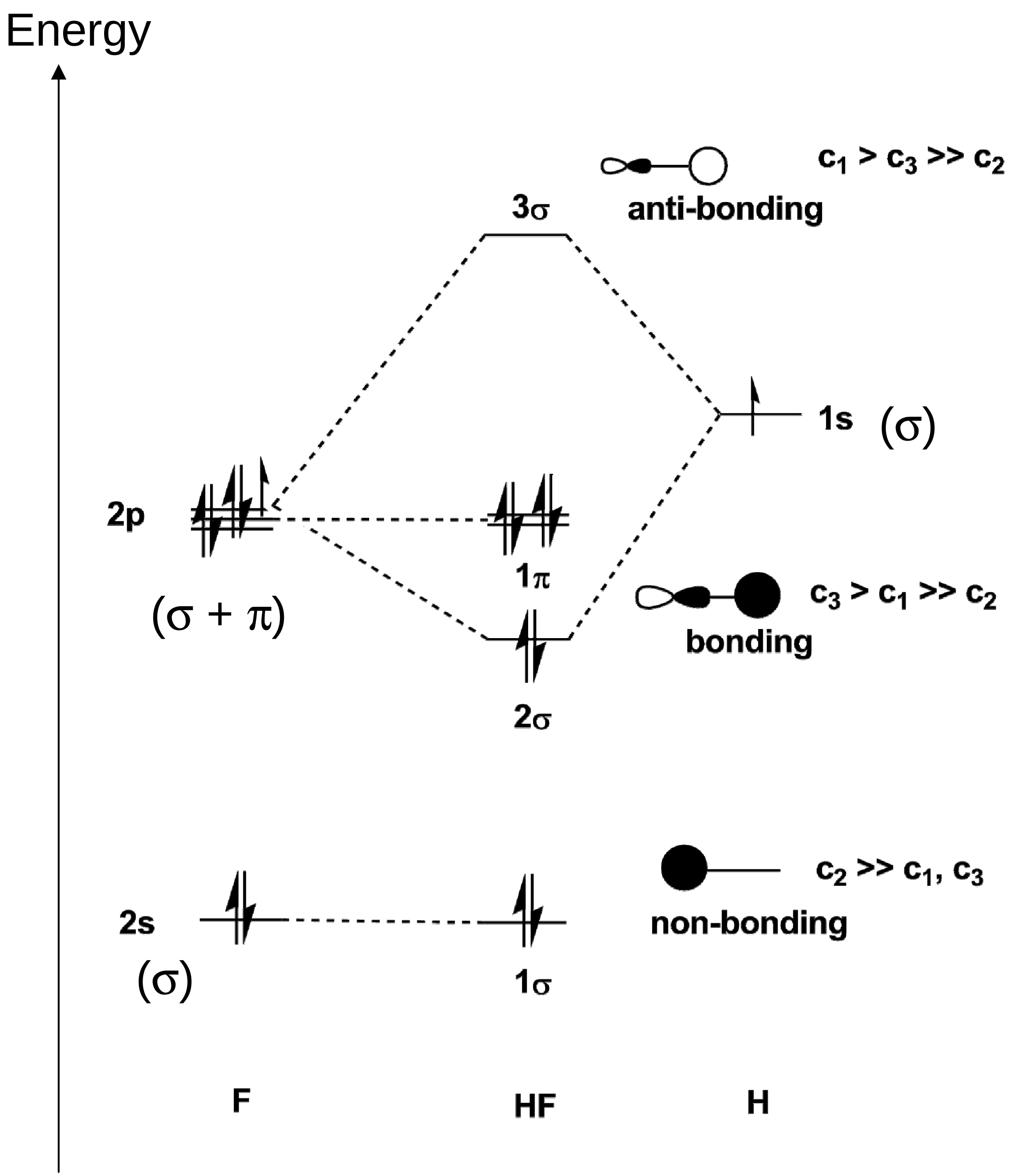
Bonding in Molecules

Lecture 2

MO theory for polyatomic molecules

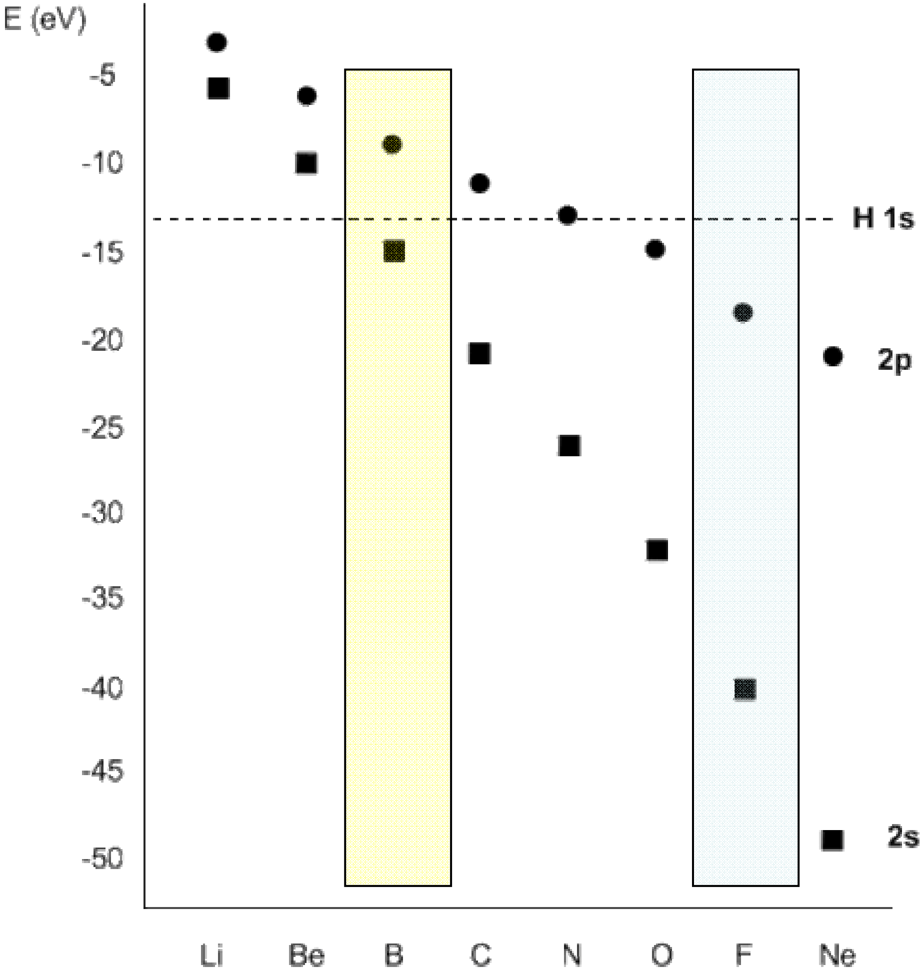


Guiding principles:
orbitals do ***not*** interact
(i) if they do not overlap
(ii) if they have very different energies

In unsymmetric cases, a given molecular orbital ‘resembles’ the atomic orbital to which it lies closest in energy

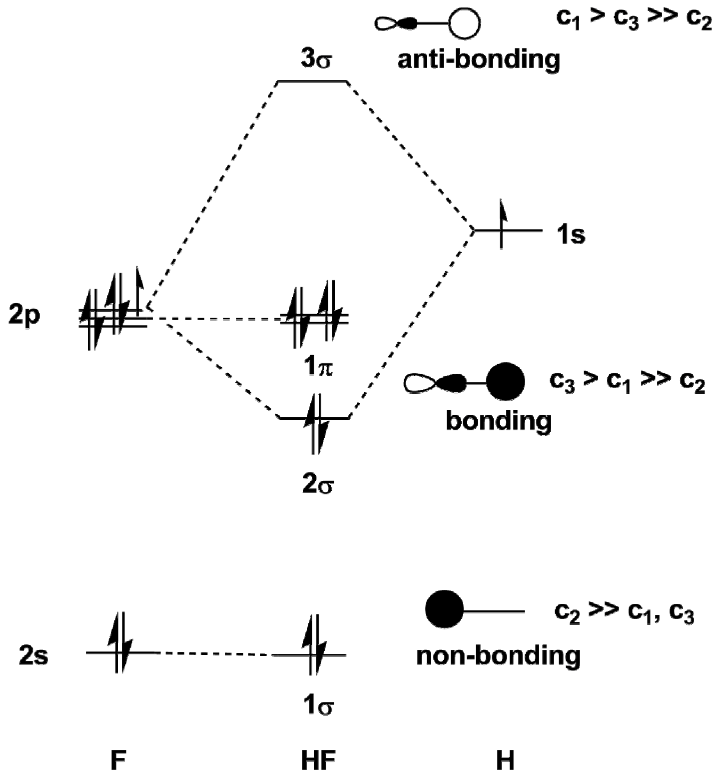
What happens for less electronegative A?

Orbital energies



Heteronuclear diatomics, AH: (HF vs HB)

more
bonding



more
onding

$$\phi(n\sigma) = c_1\chi_{1s(H)} + c_2\chi_{2s(A)} + c_2\chi_{2pz(A)}$$

s/p mixing less important

s/p mixing more important

Protocol for constructing MO diagrams for AH_n (H_2O, NH_3, CH_4)

1) Identify symmetry equivalent atoms (hydrogens in this case)

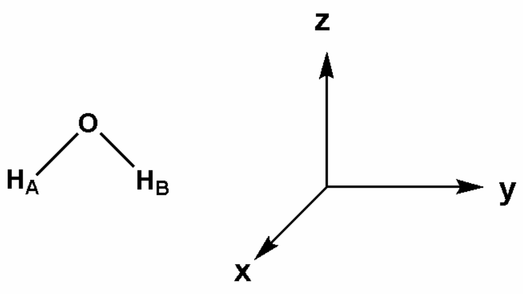
2) Generate Symmetry Adapted Linear Combinations on these identical atoms

3) Combine SALCS with orbitals on A

For more complex molecules, there may be more than 2 symmetry equivalent types of atoms. In this case, MO diagrams can be constructed from the orbitals of two chemically reasonable fragments.

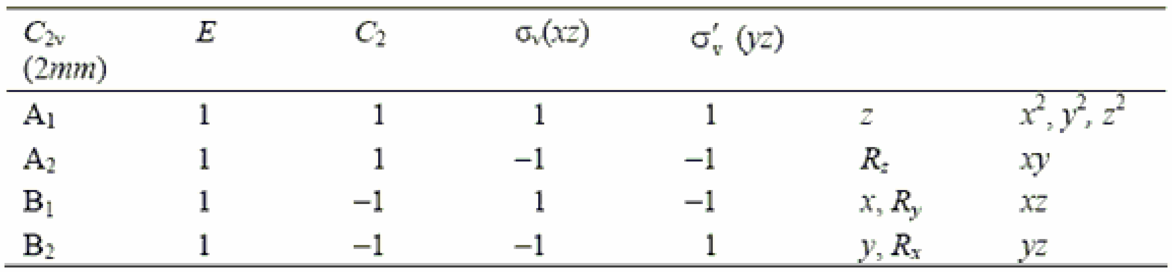
For example, the bonding in $[Cl_3Pt(C_2H_4)]^-$ can reasonably be considered in terms of the interaction between $[PtCl_3]^-$ and C_2H_4.

H_2O (C_{2v})



Valence orbitals: 2s, $2p_{x,y,z}$ on O
2 x 1s on H

Symmetry analysis:



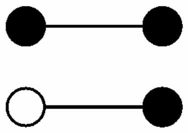
C_{2v} (2mm)	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

Γ(2 x H1s) = 2 0 0 2

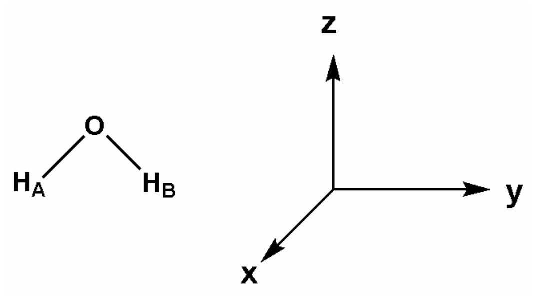
$a_1 + b_2$

A_1 $(1/2)^{1/2} (\phi_1 + \phi_2)$

B_2 $(1/2)^{1/2} (\phi_1 - \phi_2)$



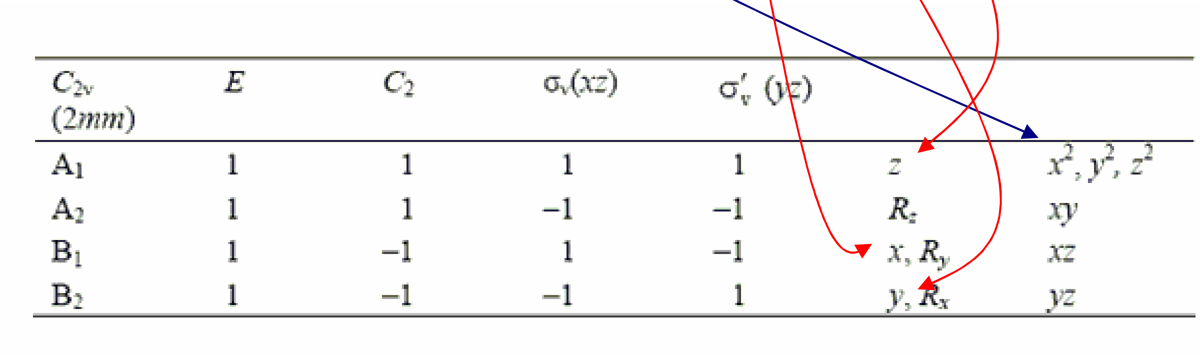
H_2O (C_{2v})



Valence orbitals: 2s, $2p_{x,y,z}$ on O
2 x 1s on H

O is on an *invariant point*

Symmetry analysis:



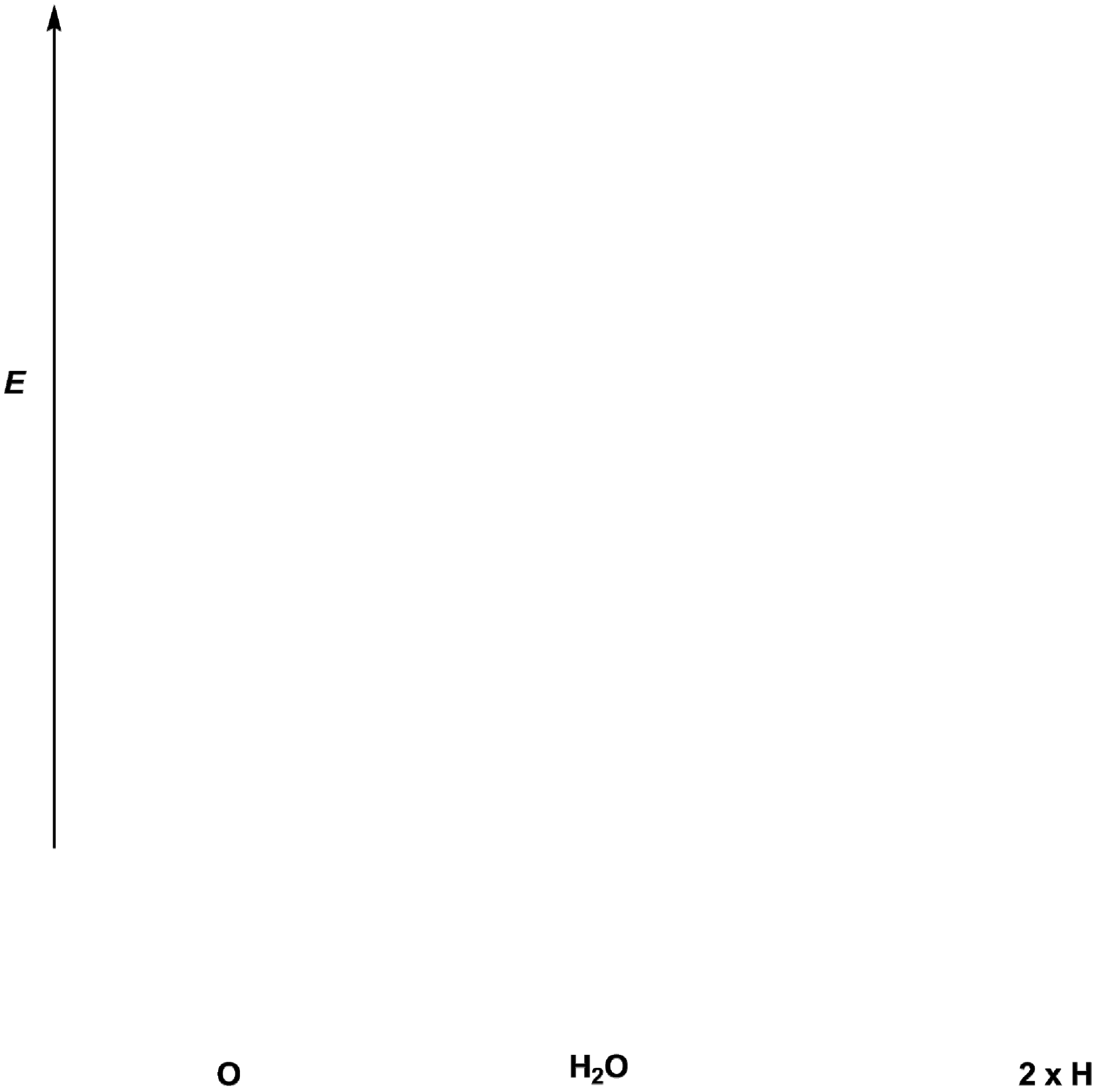
C_{2v} (2*mm*)	*E*	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$		
A_1	1	1	1	1	*z*	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	*xy*
B_1	1	−1	1	−1	x, R_y	*xz*
B_2	1	−1	−1	1	y, R_x	*yz*

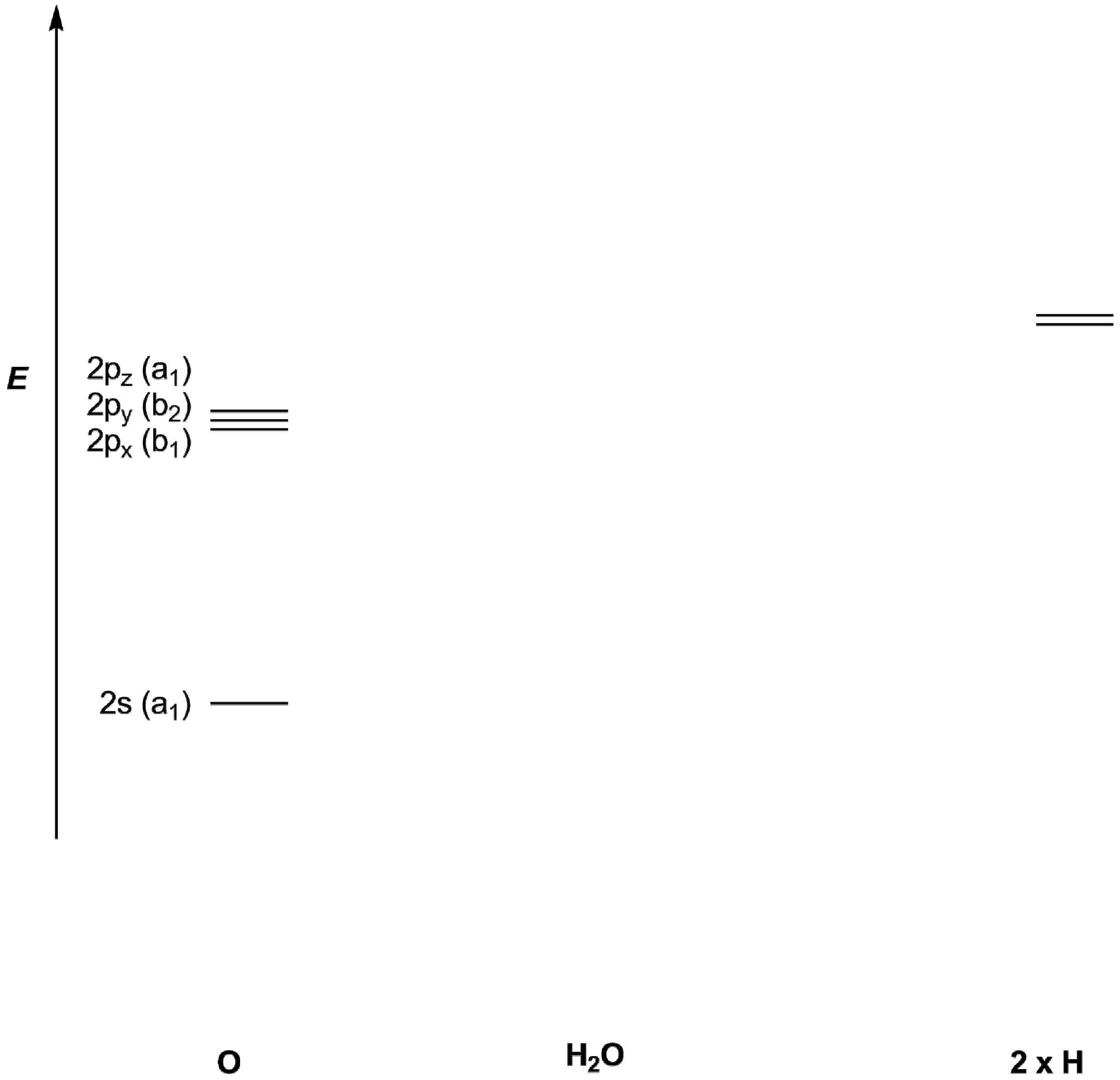
$\Gamma(O2s) = a_1$

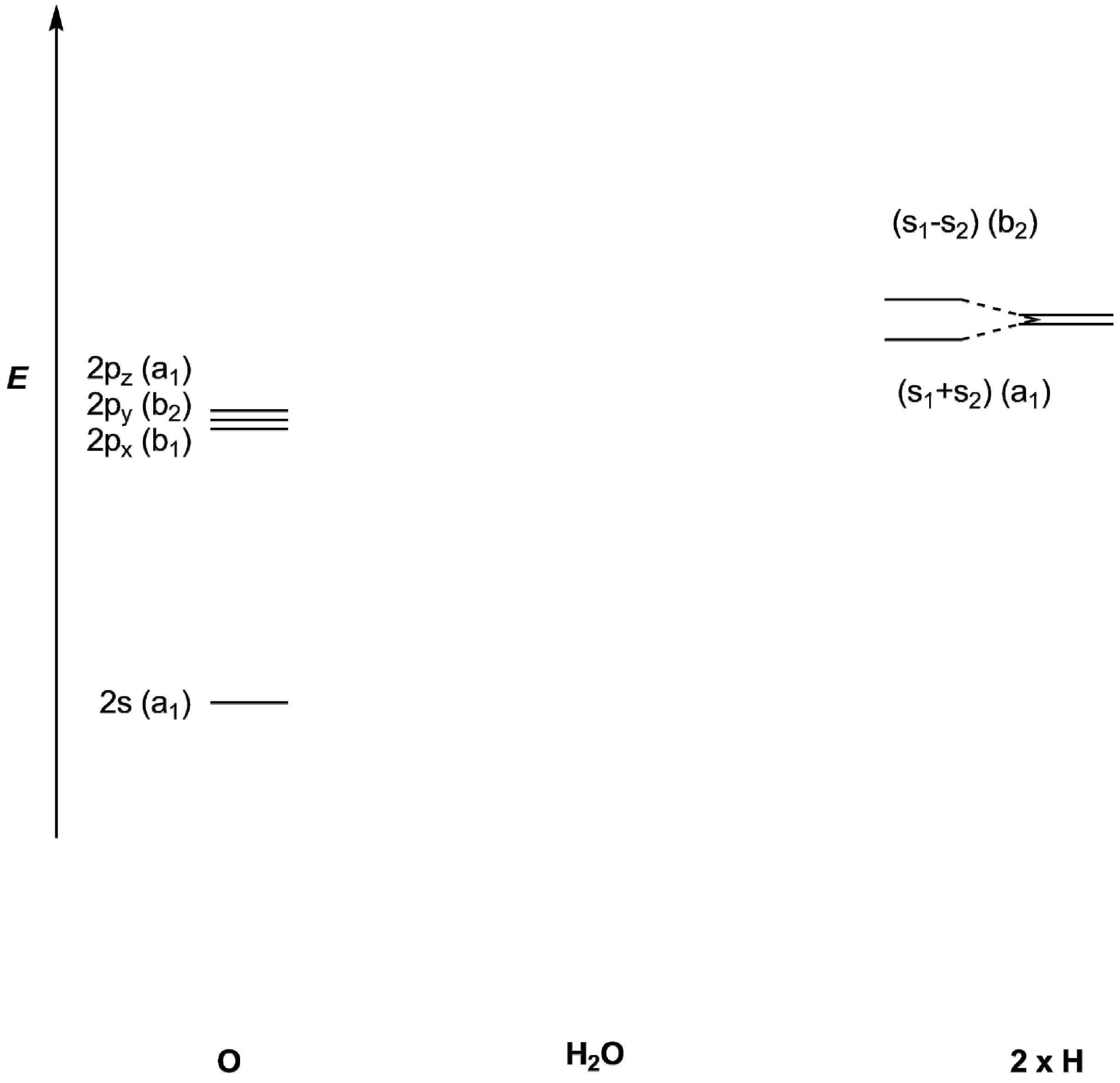
$\Gamma(O2p_x) = b_1$

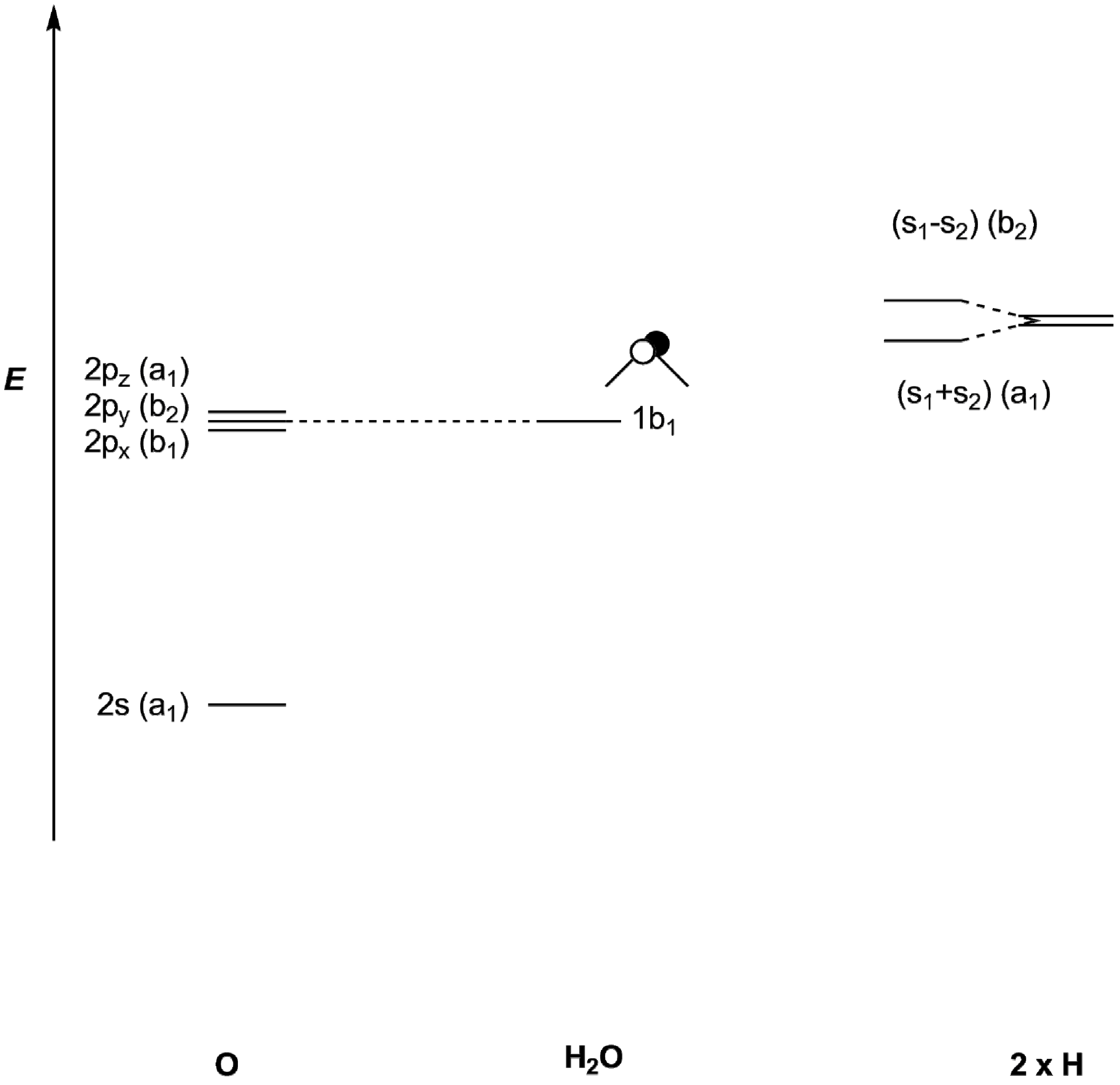
$\Gamma(O2p_y) = b_2$

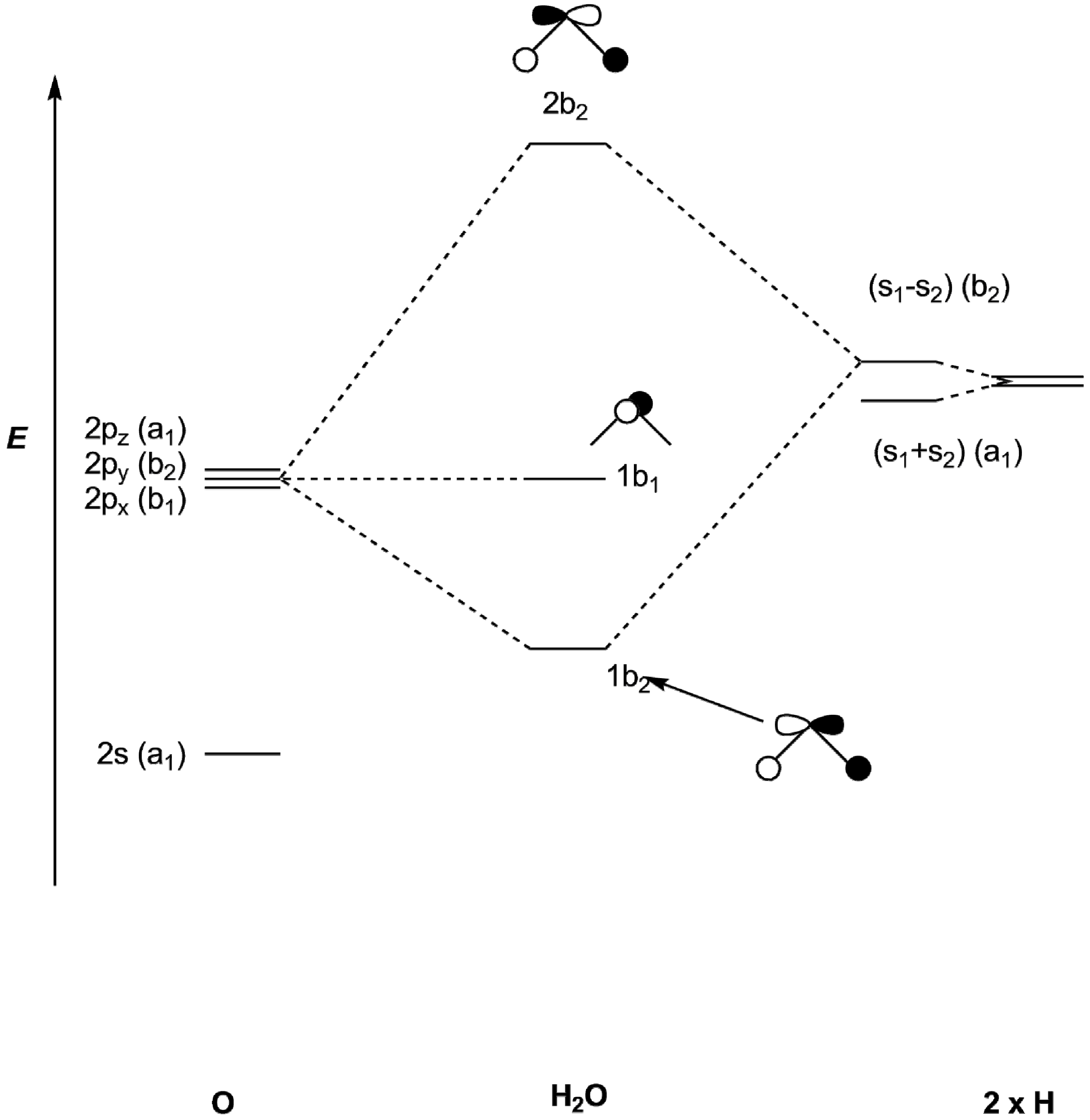
$\Gamma(O2p_z) = a_1$

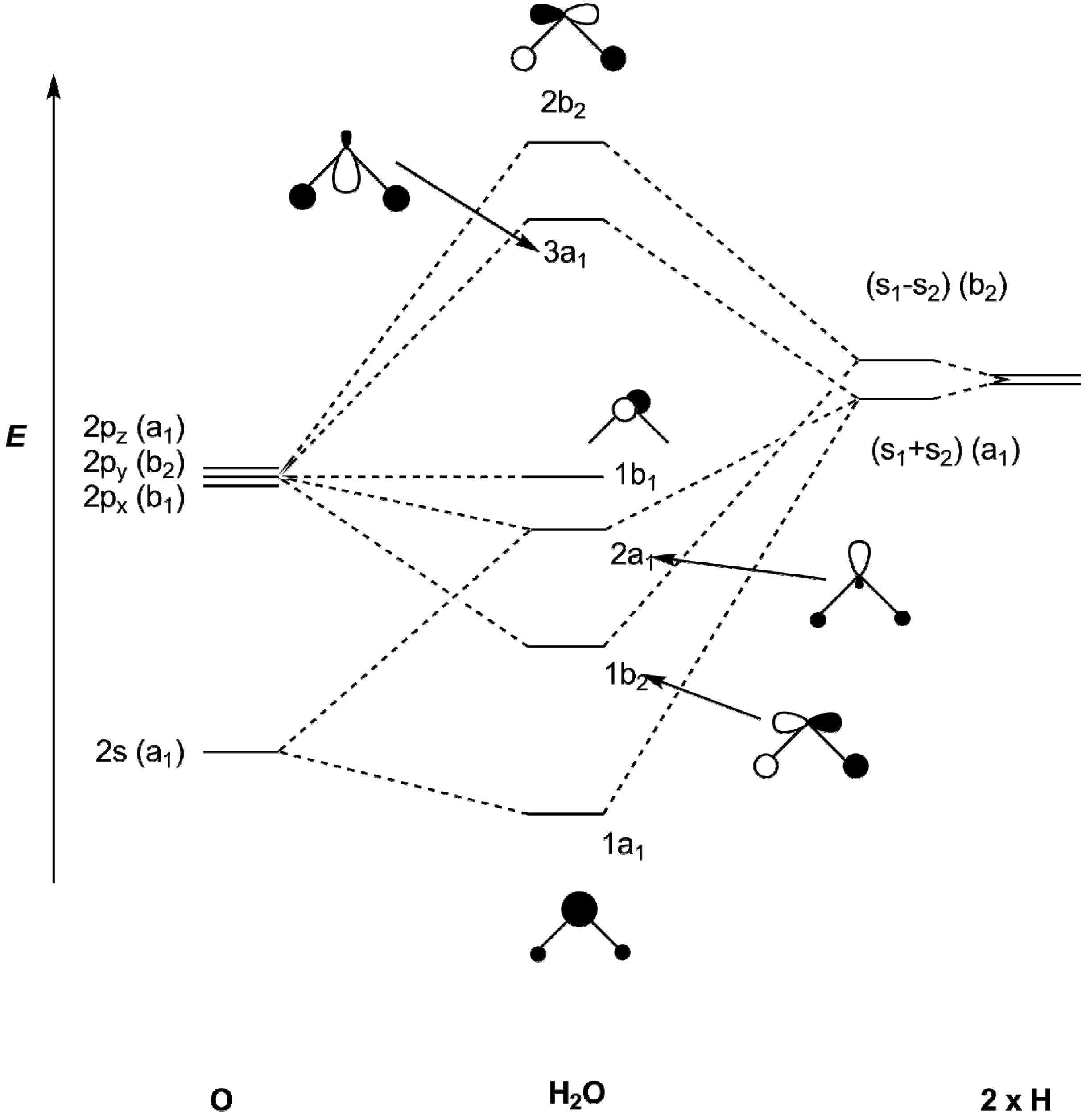

E
O
H_2O
2 x H

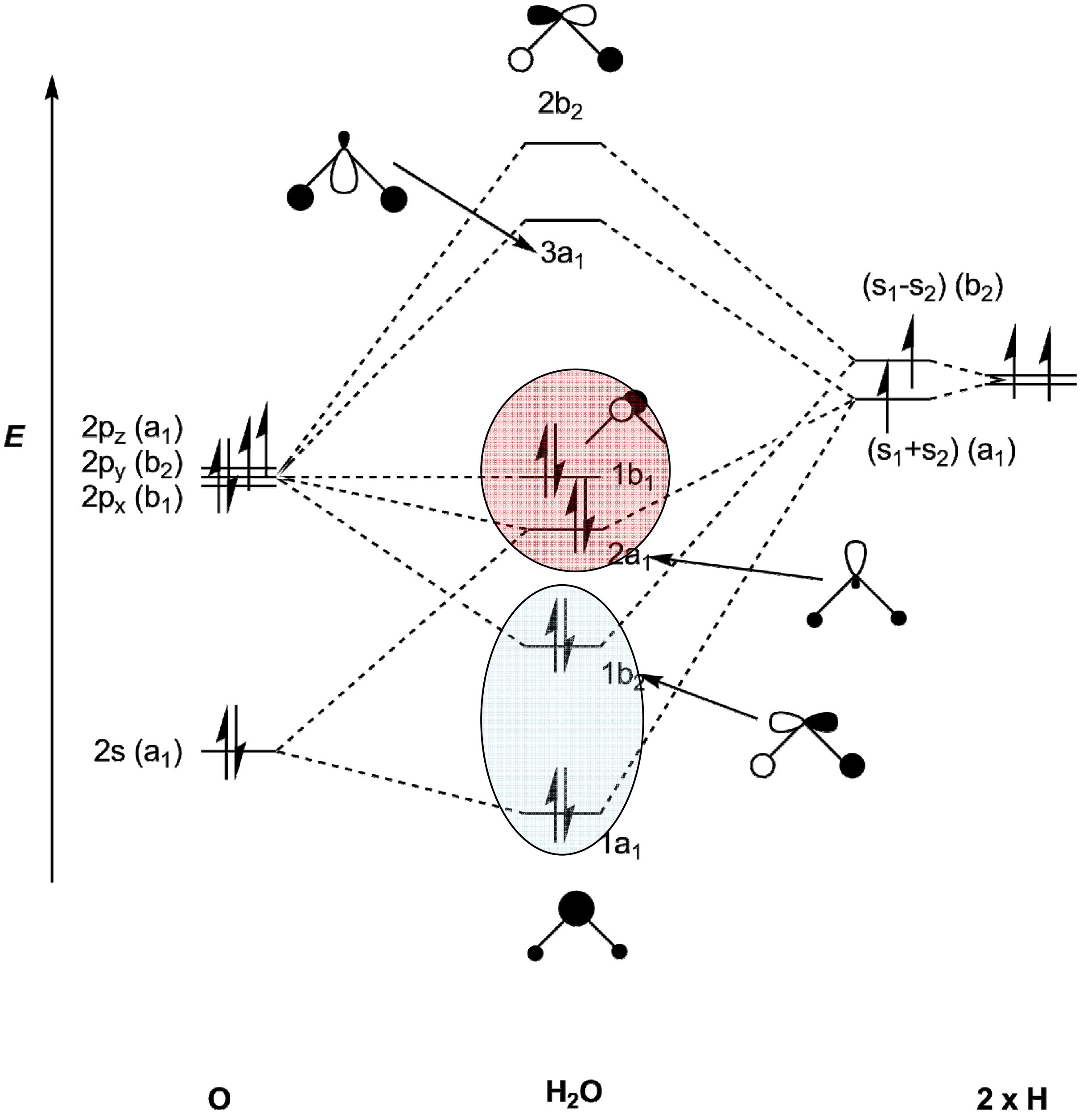

E
2pz (a1)
2py (b2)
2px (b1)
2s (a1)
O
H2O
2 x H

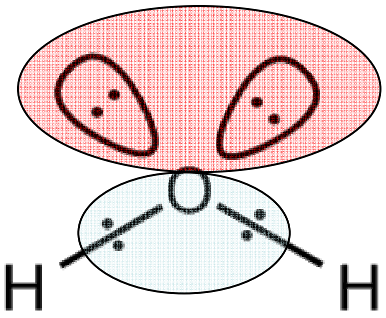

(s_1-s_2) (b_2)
(s_1+s_2) (a_1)
E
$2p_z$ (a_1)
$2p_y$ (b_2)
$2p_x$ (b_1)
2s (a_1)
O
H_2O
2 x H


E
2p$_z$ (a$_1$)
2p$_y$ (b$_2$)
2p$_x$ (b$_1$)
2s (a$_1$)
1b$_1$
(s$_1$-s$_2$) (b$_2$)
(s$_1$+s$_2$) (a$_1$)
O
H$_2$O
2 x H


$2b_2$
$(s_1 - s_2)$ (b_2)
E
$2p_z$ (a_1)
$2p_y$ (b_2)
$2p_x$ (b_1)
$1b_1$
$(s_1 + s_2)$ (a_1)
$1b_2$
$2s$ (a_1)
O
H_2O
2 x H


$2b_2$
$3a_1$
$(s_1-s_2)\ (b_2)$
E
$2p_z\ (a_1)$
$2p_y\ (b_2)$
$2p_x\ (b_1)$
$1b_1$
$(s_1+s_2)\ (a_1)$
$2a_1$
$1b_2$
$2s\ (a_1)$
$1a_1$
O
H_2O
2 x H

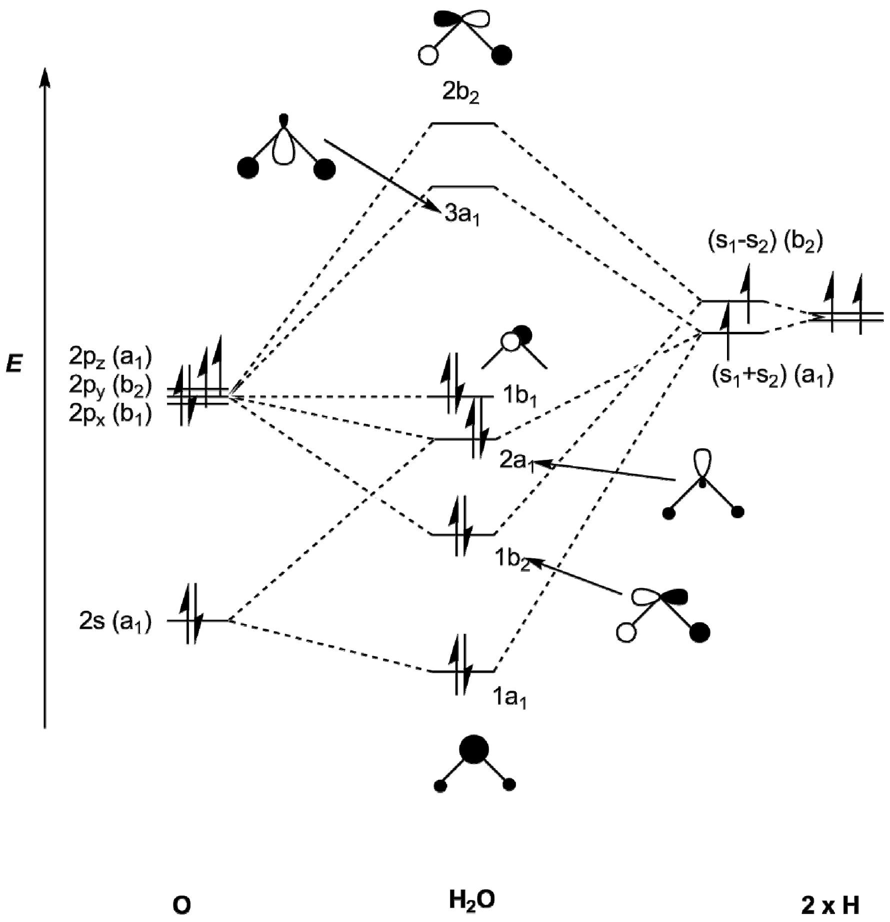


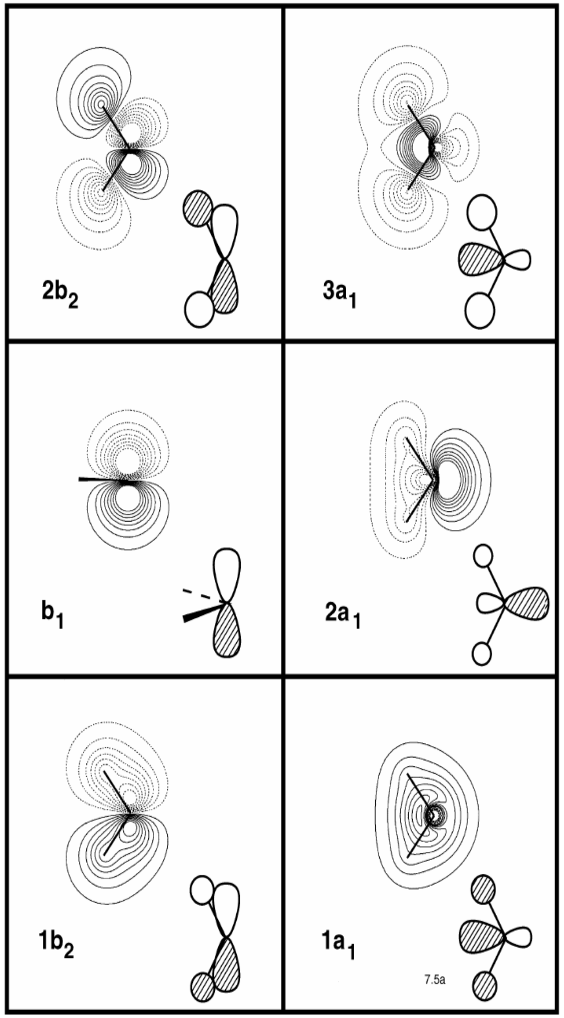


non-bonding

bonding

formal bond order:
2 (1 per O-H bond)

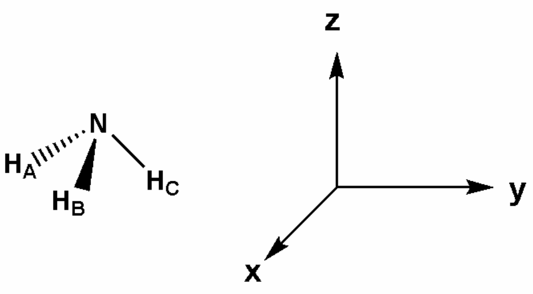




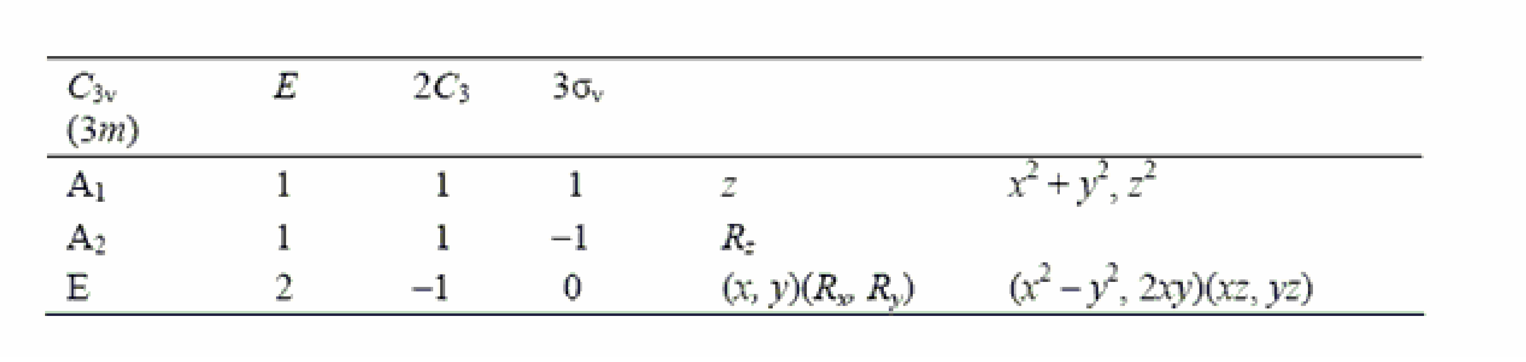
	Oxygen AO					**Hydrogen AO**	
MO	**1s**	**2s**	**2pz**	**2py**	**2px**	**1s1**	**1s2**
1a1	-0.222	0.843	-0.132	0	0	0.151	0.151
2a1	-0.093	0.516	0.787	0	0	-0.264	-0.264
1b2	0	0	0	0.624	0	0.424	-0.424
1b1	0	0	0	0	1	0	0

NH_3 (C_{3v})

Valence orbitals: $2s$, $2p_{x,y,z}$ on N
$3 \times 1s$ on H



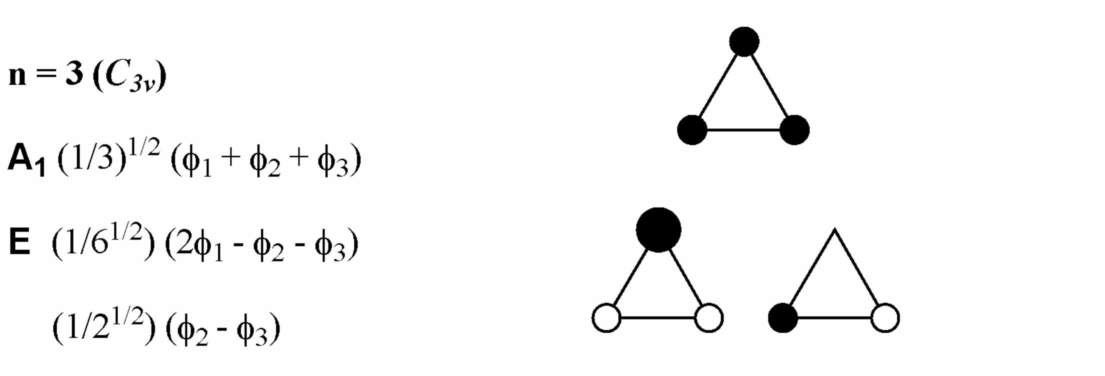
Symmetry analysis:



C_{3v} (3m)	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y)(R_x, R_y)$	$(x^2-y^2, 2xy)(xz, yz)$

$\Gamma(3 \times H1s)$ = 3 0 1

$a_1 + e$



n = 3 (C_{3v})

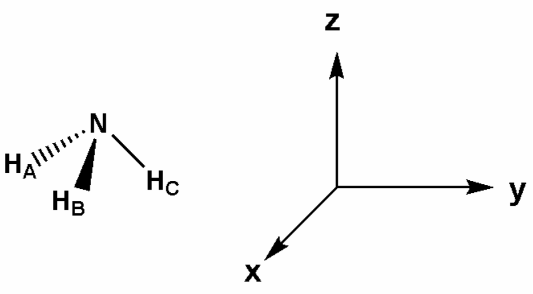
A_1 $(1/3)^{1/2}$ $(\phi_1 + \phi_2 + \phi_3)$

E $(1/6^{1/2})$ $(2\phi_1 - \phi_2 - \phi_3)$

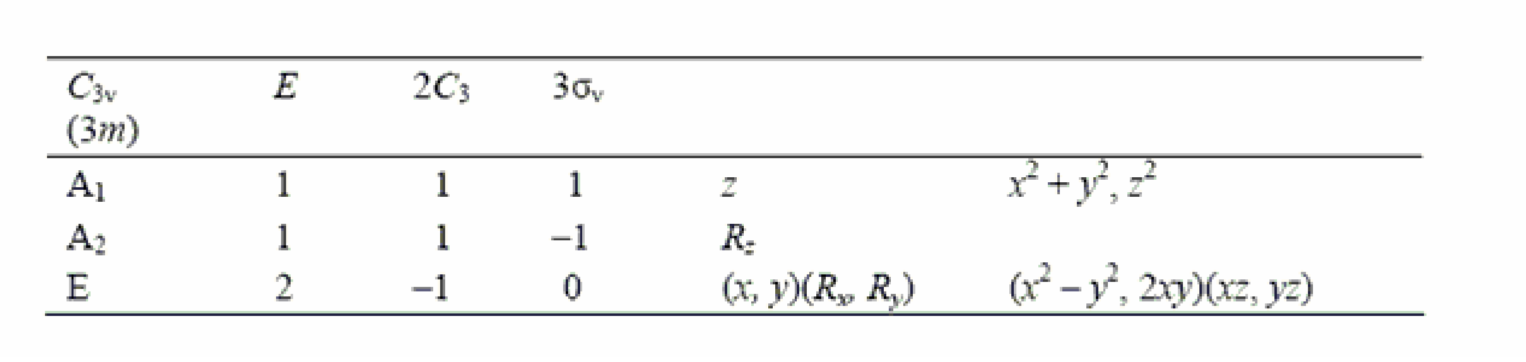
$(1/2^{1/2})$ $(\phi_2 - \phi_3)$

NH_3 (C_{3v})

Valence orbitals: 2s, $2p_{x,y,z}$ on N
3 x 1s on H



Symmetry analysis:

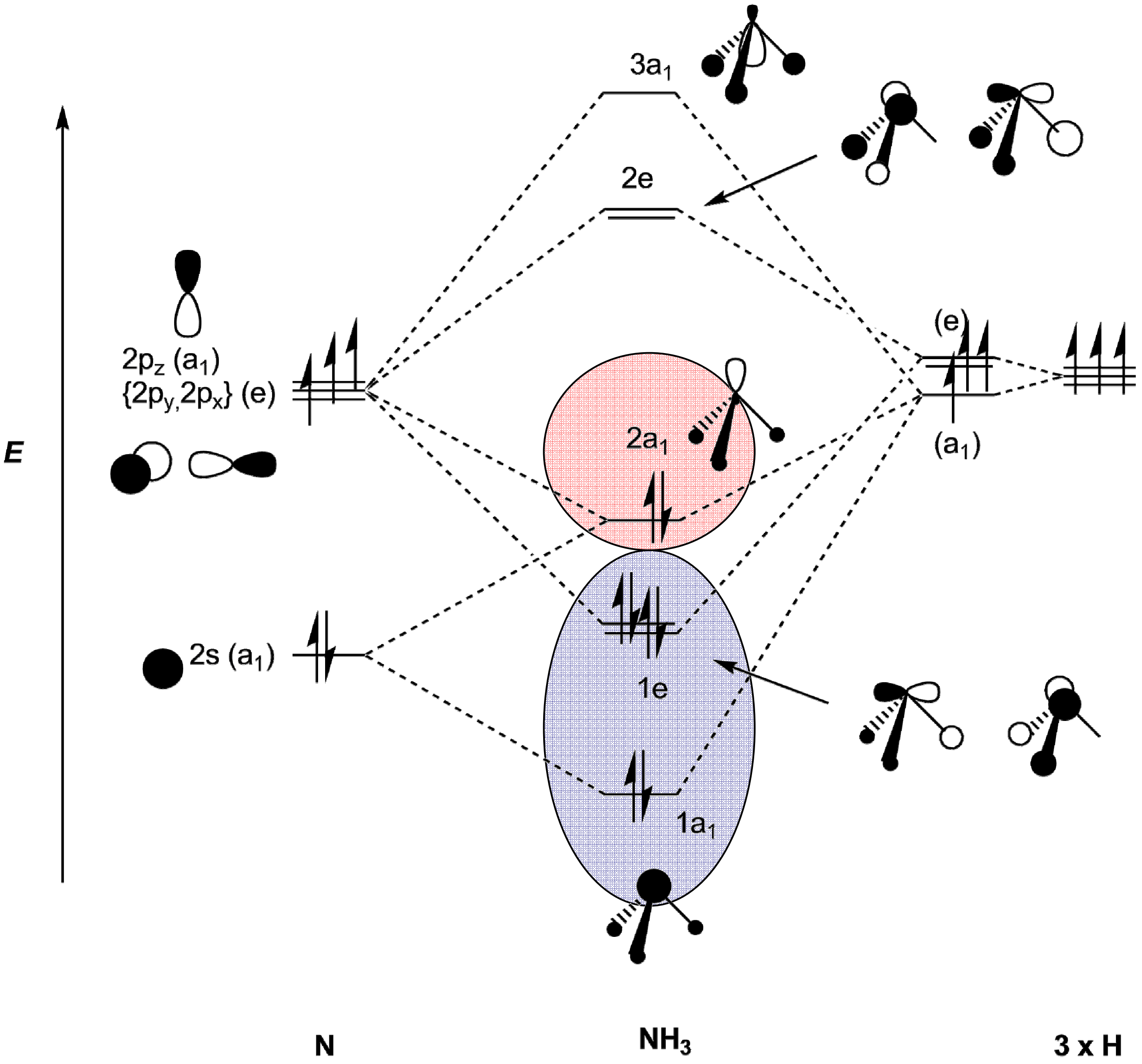


C_{3v} (3m)	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y)(R_x, R_y)$	$(x^2-y^2, 2xy)(xz, yz)$

$\Gamma(N2s) = a_1$

$\Gamma(N2p_x + N2p_y) = e_1$

$\Gamma(N2p_z) = a_1$



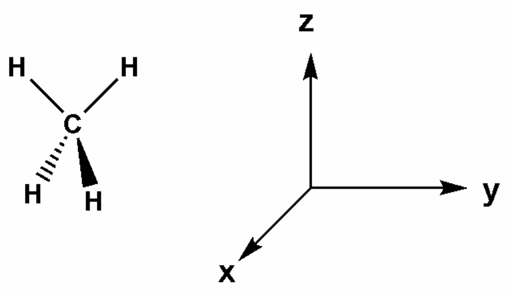
lone pair

bonding pairs

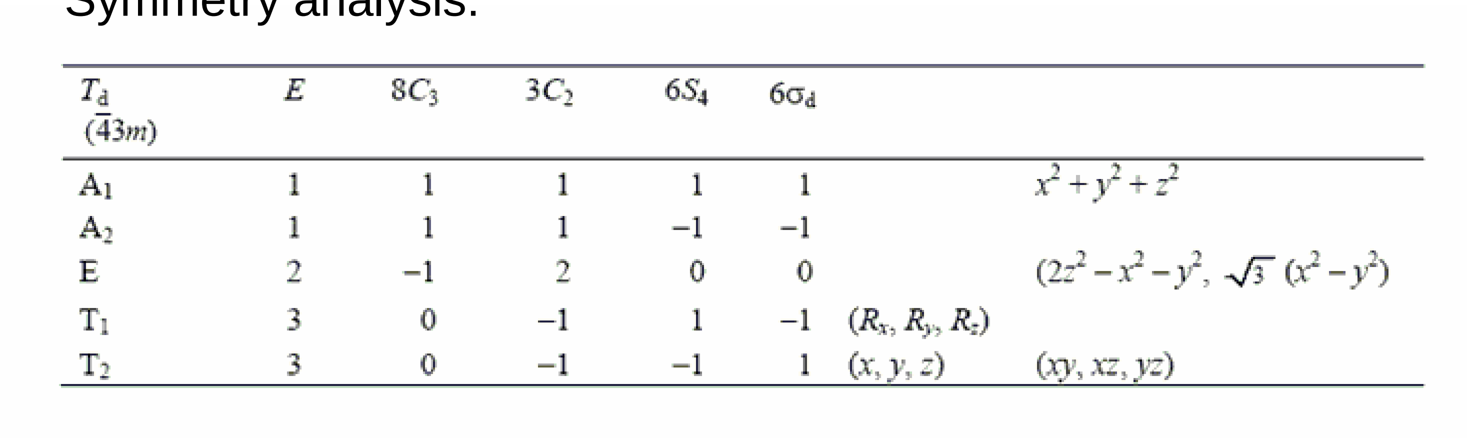
formal bond order:
3 (1 per N-H bond)

CH_4 (T_d)

Valence orbitals: $2s$, $2p_{x,y,z}$ on C
$4 \times 1s$ on H



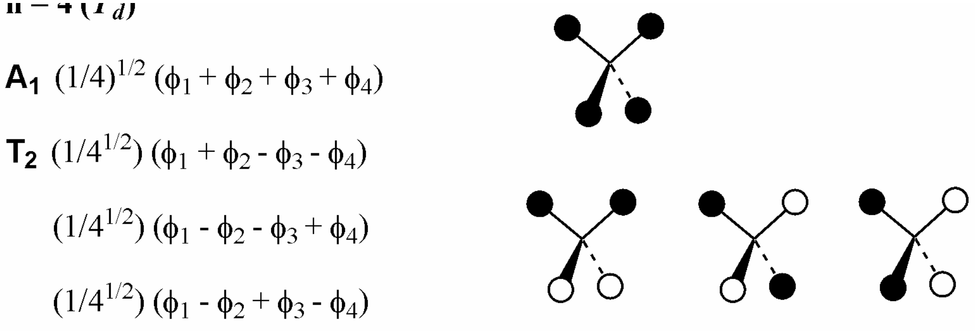
Symmetry analysis:



T_d ($\bar{4}3m$)	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	−1	−1		
E	2	−1	2	0	0		$(2z^2-x^2-y^2, \sqrt{3}\,(x^2-y^2)$
T_1	3	0	−1	1	−1	(R_x, R_y, R_z)	
T_2	3	0	−1	−1	1	(x, y, z)	(xy, xz, yz)

$\Gamma(4 \times H1s) = \quad 4 \quad 1 \quad 0 \quad 0 \quad 2$

$a_1 + t_2$



n = 4 (T_d)

A_1 $(1/4)^{1/2}(\phi_1+\phi_2+\phi_3+\phi_4)$

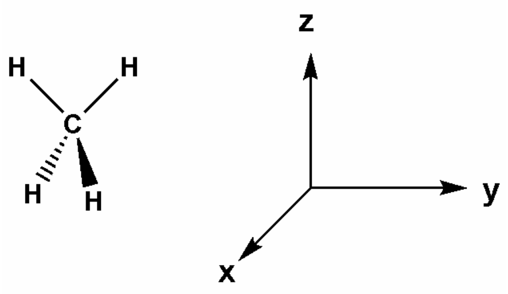
T_2 $(1/4^{1/2})(\phi_1+\phi_2-\phi_3-\phi_4)$

$(1/4^{1/2})(\phi_1-\phi_2-\phi_3+\phi_4)$

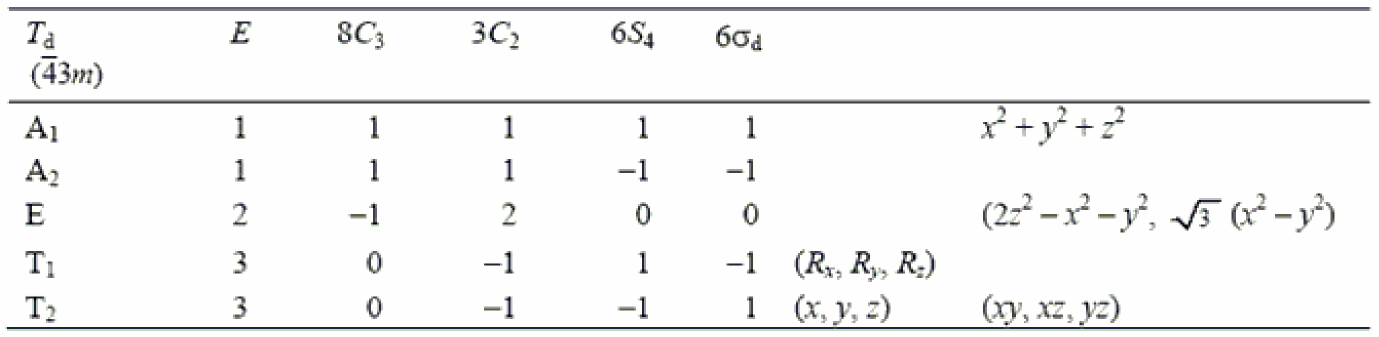
$(1/4^{1/2})(\phi_1-\phi_2+\phi_3-\phi_4)$

CH_4 (T_d)

Valence orbitals: 2s, $2p_{x,y,z}$ on C
4 x 1s on H



Symmetry analysis:

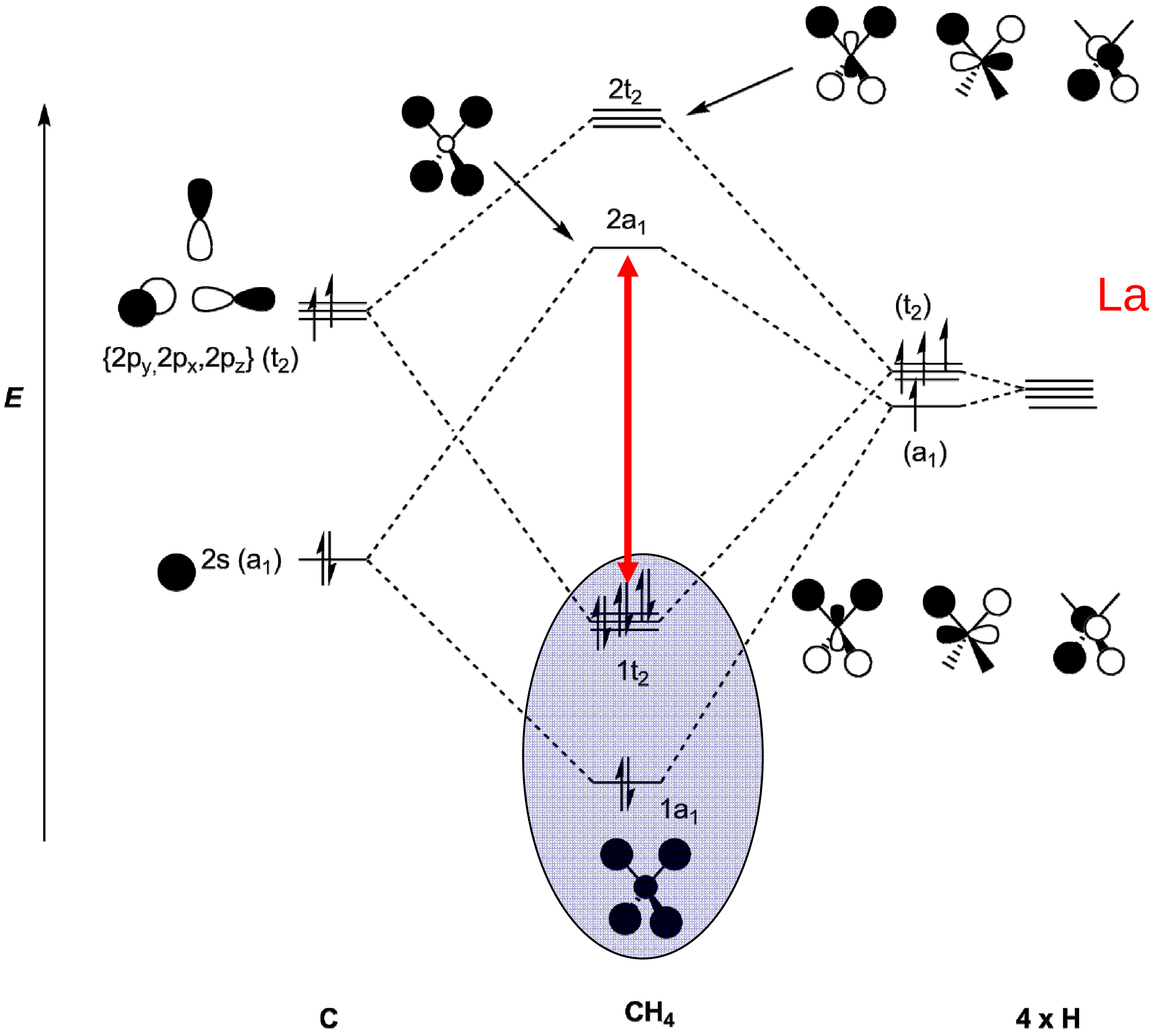


T_d $(\bar{4}3m)$	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	−1	−1		
E	2	−1	2	0	0		$(2z^2-x^2-y^2, \sqrt{3}\,(x^2-y^2))$
T_1	3	0	−1	1	−1	(R_x, R_y, R_z)	
T_2	3	0	−1	−1	1	(x, y, z)	(xy, xz, yz)

Γ(C2s) = a_1

Γ($C2p_{x,y,z}$) = t_2

n.b ***no*** s-p mixing

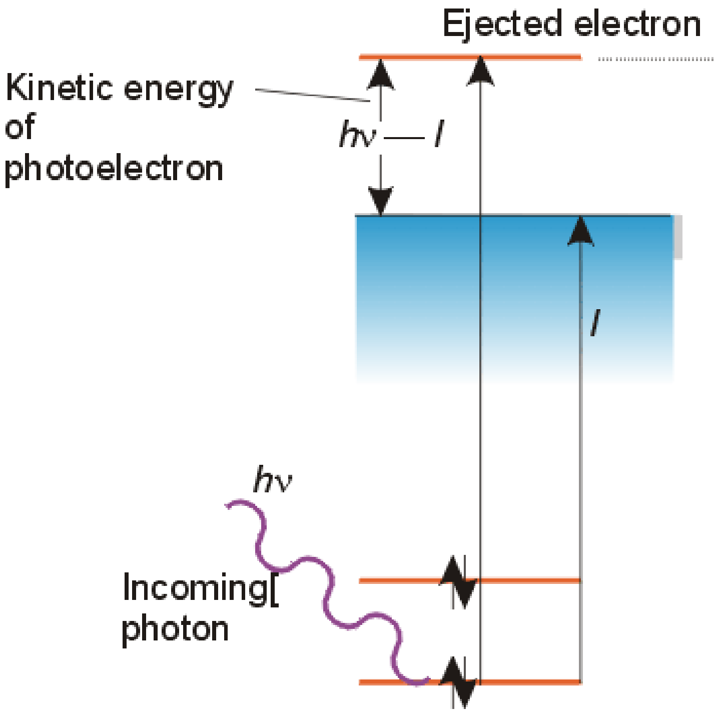


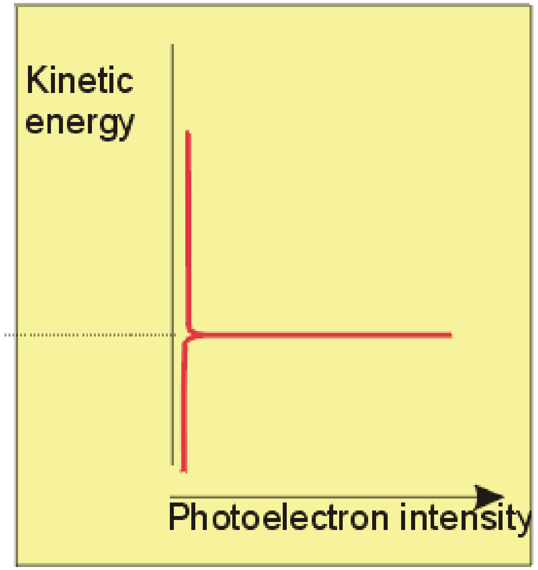
Large HOMO-LUMO gap

bonding pairs

formal bond order:
4 (1 per C-H bond)

An experimental test: Photoelectron Spectroscopy

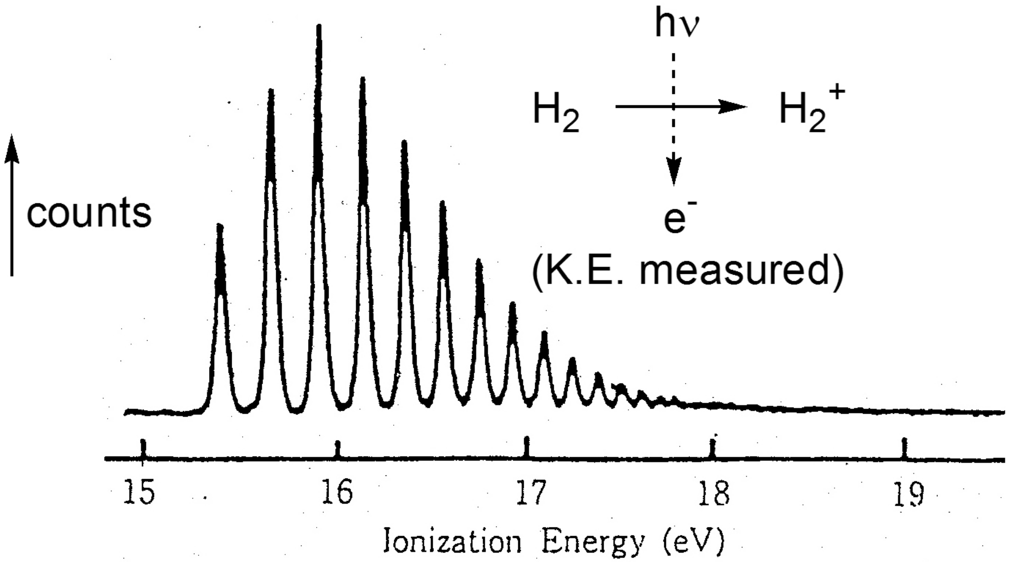




$$KE = h\nu - IE$$

Relates PES to MO diagrams through Koopmans’ approximation: $IE = -\varepsilon_i$

PES of H_2



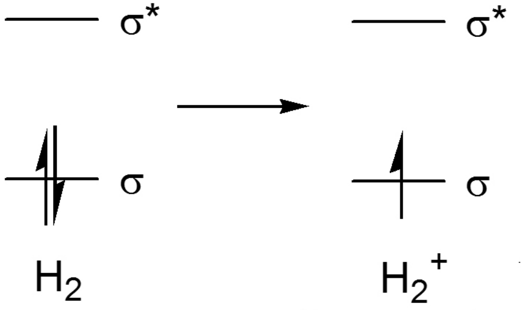
$h\nu$

$H_2 \rightarrow H_2^+$

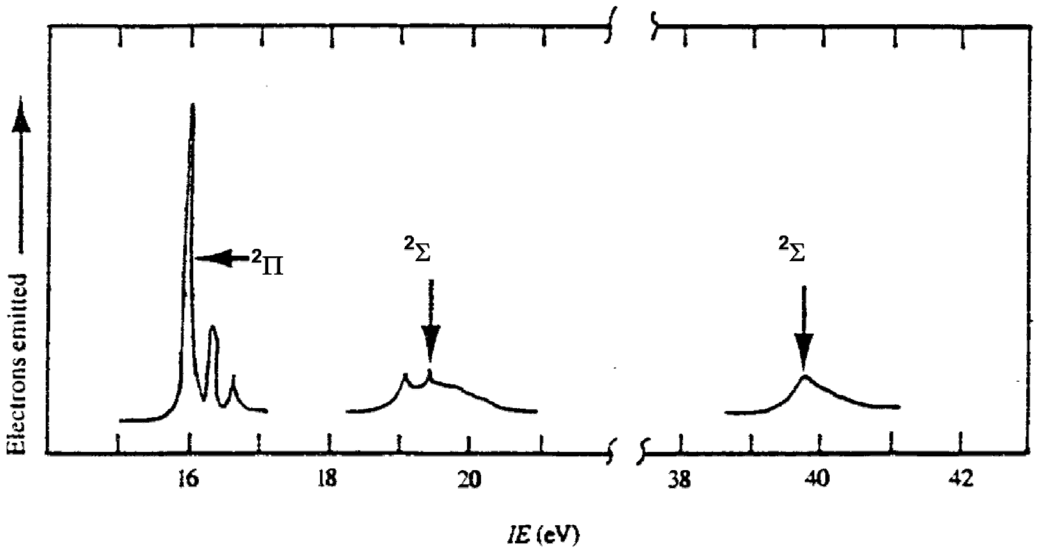
e^-

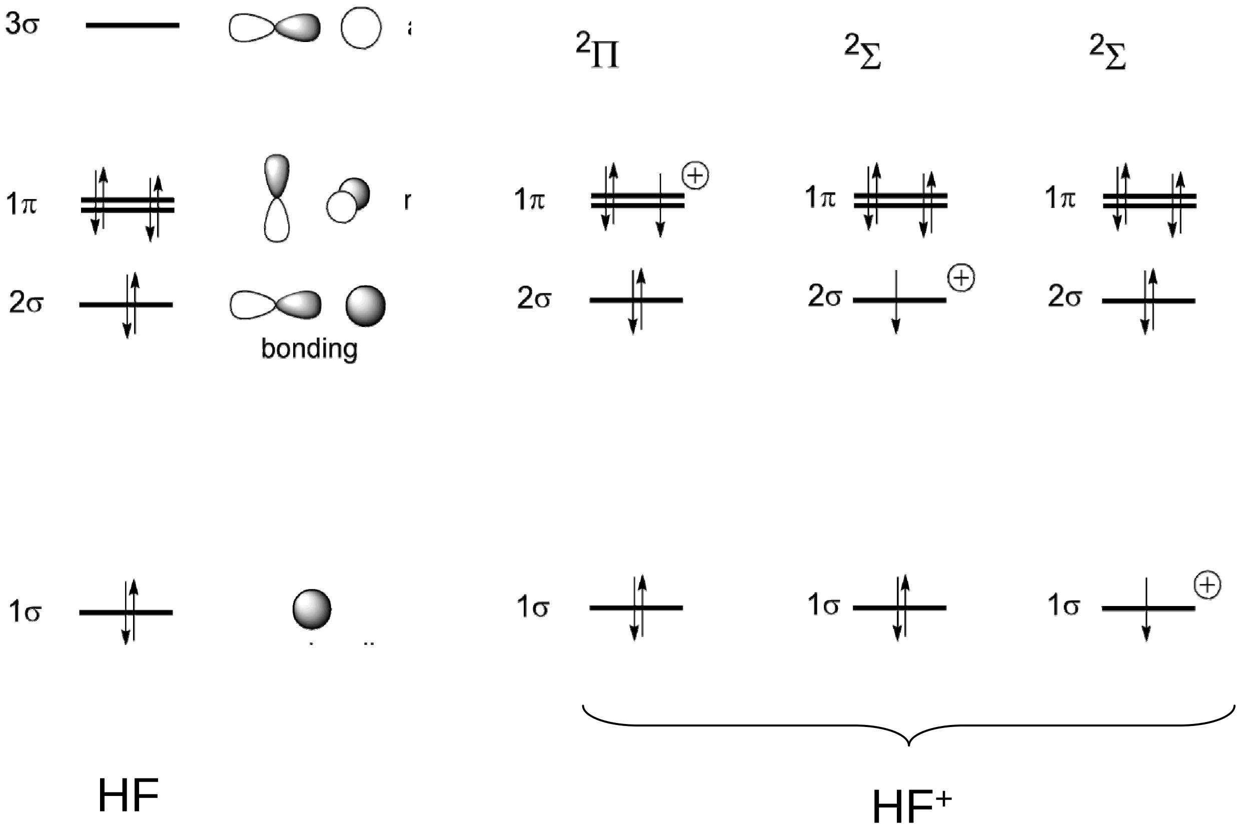
(K.E. measured)

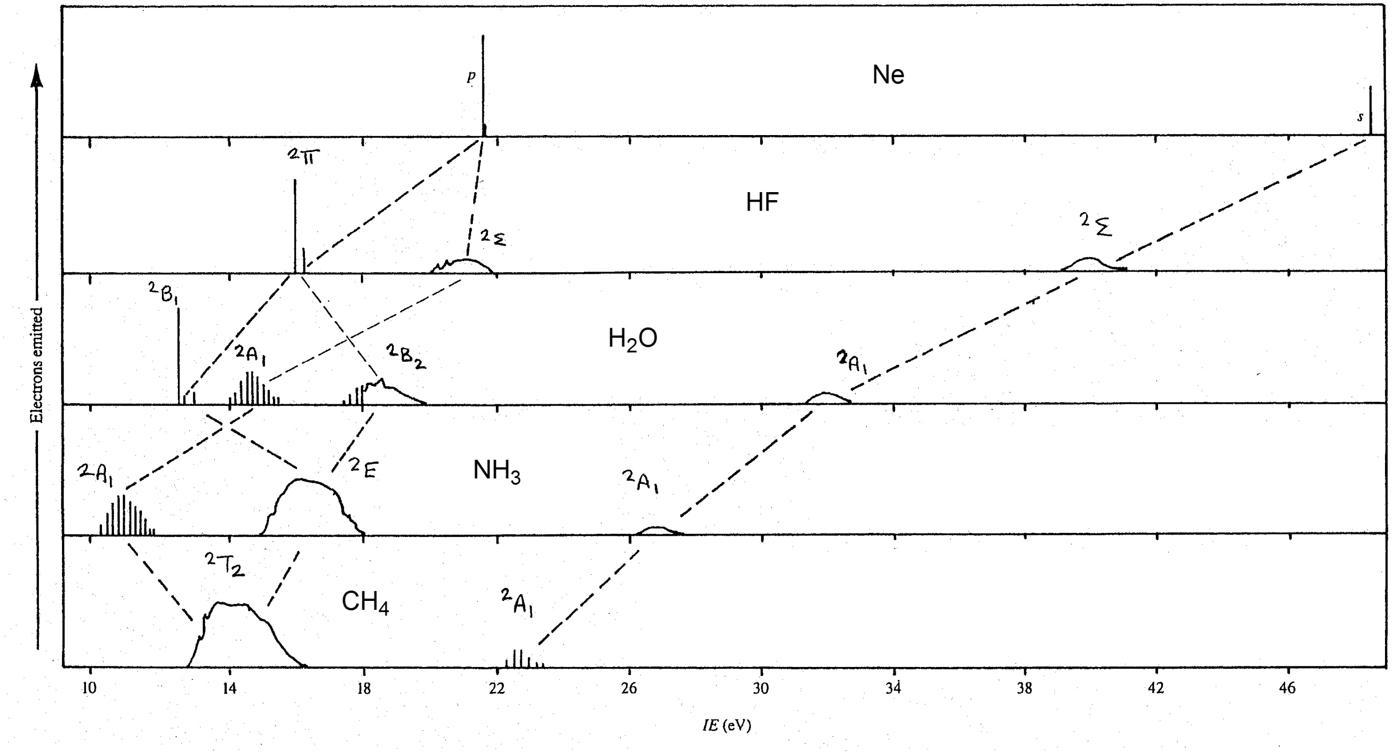
Extensive fine structure



PES of HF

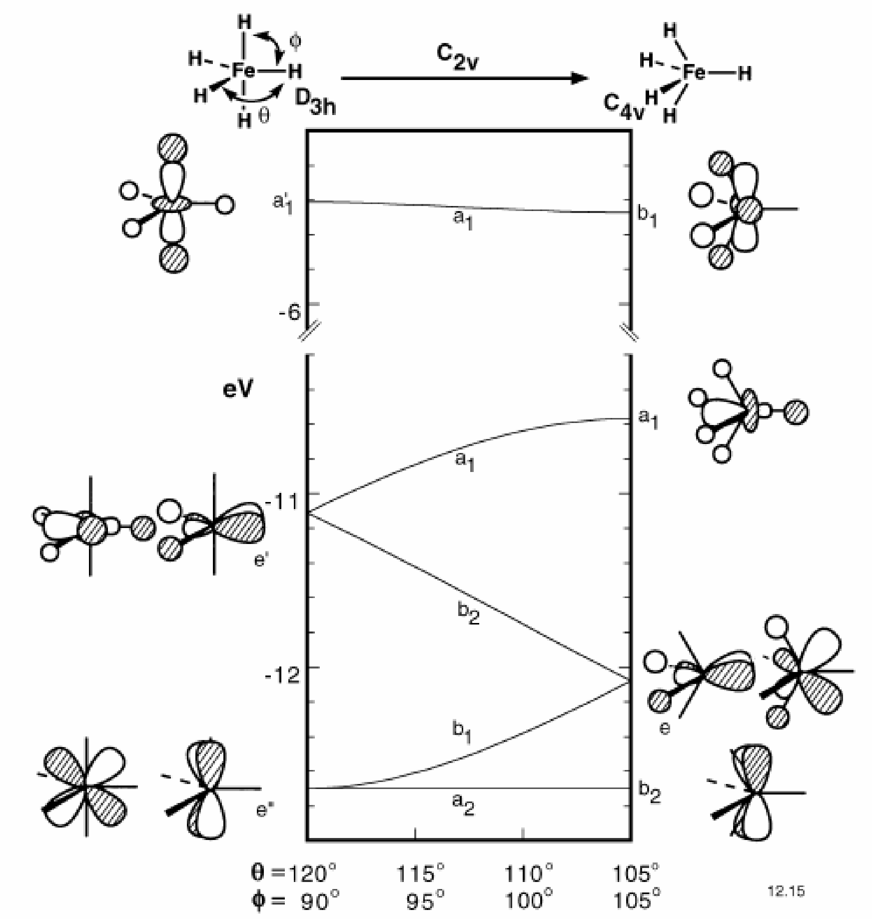

Electrons emitted
²Π
²Σ
²Σ
16
18
20
38
40
42
IE (eV)


3σ
1π
2σ
bonding
1σ
HF
²Π
²Σ
²Σ
1π
2σ
1σ
1π
2σ
1σ
1π
2σ
1σ
⊕
⊕
⊕
HF⁺



	symmetry	no. of bands	orbital symmetries
CH_4	T_d	2	t_2, a_1
NH_3	C_{3v}	3	$2a_1$, e, $1a_1$
H_2O	C_{2v}	4	b_1, $2a_1$, b_2, $1a_1$
HF	$C_{\infty v}$	3	π, 2σ, 1σ
Ne	R	2	π, σ

Shapes of molecules: Walsh diagrams



Walsh's rule

A molecule adopts the structure that best stabilises the HOMO.

If the HOMO is unperturbed by the structural change under consideration, then the occupied MO lying closest to it governs the geometric preference.

In most cases this means that molecules tend to adopt the geometry that maximises the HOMO-LUMO gap.

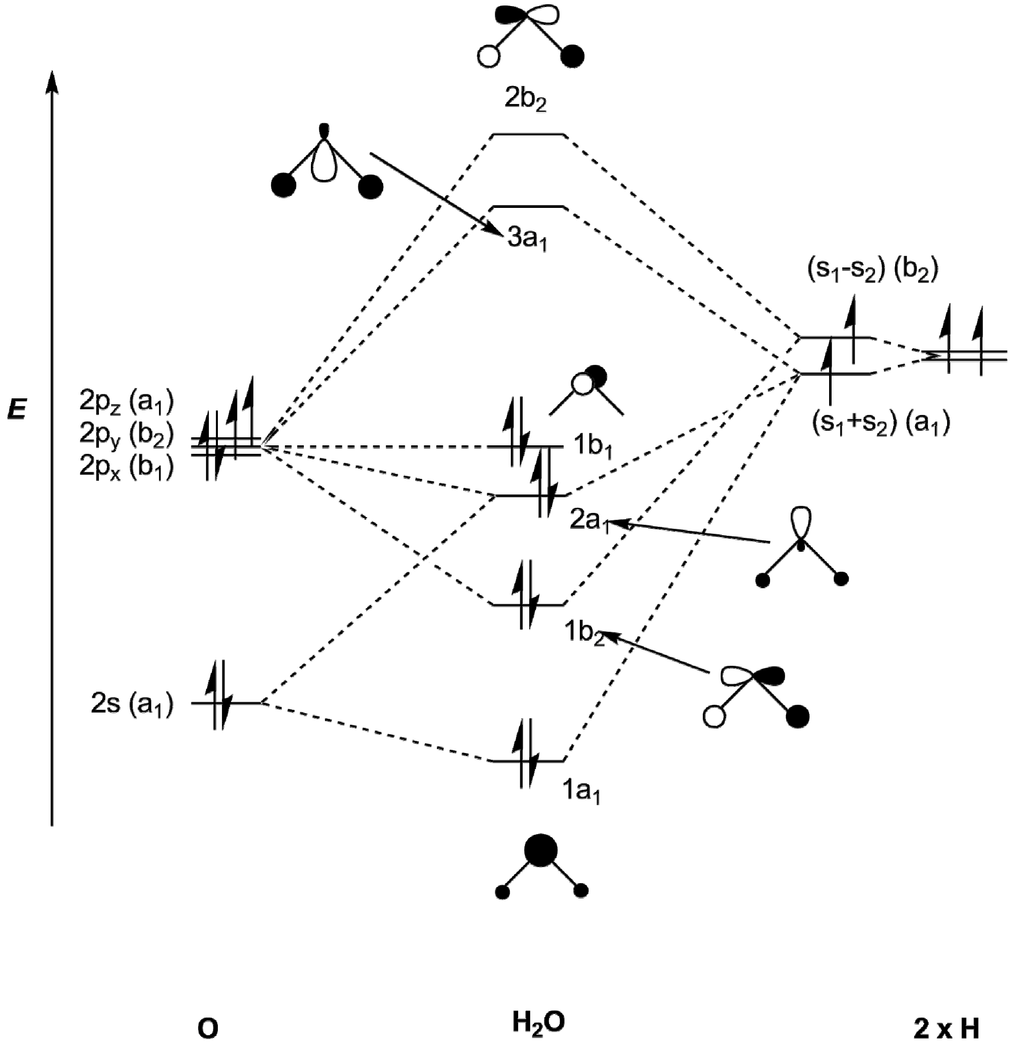
Consider AH_2 molecules

Known shape of some AH2 molecules		
Molecular species	No. of valence electrons	Shape
LiH_2^+	2	Bent
LiH_2, BeH_2^+	3	Linear
BeH_2, BH_2^+	4	Linear
BH_2, AlH_2, CH_2^+	5	Bent
CH_2, SiH_2, BH_2^-, NH_2^+	6	Bent
NH_2, PH_2, CH_2^-, OH_2^+	7	Bent
OH_2, SH_2, NH_2^-, FH_2^+	8	Bent

Molecular species	angle
BH_2	131
CH_2	110
SiH_2	93
NH_2	103
OH_2	104.5
SH_2	92.1
FH_2^+	118

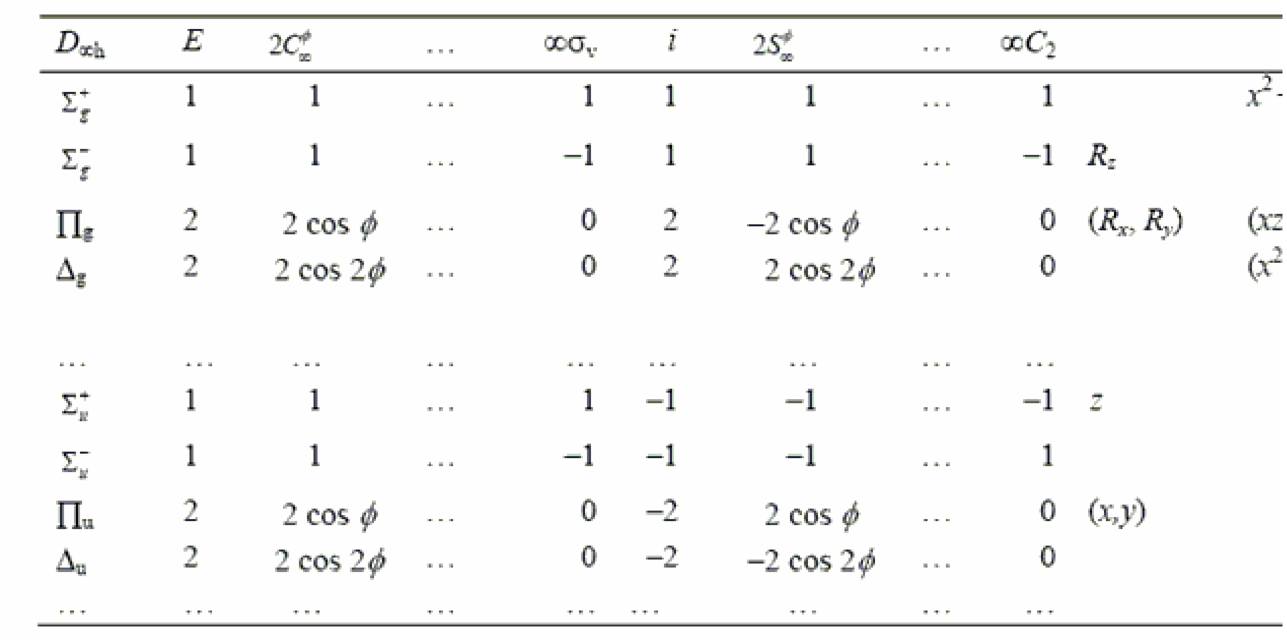
First consider bonding at the 2 limits (C_{2v} and $D_{\infty h}$)

C_{2v}



First consider bonding at the 2 limits (C_{2v} and $D_{\infty h}$)

$D_{\infty h}$



$D_{\infty h}$	E	$2C_\infty^\phi$	…	$\infty\sigma_v$	i	$2S_\infty^\phi$	…	∞C_2		
Σ_g^+	1	1	…	1	1	1	…	1		x^2-
Σ_g^-	1	1	…	−1	1	1	…	−1	R_z	
Π_g	2	$2\cos\phi$	…	0	2	$-2\cos\phi$	…	0	(R_x, R_y)	(xz
Δ_g	2	$2\cos 2\phi$	…	0	2	$2\cos 2\phi$	…	0		(x^2
…	…	…	…	…	…	…	…	…		
Σ_u^+	1	1	…	1	−1	−1	…	−1	z	
Σ_u^-	1	1	…	−1	−1	−1	…	1		
Π_u	2	$2\cos\phi$	…	0	−2	$2\cos\phi$	…	0	(x,y)	
Δ_u	2	$2\cos 2\phi$	…	0	−2	$-2\cos 2\phi$	…	0		
…	…	…	…	…	…	…	…	…		

Symmetry analysis: For the A atom (4 AOs):

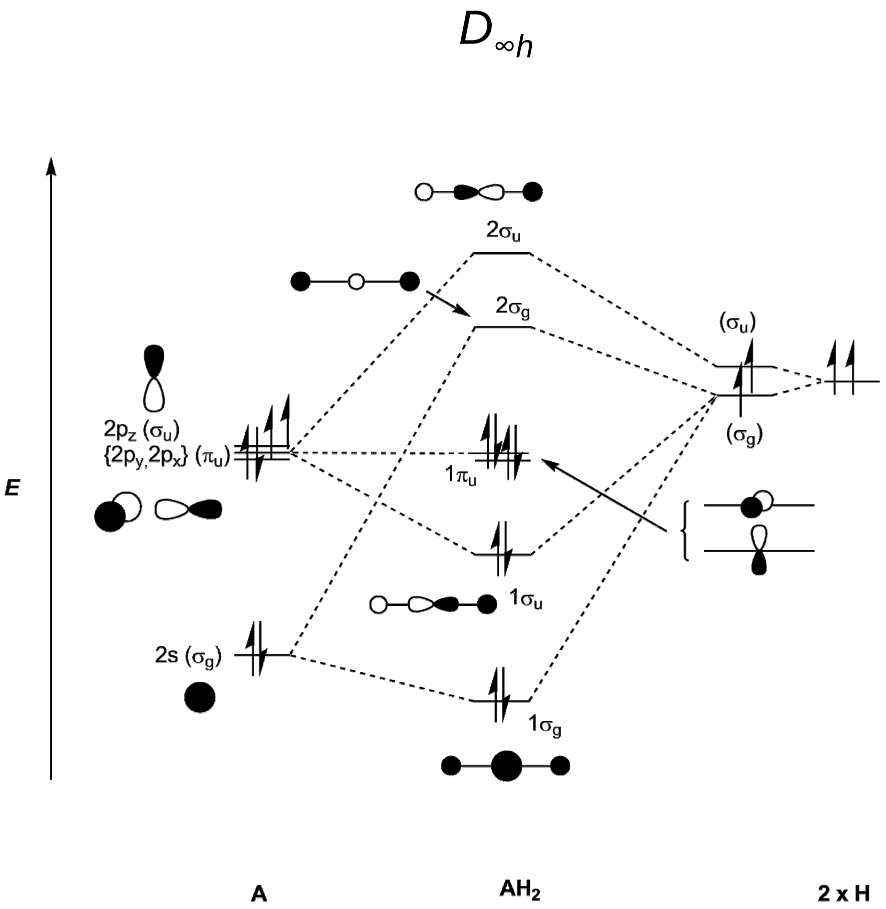
Γ (2s) = σ_g Γ ($2p_z$) = σ_u Γ ($2p_{x,y}$) = π_u

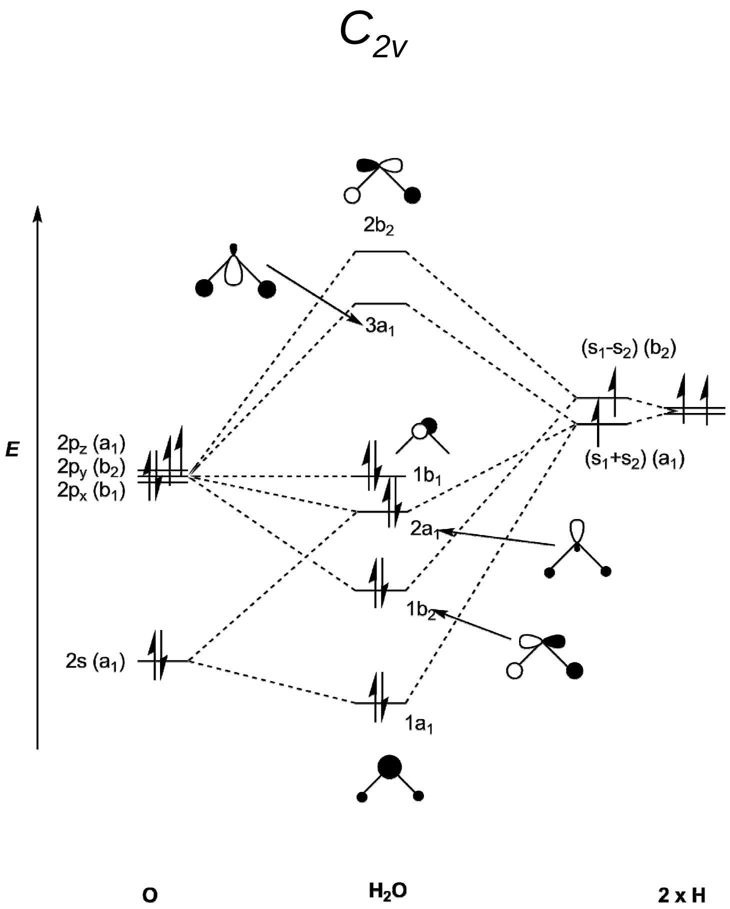
For the H atoms (2 x 1s AO):

Γ (2 x 1s) = $\sigma_g + \sigma_u$

σ_g

σ_u


$D_{\infty h}$
E
$2\sigma_u$
$2\sigma_g$
(σ_u)
(σ_g)
$2p_z$ (σ_u)
$\{2p_y, 2p_x\}$ (π_u)
$1\pi_u$
$1\sigma_u$
2s (σ_g)
$1\sigma_g$
A
AH_2
2 x H


C_{2v}
E
$2b_2$
$3a_1$
(s_1-s_2) (b_2)
(s_1+s_2) (a_1)
$2p_z$ (a_1)
$2p_y$ (b_2)
$2p_x$ (b_1)
$1b_1$
$2a_1$
$1b_2$
2s (a_1)
$1a_1$
O
H_2O
2 x H