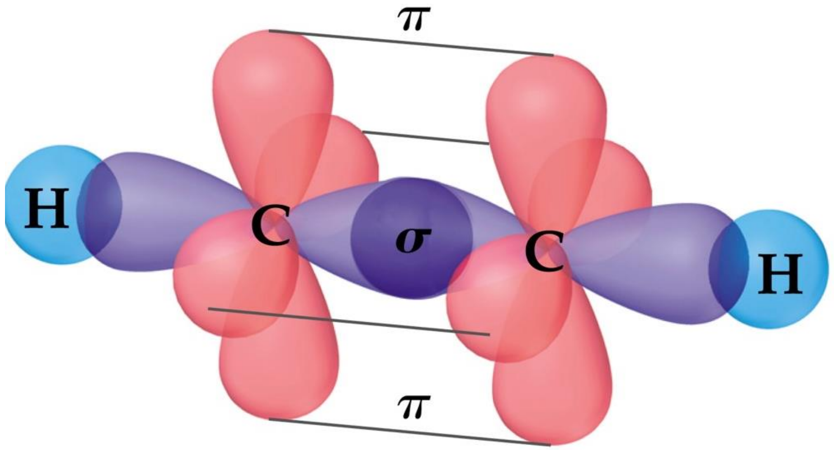
sp

$$\psi_{sp} = \frac{1}{\sqrt{2}}(2s \pm 2p_z)$$





Etino $H{-}C{\equiv}C{-}H$



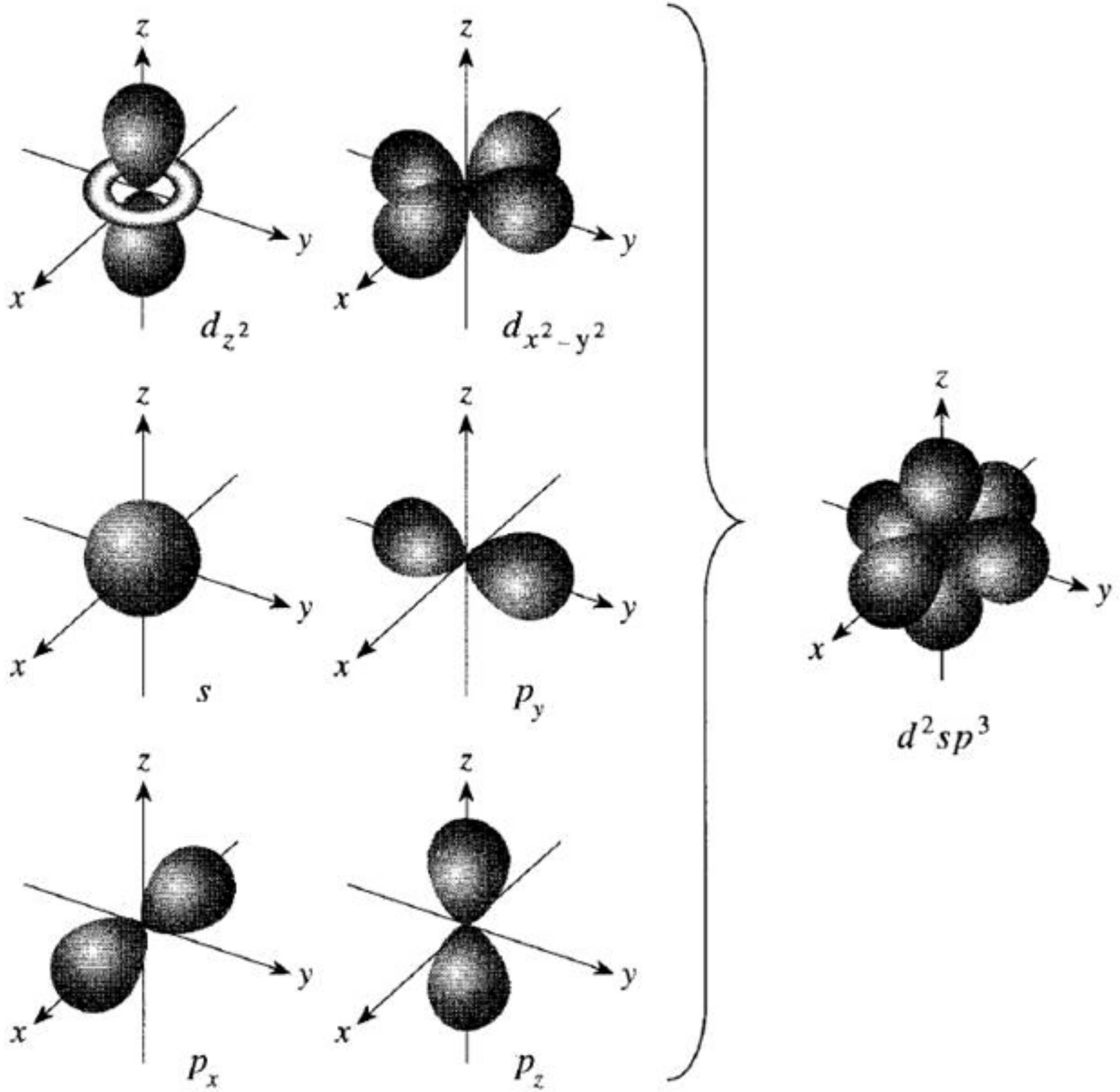

z
y
x
d_{z^2}
$d_{x^2-y^2}$
s
p_y
p_x
p_z
d^2sp^3

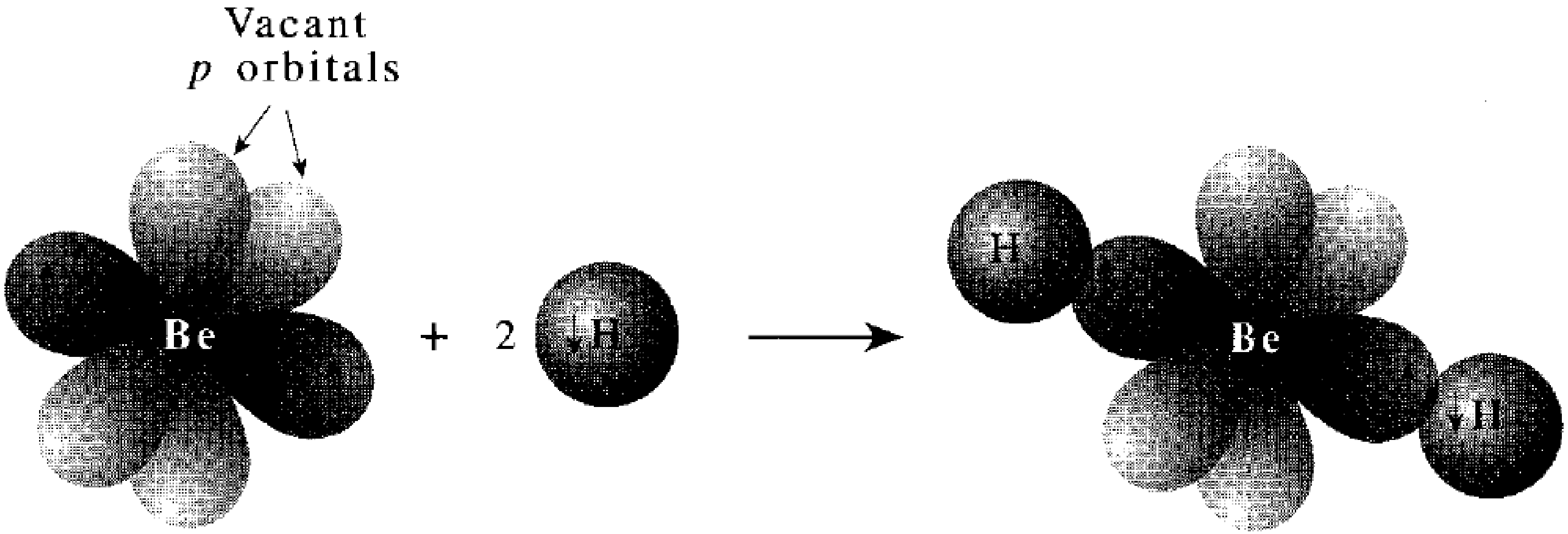
Table 11.1* Some hybridization schemes

Coordination number	Arrangement	Composition
2	Linear	sp, pd, sd
	Angular	sd
3	Trigonal planar	sp^2, p^2d
	Unsymmetrical planar	spd
	Trigonal pyramidal	pd^2
4	Tetrahedral	sp^3, sd^3
	Irregular tetrahedral	spd^2, p^3d, dp^3
	Square planar	p^2d^2, sp^2d
5	Trigonal bipyramidal	sp^3d, spd^3
	Tetragonal pyramidal	sp^2d^2, sd^4, pd^4, p^3d^2
	Pentagonal planar	p^2d^3
6	Octahedral	sp^3d^2
	Trigonal prismatic	spd^4, pd^5
	Trigonal antiprismatic	p^3d^2

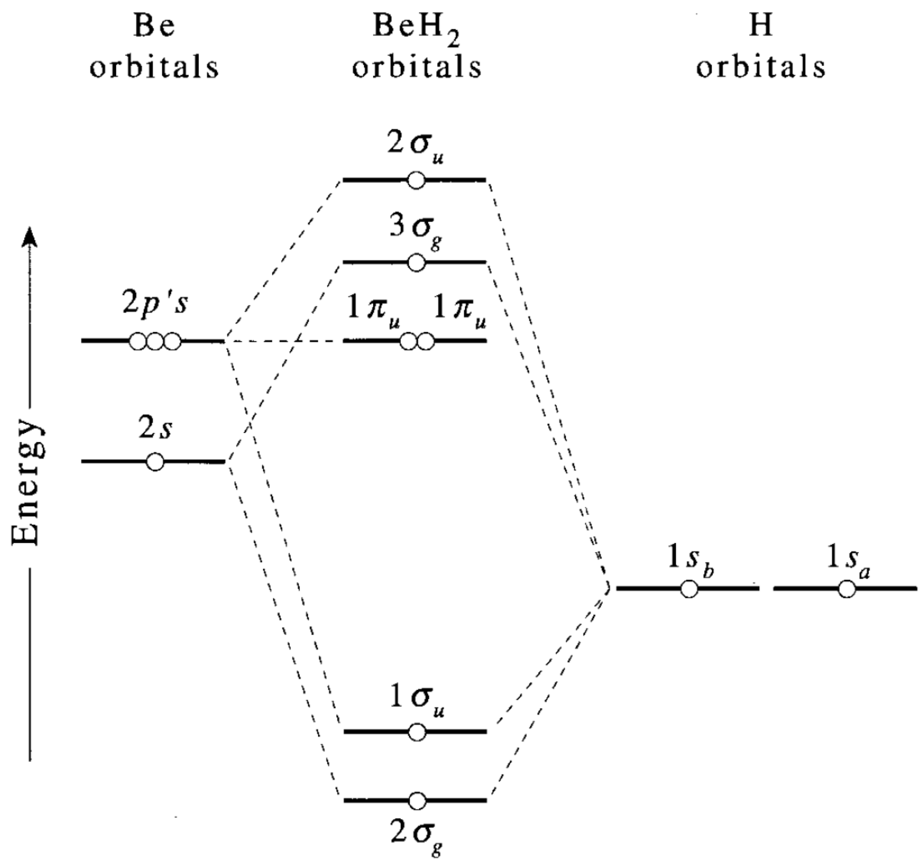
* Source: H. Eyring, J. Walter, and G.E. Kimball, *Quantum chemistry*, Wiley (1944).

H–Be–H

$$\psi_{\mathrm{Be-H}} = \boxed{c_1\psi_{\mathrm{Be}(2s)} + c_2\psi_{\mathrm{Be}(2p)}} + c_3\psi_{\mathrm{H}(1s)}$$

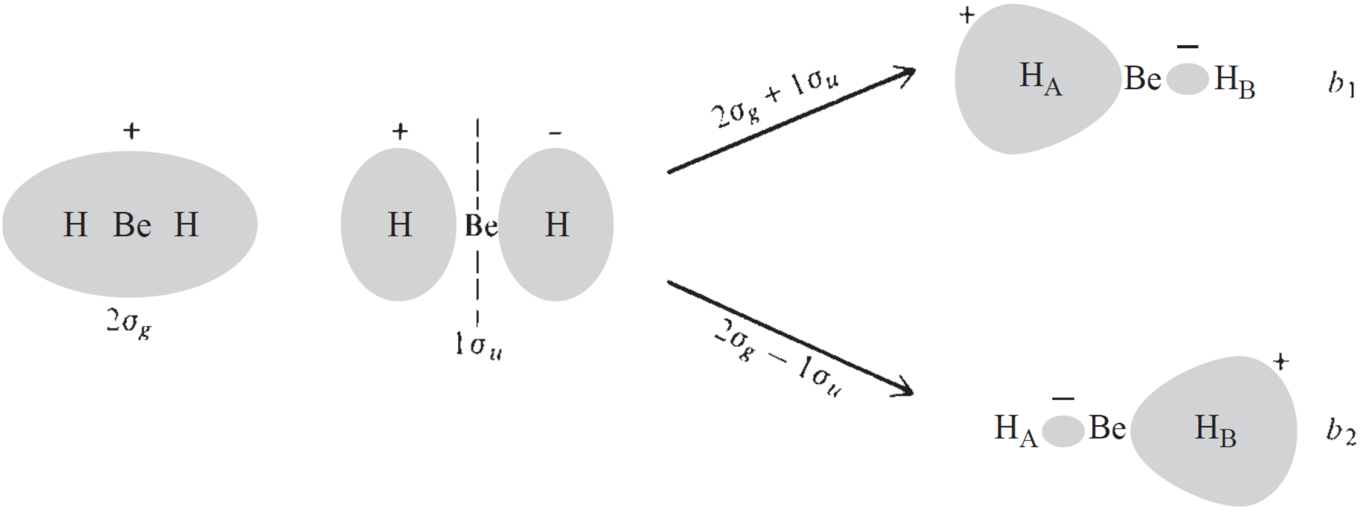


D. McQuarrie, J. D. Simon, *Physical Chemistry*, Univ. Sc. Books, 1997, cap. 10.1



$$b_1 = 2^{-1/2}(2\sigma_g + 1\sigma_u) \approx 2^{-1/2}[c_1(\mathrm{Be}2s + \mathrm{Be}2p_z) + 2c_2\mathrm{H_A}1s]$$

$$b_2 = 2^{-1/2}(2\sigma_g - 1\sigma_u) \approx 2^{-1/2}[c_1(\mathrm{Be}2s - \mathrm{Be}2p_z) + 2c_2\mathrm{H_B}1s]$$



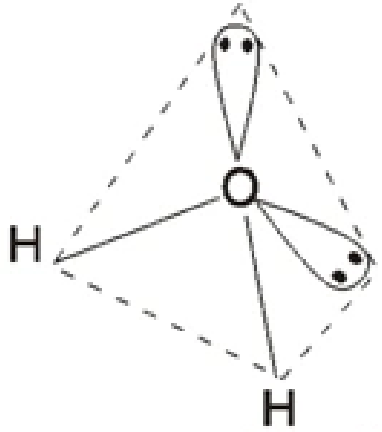
$$1\sigma_u = 0.44(\mathrm{Be}2p_z) + 0.44(\mathrm{H_A}1s - \mathrm{H_B}1s)$$

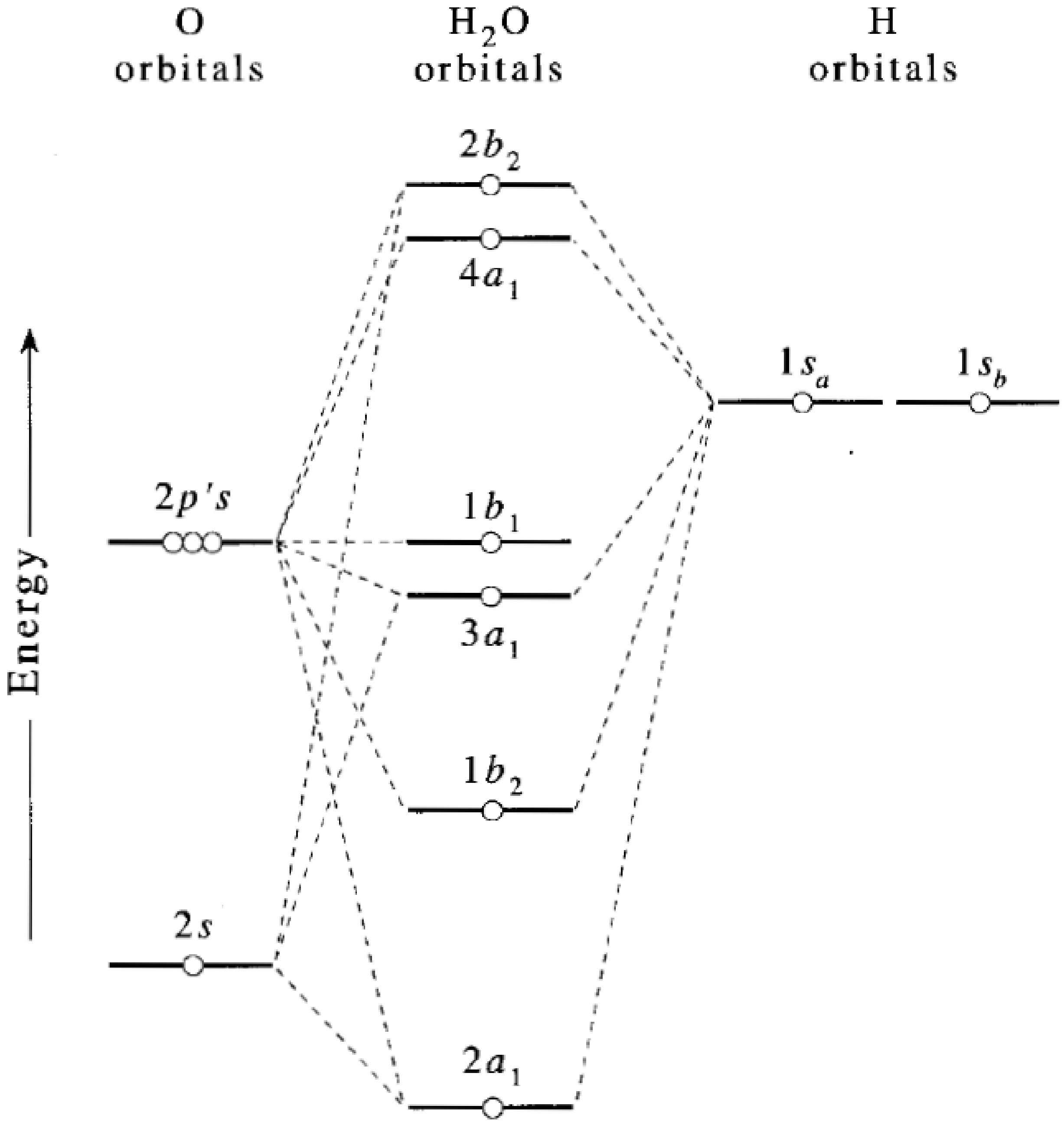
$$2\sigma_g = -0.09(\mathrm{Be}1s) + 0.40(\mathrm{Be}2s) + 0.45(\mathrm{H_A}1s + \mathrm{H_B}1s)$$

I. N. Levine, *Quantum Chemistry*,
Prentice Hall, 5ª ed., 2000, cap. 19.6

H_2O

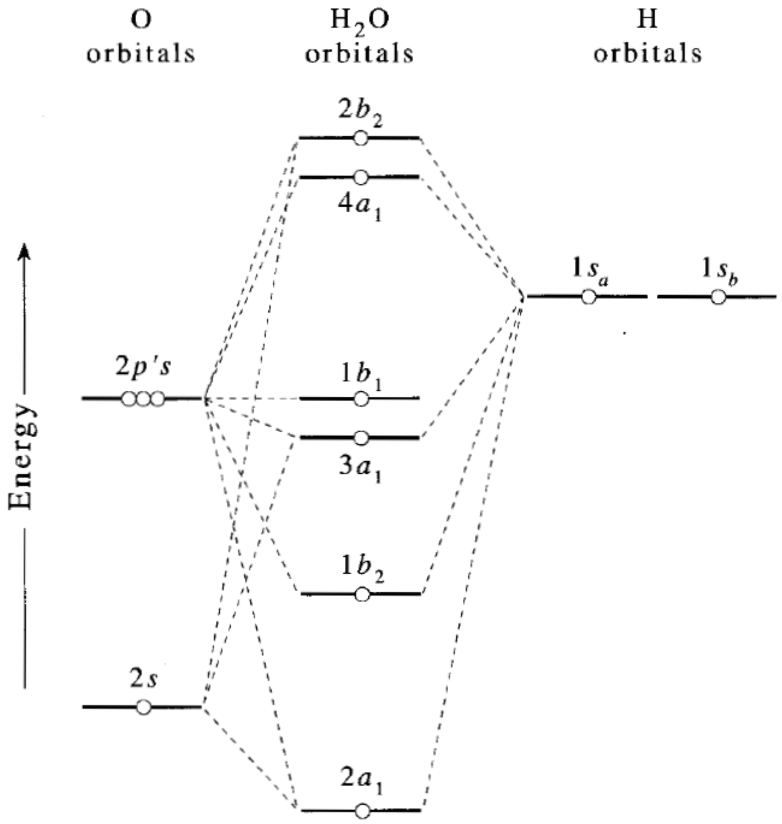
$(1\,a_1)^2\,(2\,a_1)^2\,(1\,b_2)^2\,(3\,a_1)^2\,(1\,b_1)^2$





H_2O

$(1\,a_1)^2\,(2\,a_1)^2\,(1\,b_2)^2\,(3\,a_1)^2\,(1\,b_1)^2$



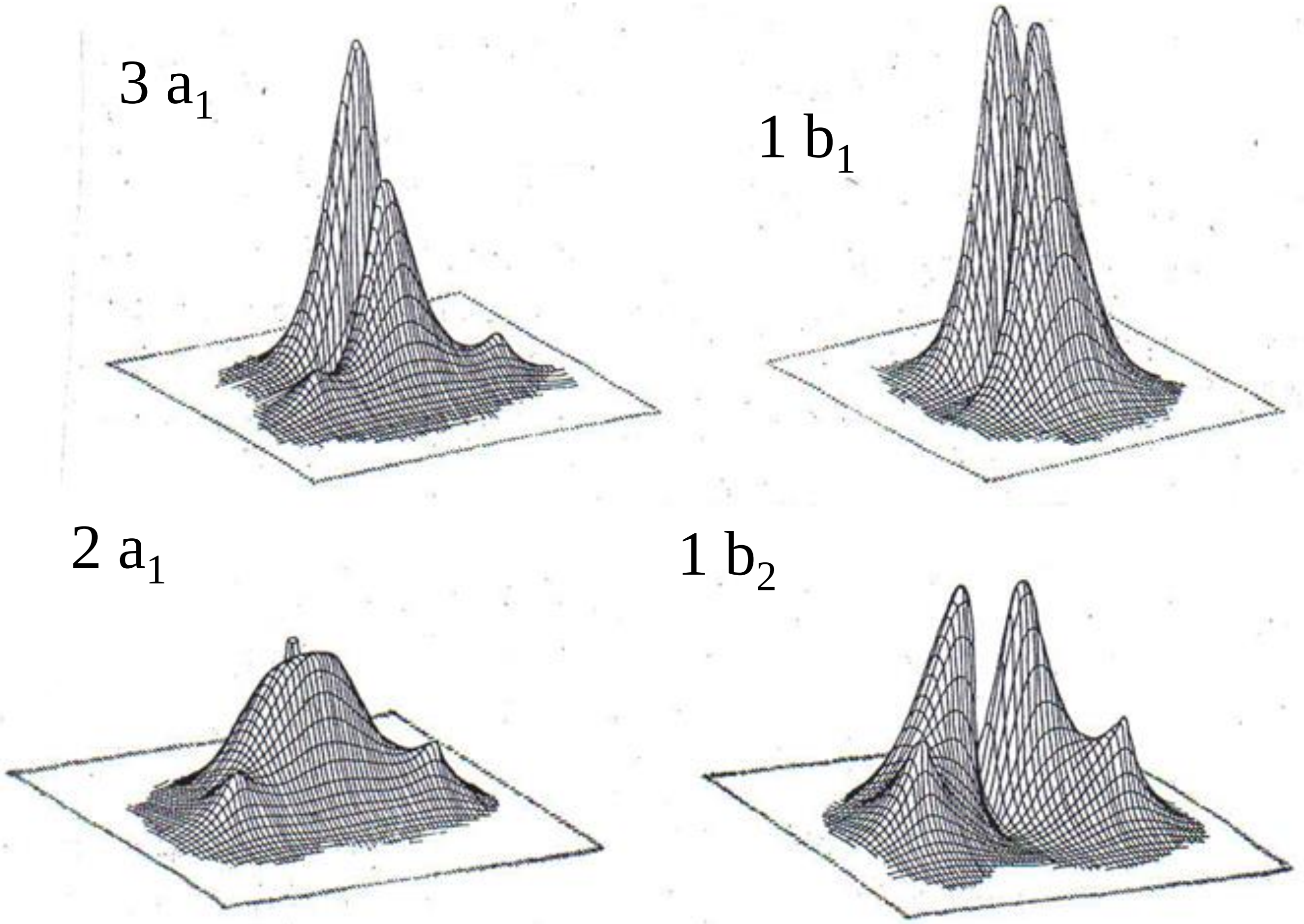
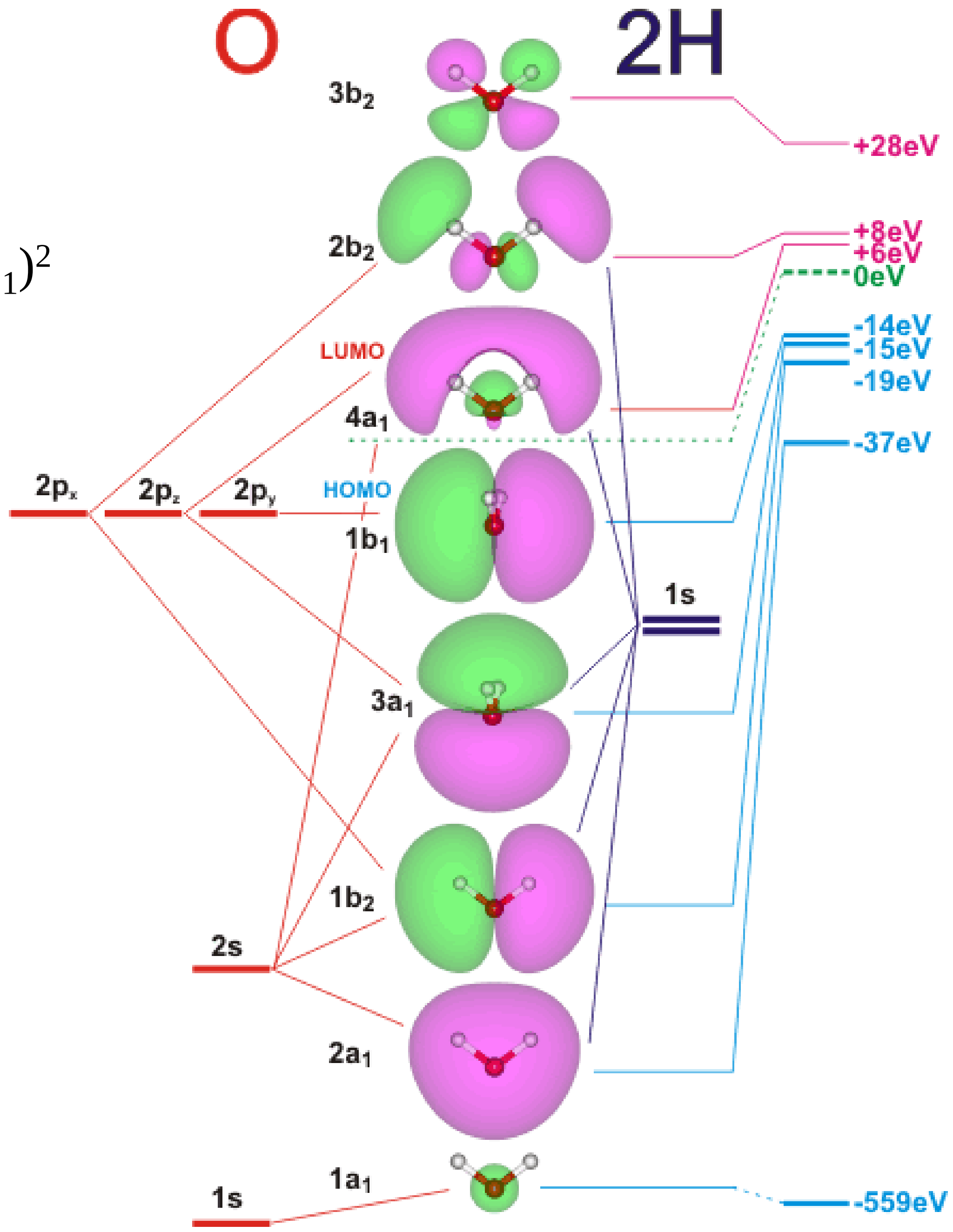


Fig. 11.5 — Gráficos de densidade electrónica, $\psi^*\psi$, em várias bases de funções para as orbitais moleculares simetrizadas dos electrões de valência da molécula de água. As densidades representadas referem-se aos pontos de um plano basal que passa pelos três núcleos da molécula, excepto na orbital molecular $1b_1$ onde o plano basal é perpendicular ao plano da molécula, passa pelo núcleo do átomo de oxigénio e bissecta o ângulo das ligações.

H_2O

$(1\,a_1)^2\,(2\,a_1)^2\,(1\,b_2)^2\,(3\,a_1)^2\,(1\,b_1)^2$



1 eV = 96 kJ/mol

H_2O

$(1\,a_1)^2\,(2\,a_1)^2\,(1\,b_2)^2\,(3\,a_1)^2\,(1\,b_1)^2$

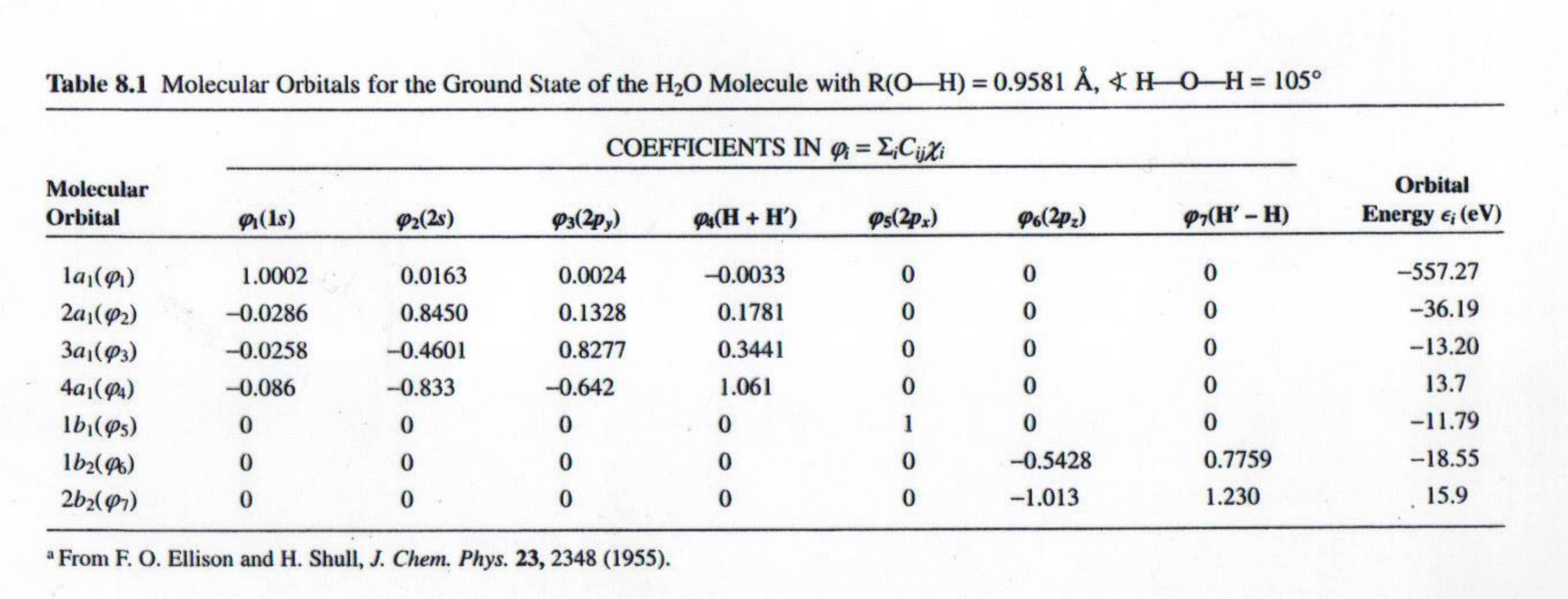
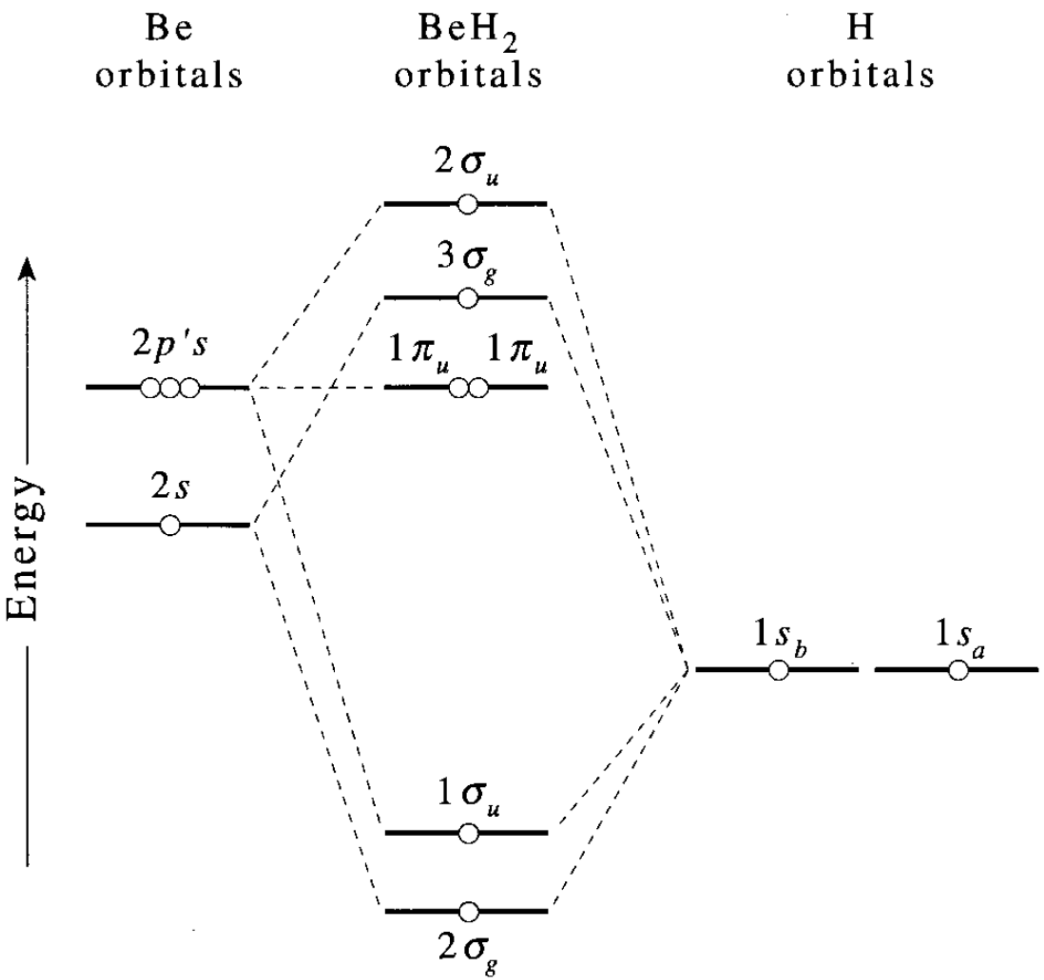


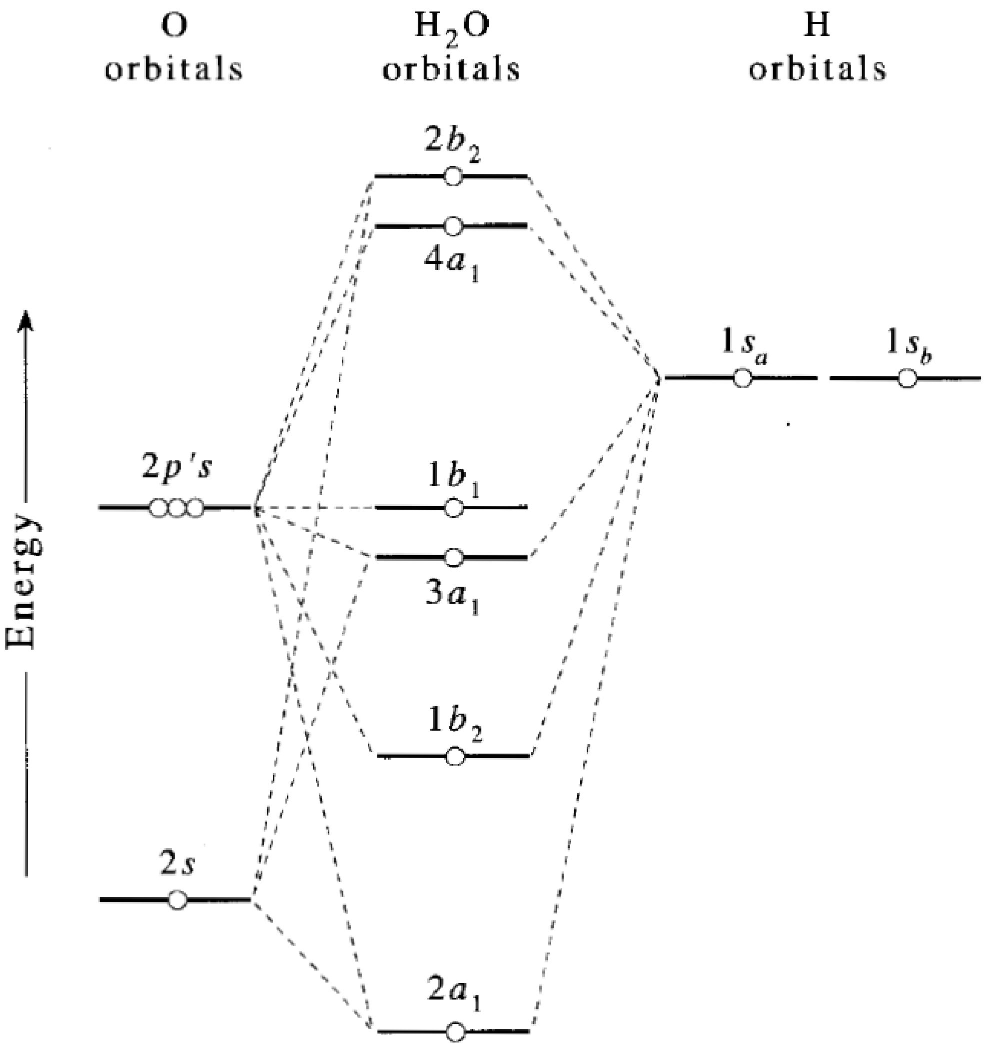
Table 8.1 Molecular Orbitals for the Ground State of the H_2O Molecule with R(O—H) = 0.9581 Å, ∢ H—O—H = 105°

Molecular Orbital	COEFFICIENTS IN $\varphi_i = \Sigma_i C_{ij}\chi_i$							Orbital Energy ϵ_i (eV)
	$\varphi_1(1s)$	$\varphi_2(2s)$	$\varphi_3(2p_y)$	$\varphi_4(\text{H + H}')$	$\varphi_5(2p_x)$	$\varphi_6(2p_z)$	$\varphi_7(\text{H}' - \text{H})$	
$1a_1(\varphi_1)$	1.0002	0.0163	0.0024	−0.0033	0	0	0	−557.27
$2a_1(\varphi_2)$	−0.0286	0.8450	0.1328	0.1781	0	0	0	−36.19
$3a_1(\varphi_3)$	−0.0258	−0.4601	0.8277	0.3441	0	0	0	−13.20
$4a_1(\varphi_4)$	−0.086	−0.833	−0.642	1.061	0	0	0	13.7
$1b_1(\varphi_5)$	0	0	0	0	1	0	0	−11.79
$1b_2(\varphi_6)$	0	0	0	0	0	−0.5428	0.7759	−18.55
$2b_2(\varphi_7)$	0	0	0	0	0	−1.013	1.230	15.9

[a] From F. O. Ellison and H. Shull, *J. Chem. Phys.* **23,** 2348 (1955).

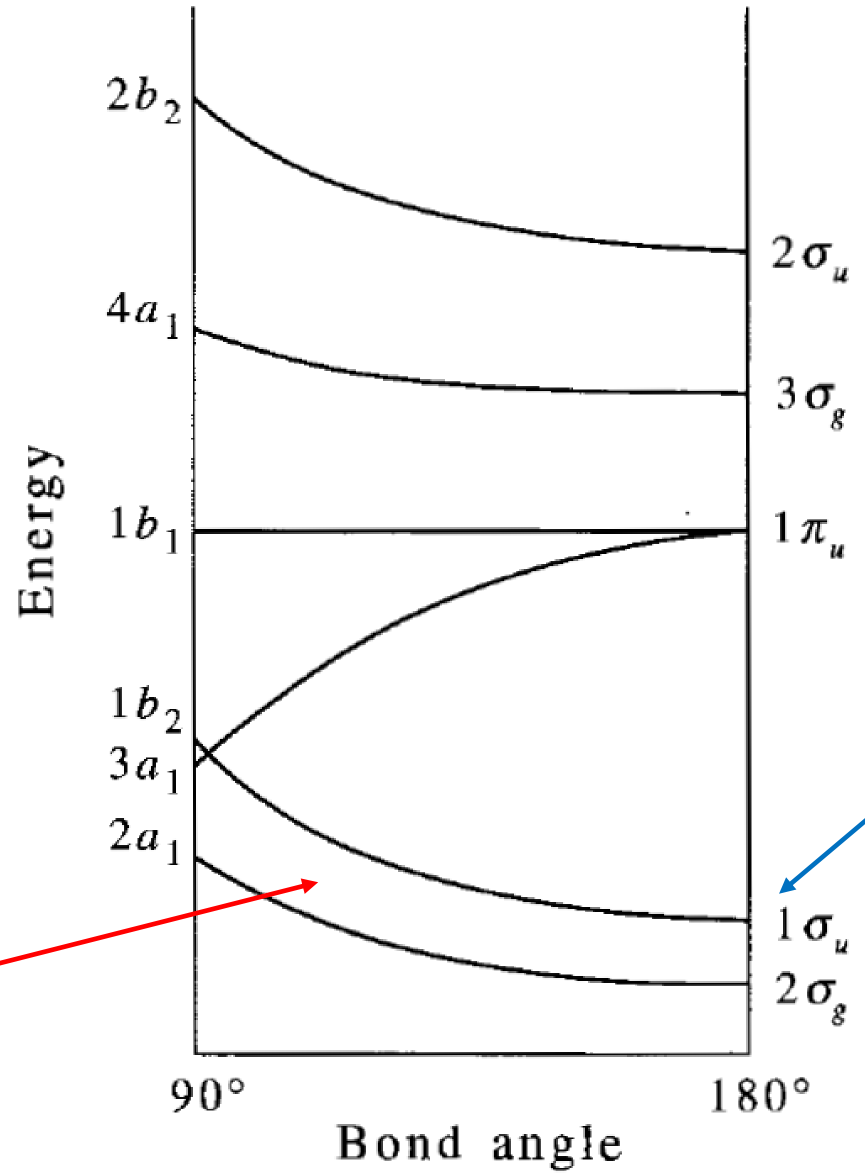


BeH$_2$, 4 elétrons de valência: $(2\sigma_g)^2(1\sigma_u)^2$



H$_2$O, 8 elétrons de valência: $(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2$

Diagrama de correlação de Walsh



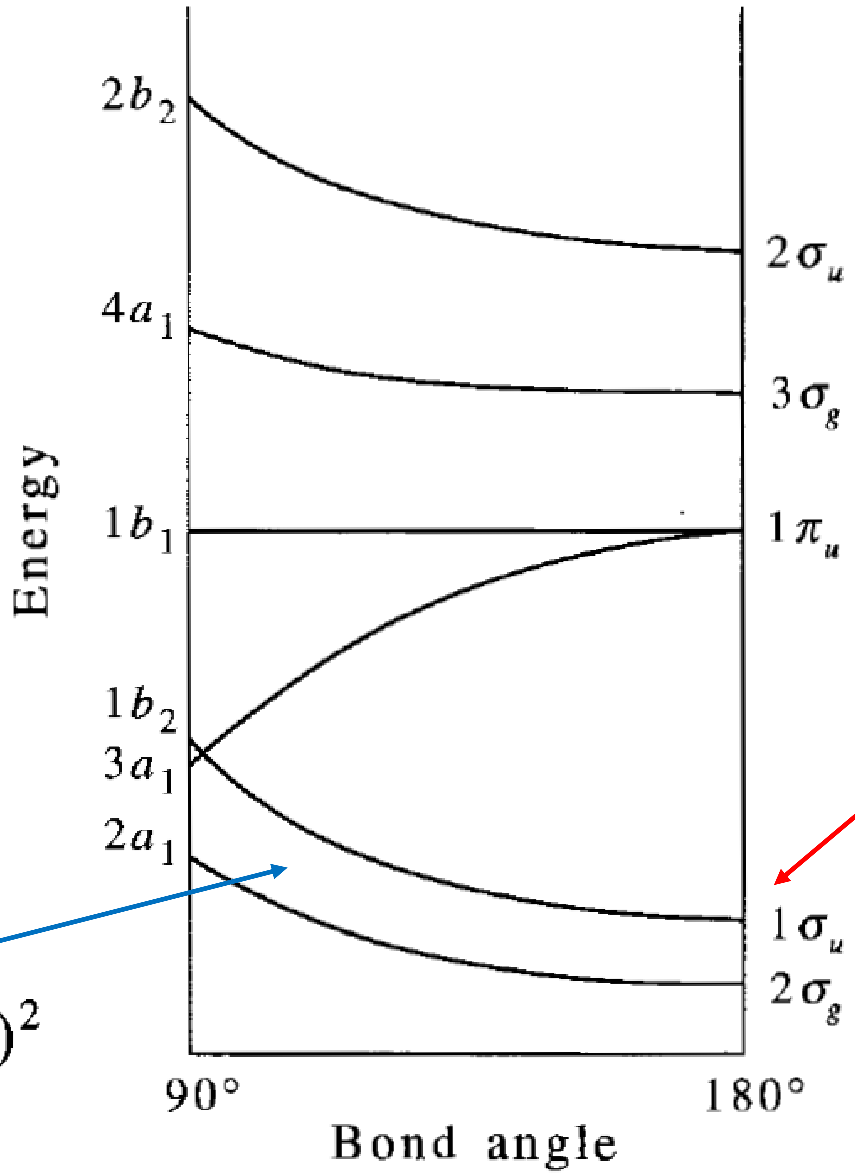
BeH$_2$ linear

$(2\sigma_g)^2(1\sigma_u)^2$

BeH$_2$ não-linear

$(2a_1)^2(3a_1)^2$

Diagrama de correlação de Walsh



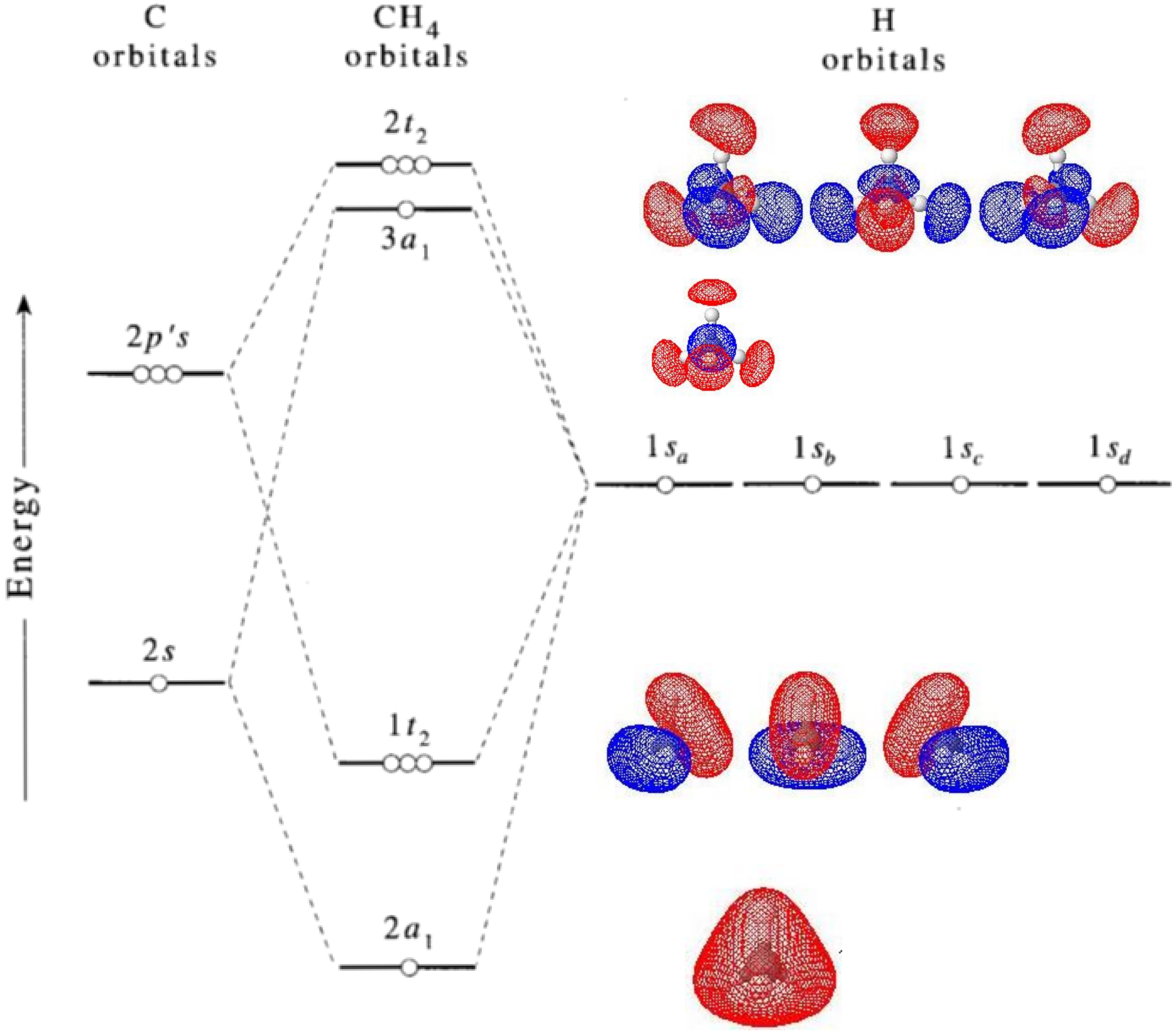
H_2O linear

$(2\sigma_g)^2(1\sigma_u)^2(1\pi_u)^4$

H_2O não-linear

$(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2$

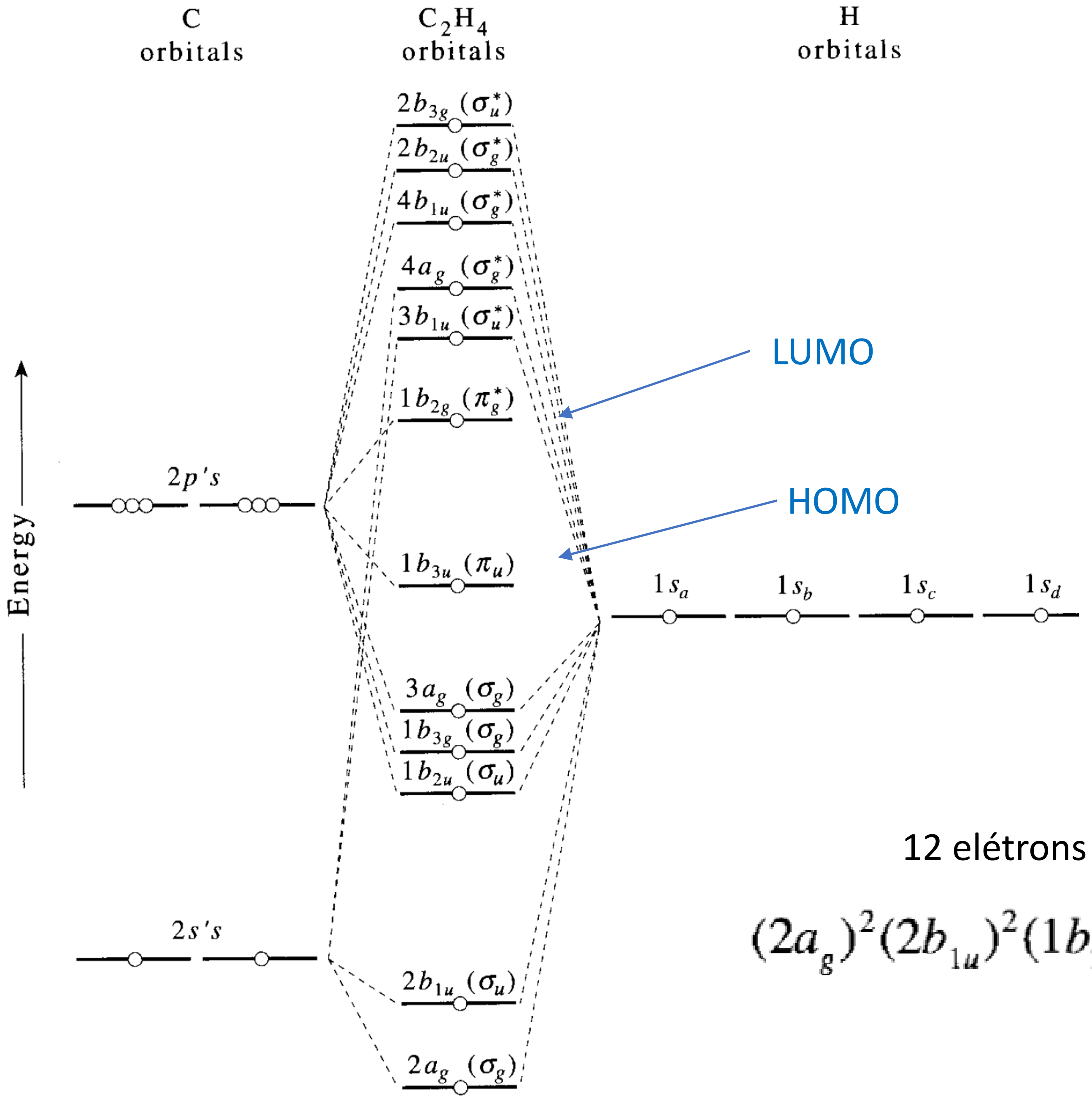
CH$_4$



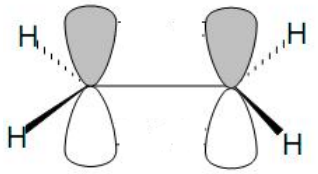
8 elétrons de valência:

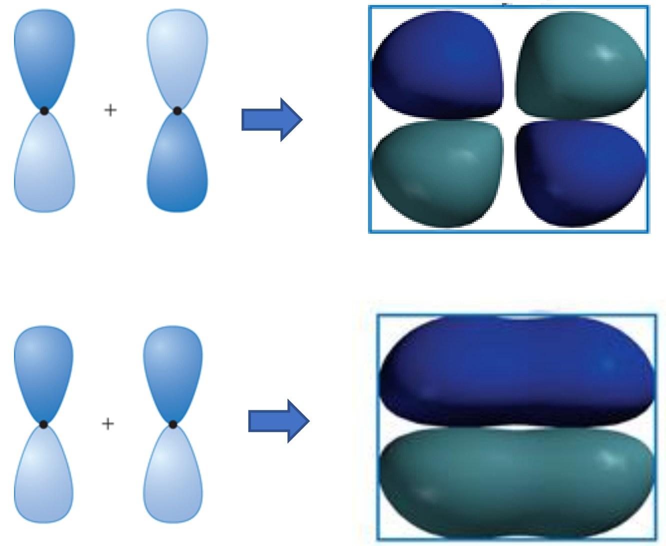
$(2a_1)^2(1t_2)^6$

C_2H_4



Teoria de Hückel





12 elétrons de valência:

$$(2a_g)^2(2b_{1u})^2(1b_{2u})^2(1b_{3g})^2(3a_g)^2(1b_{3u})^2$$