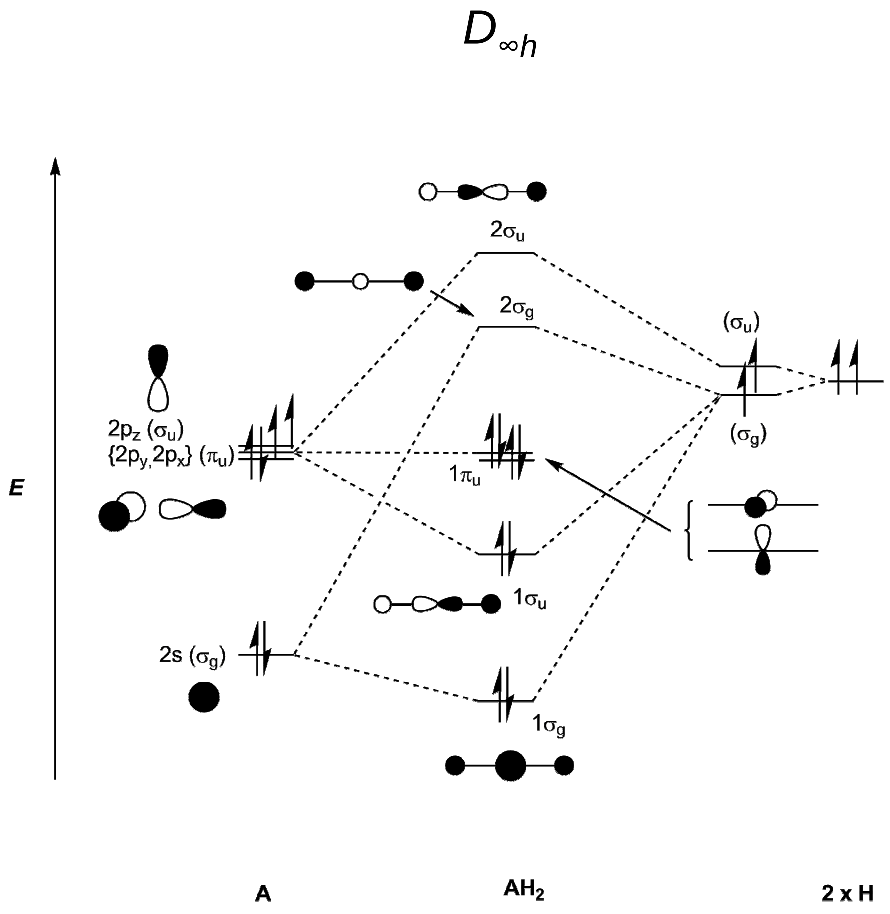
Bonding in Molecules

Lecture 3

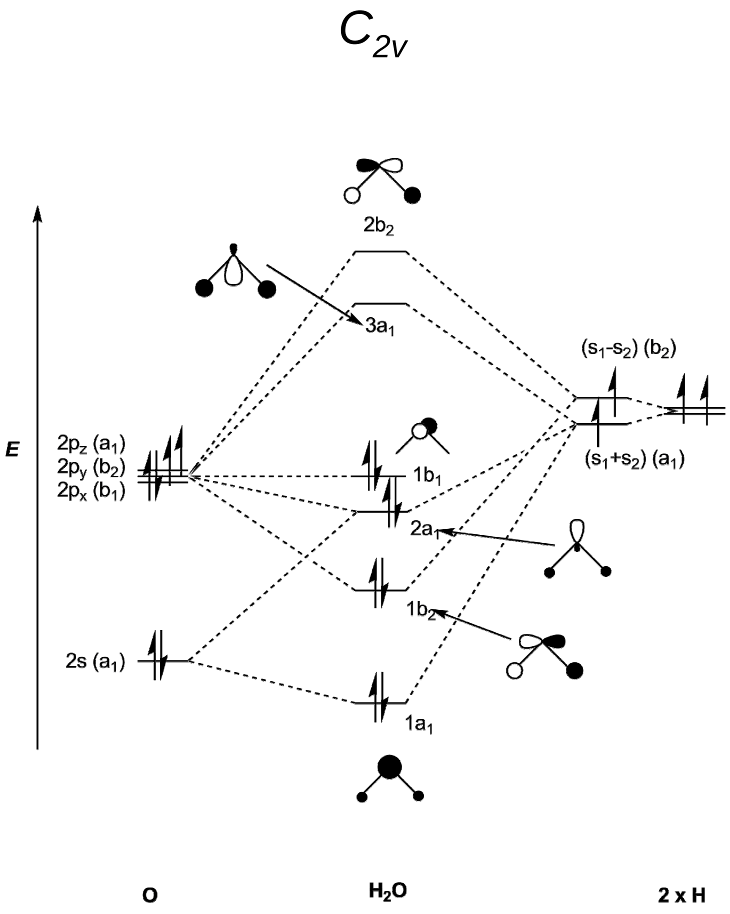
Molecular shapes

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

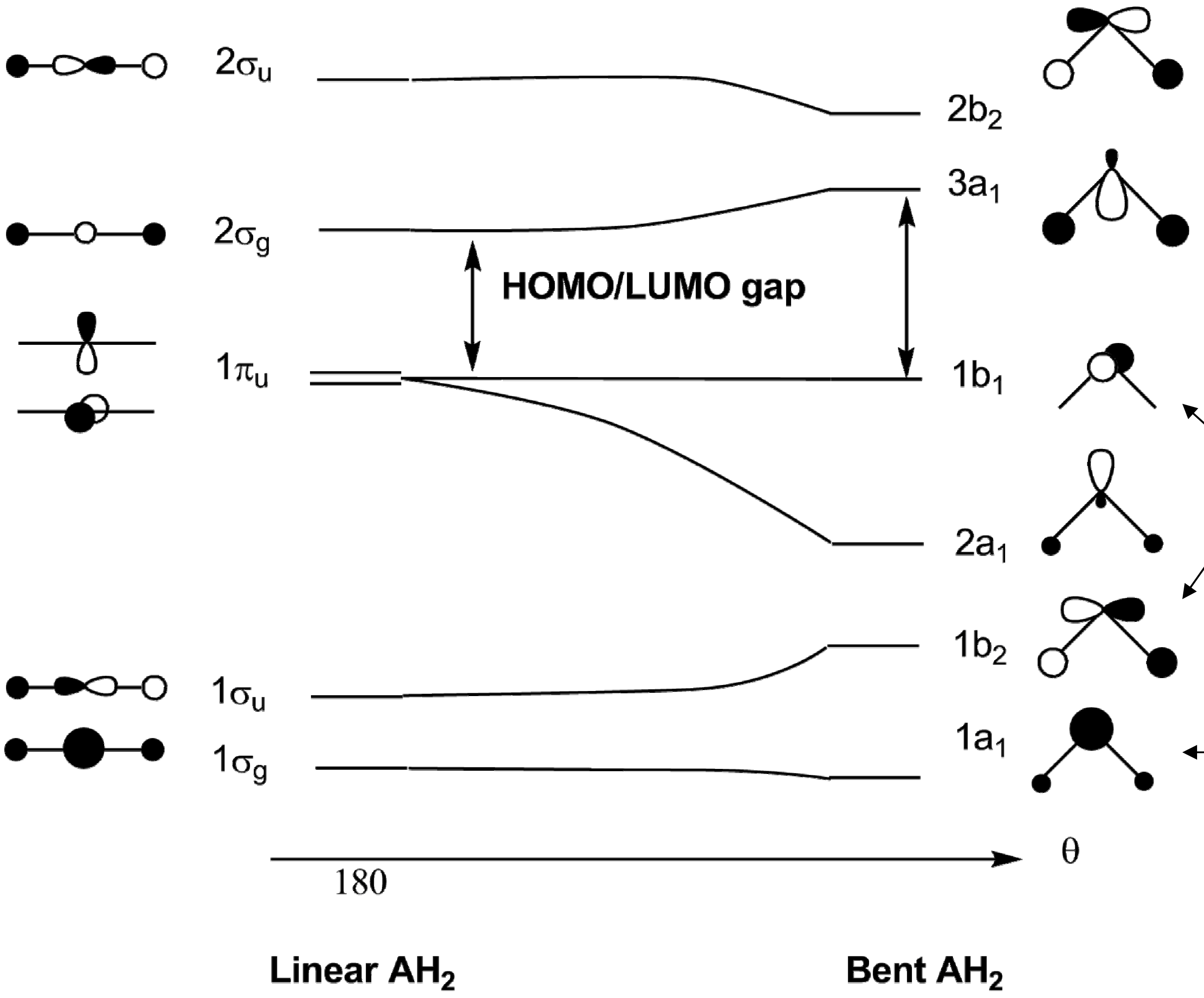


$D_{\infty h}$
E
$2\sigma_u$
$2\sigma_g$
(σ_u)
$2p_z$ (σ_u)
$\{2p_y, 2p_x\}$ (π_u)
$1\pi_u$
(σ_g)
$1\sigma_u$
2s (σ_g)
$1\sigma_g$
A
AH_2
2 x H



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

Walsh diagram



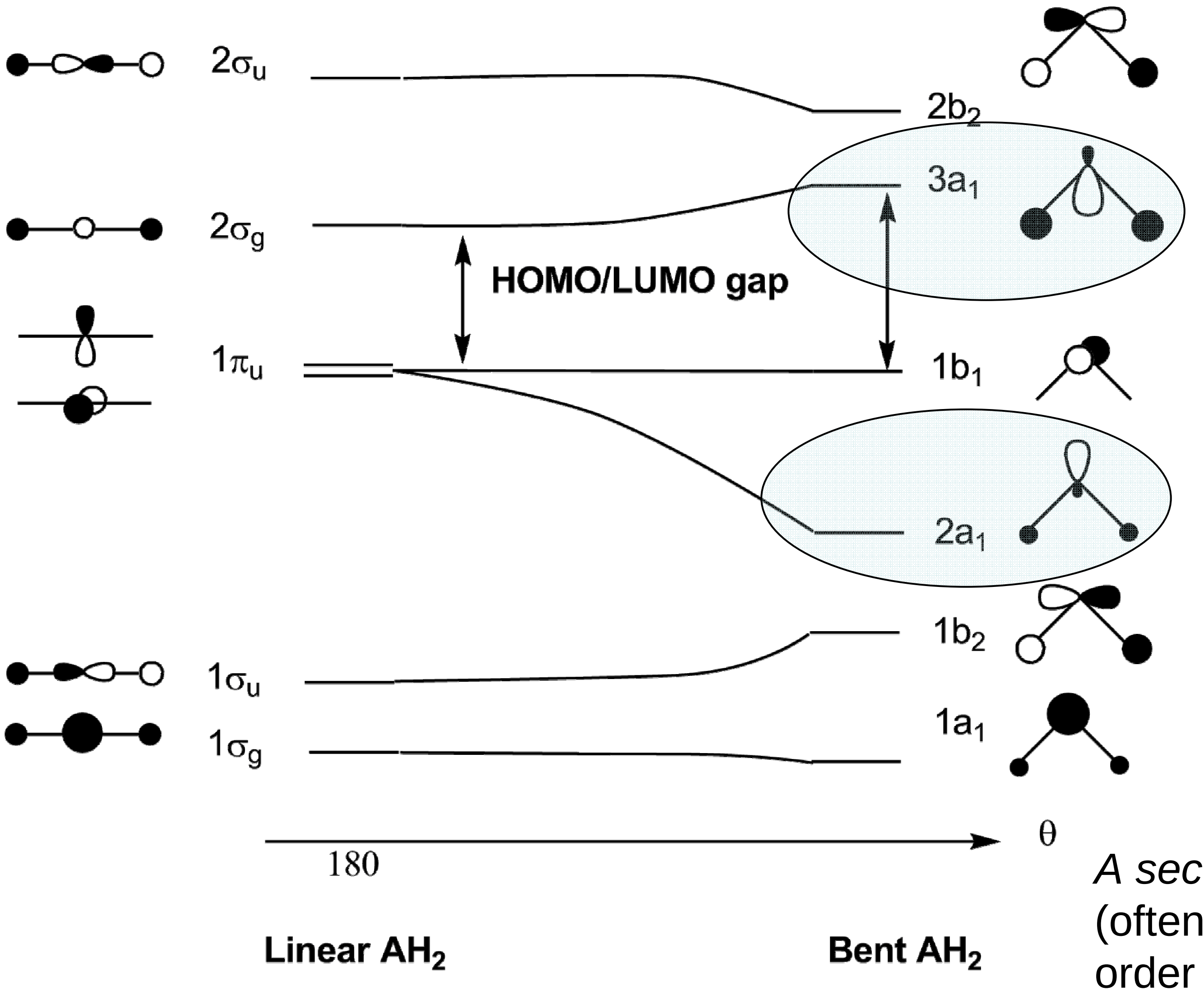
poorer overlap of H1s with $2p_x$

remains non-bonding

better overlap of H 1s orbitals

First order effects

Walsh diagram

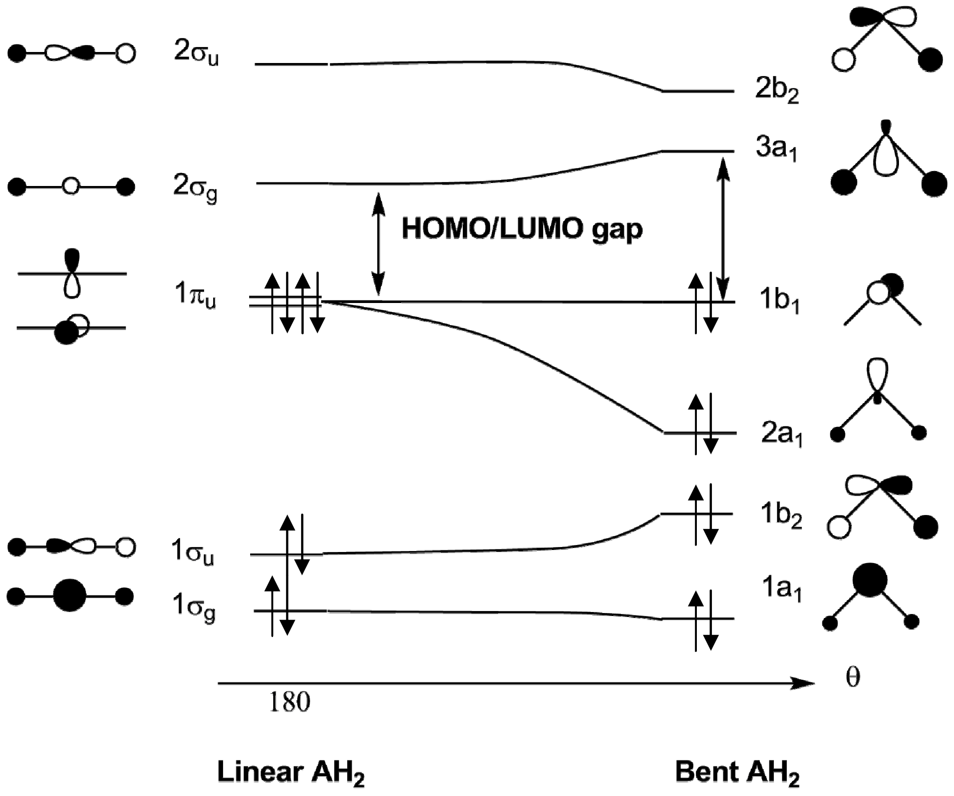


mixing can occur
between 2 orbitals
because they both
transform
as a_1 in the lower
symmetry

A second order effect
(often called a second
order Jahn Teller distortion)

$$\propto \frac{1}{\Delta E}$$

Walsh diagram



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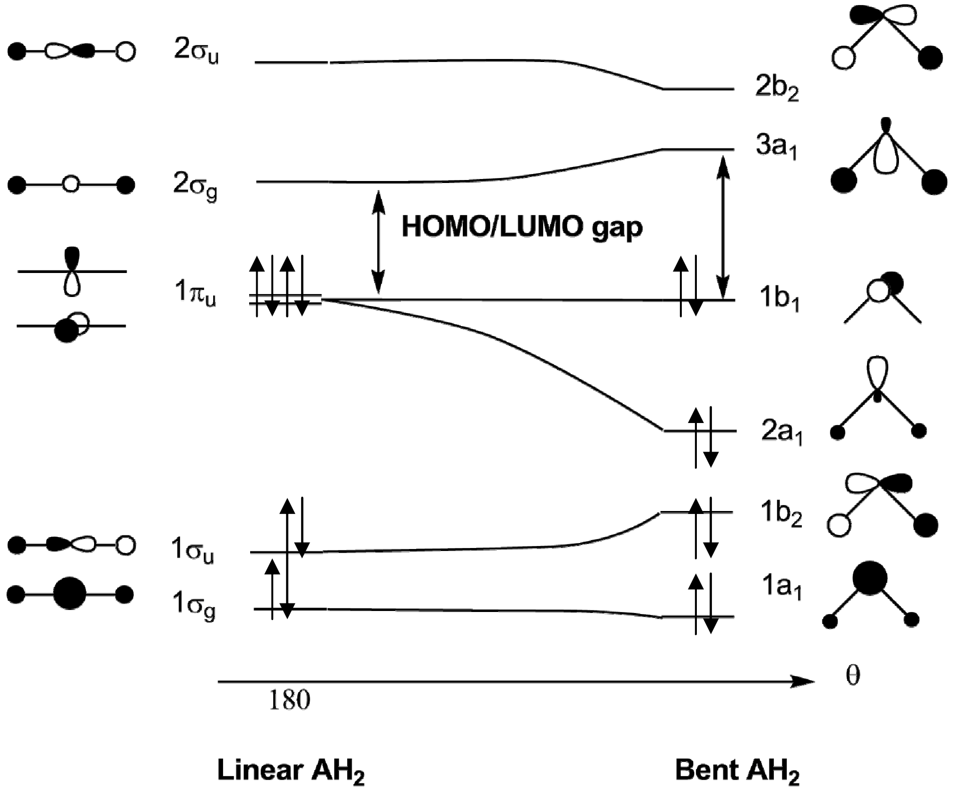
Recall: a molecule adopts the structure that best stabilises the HOMO. If the HOMO is unperturbed by the structural change under consideration, then the occupied MO lying closest to it governs the geometric preference.

Walsh diagram



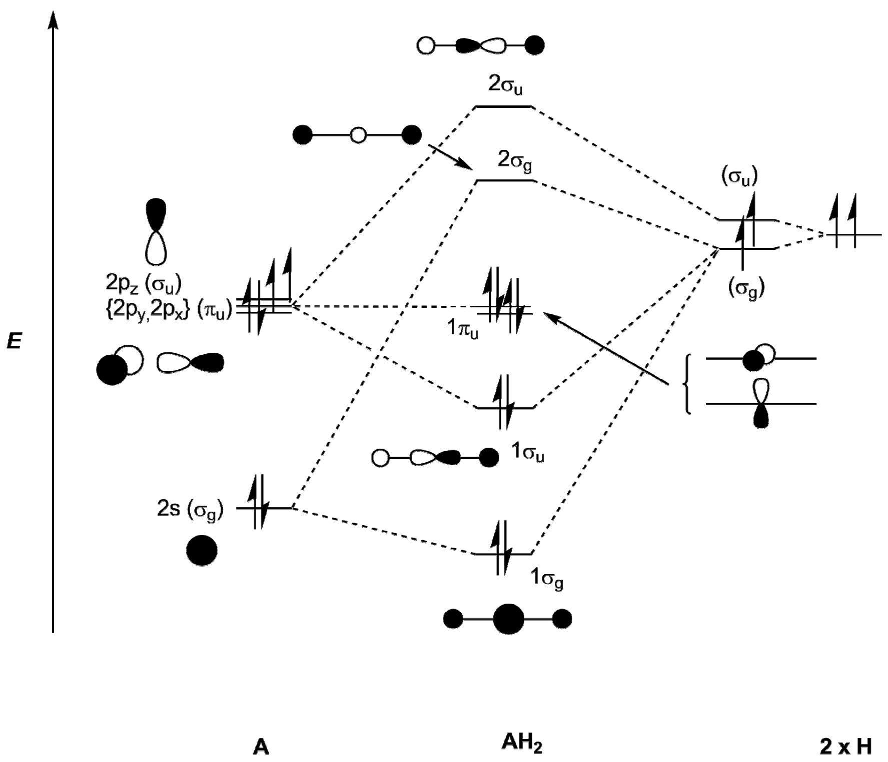
OH_2 *vs* SH_2 *vs* SeH_2?

VSEPR?

Decreased s/p hybridisation?
(note bonding with pure p orbitals implies 90° angles)

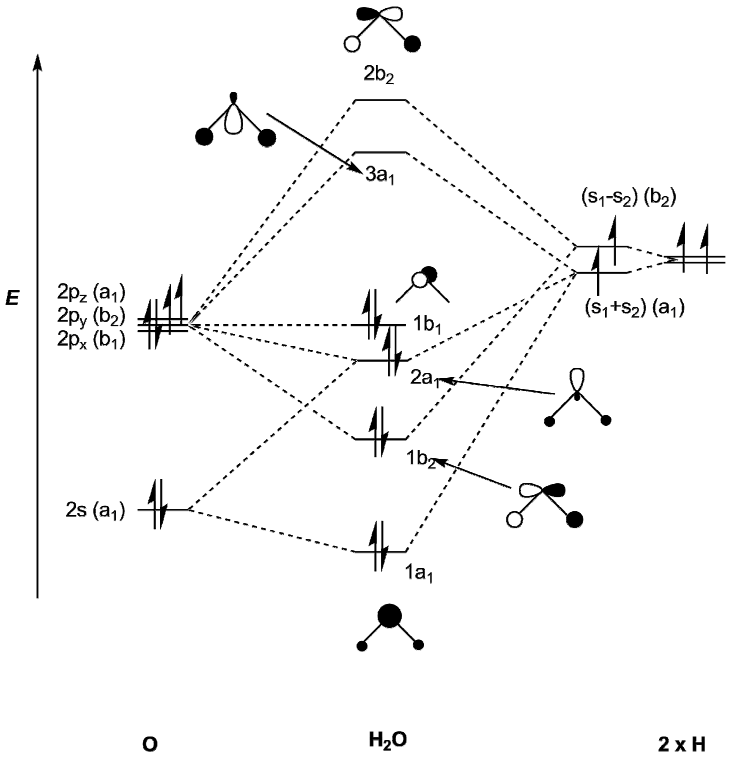
$1a_1^2\ 1b_2^2$ +	$2a_1^1$		$2a_1^2$		$2a_1^2\ 1b_1^1$		$2a_1^2\ 1b_1^2$	
	BH_2	131	CH_2	110	NH_2	103	OH_2	104.5
			NH_2^+	115-120	OH_2^+	110.5	FH_2^+	118
			BH_2-	102	CH_2-	99	NH_2^-	104
	AlH_2	119	SiH_2	93	PH_2	92	SH_2	92.1
					AsH_2	91	SeH_2	90.6
							TeH_2	90

$D_{\infty h}$



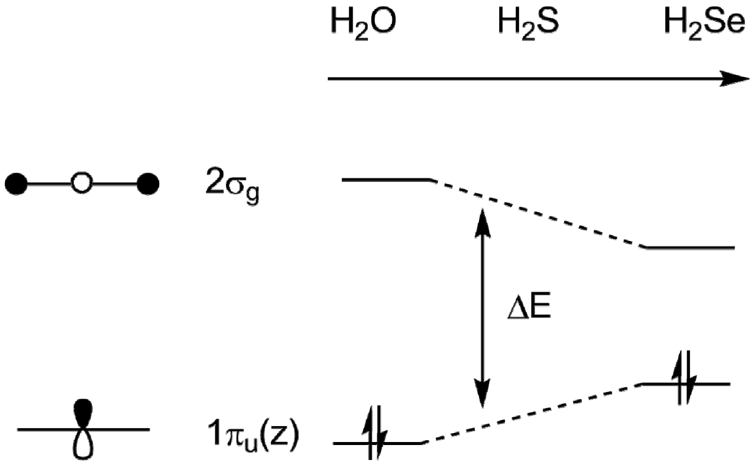
2 x ‘sp’ hybrids + 2 x p lone pairs

C_{2v}



3 x ‘sp^2’ hybrids + 1 x p lone pair

more p character in bonding orbitals



2nd order JT effect mixes s character (originally in 2σ_g) into the lone pair (1π_u) so more p character accumulates in the bonding orbitals.

Strength of 2^{nd} order JT effect proportional to 1/ΔE

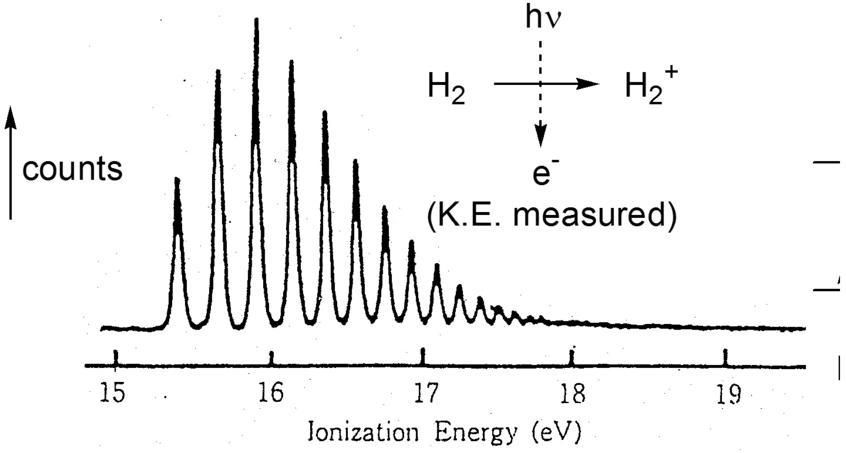
2 factors to consider:

Decrease in electronegativity destabilises π_u

3/4s orbitals of S/Se are lower than 2s of O (increased penetration) and also overlap more weakly with H 1s because they are diffuse. Both factors stabilise σ_g

both make 2^{nd} order JT effect stronger in the heavier elements

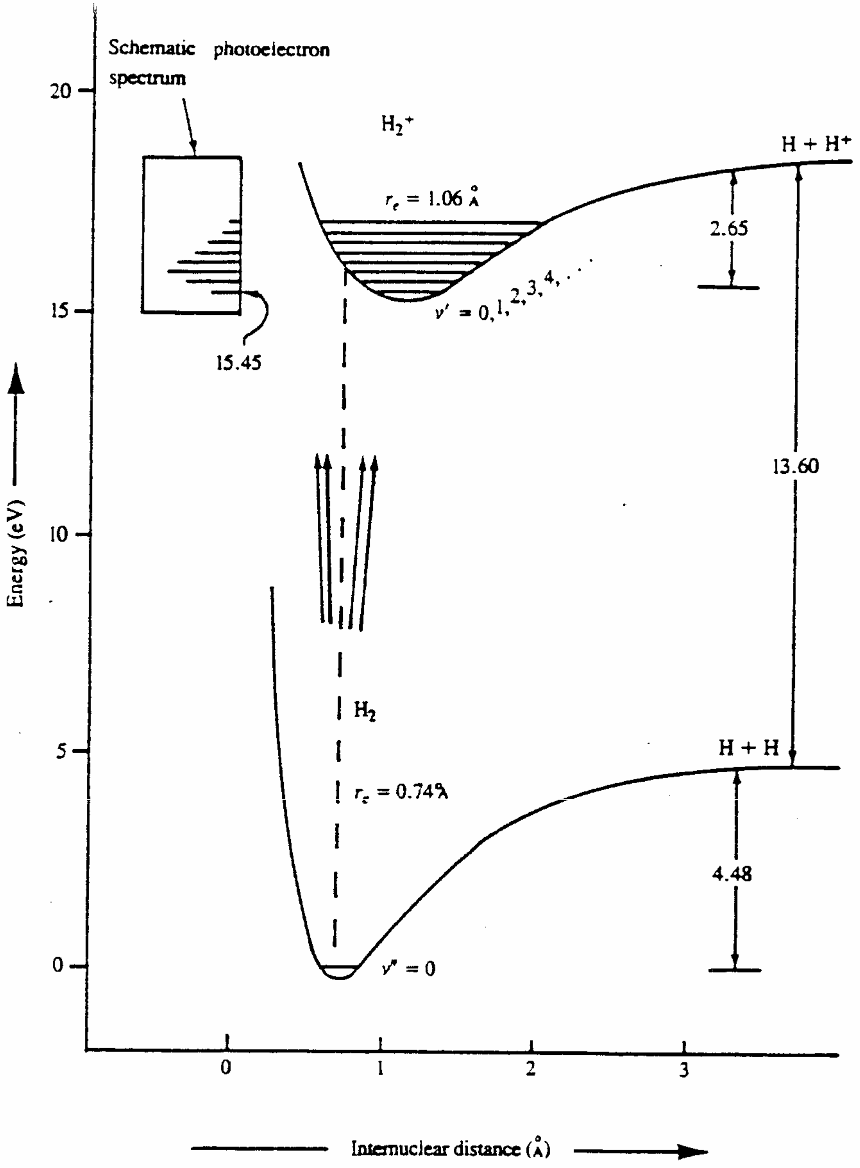
PES revisited: origin of fine structure



$H_2 \xrightarrow{h\nu} H_2^+$

e^-

(K.E. measured)



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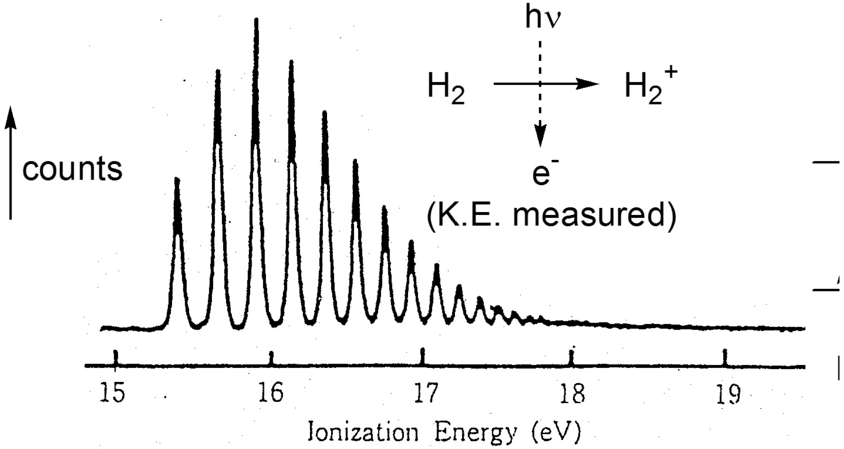

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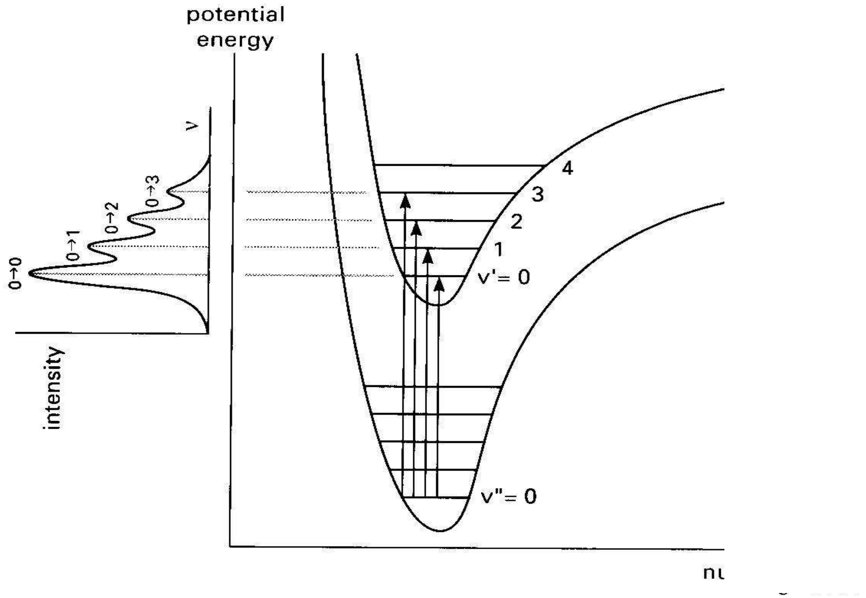
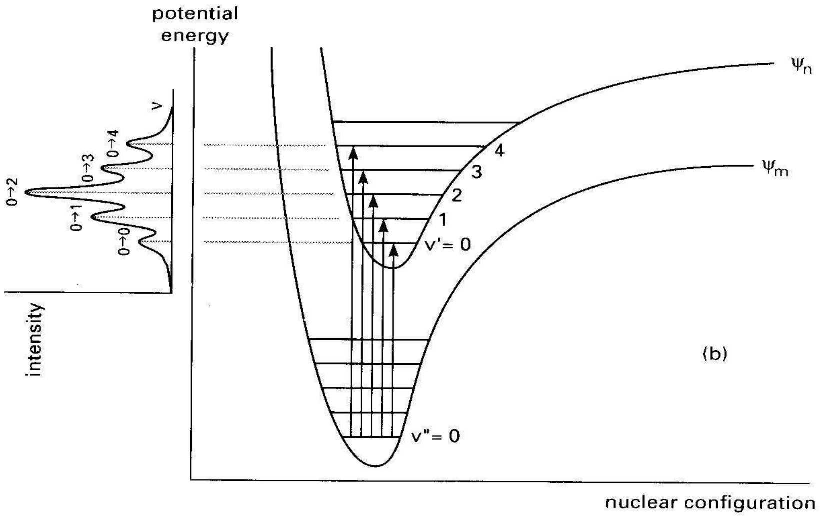
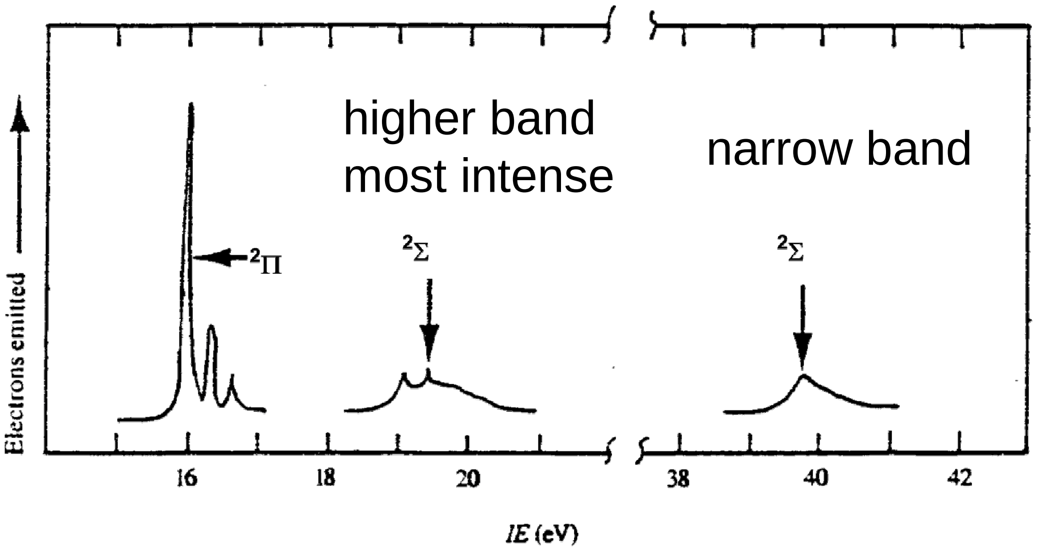




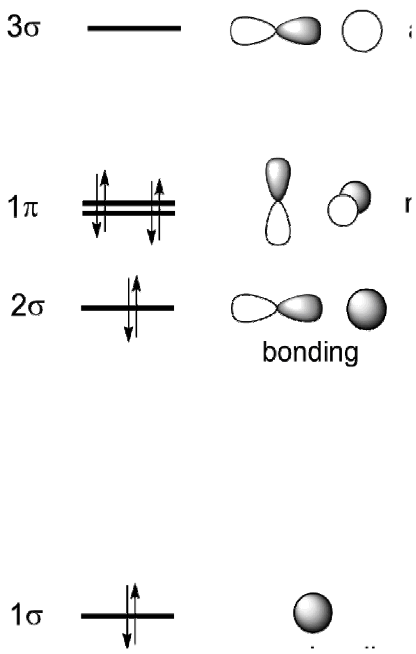
PES revisited: HF

(0,0) band
most intense



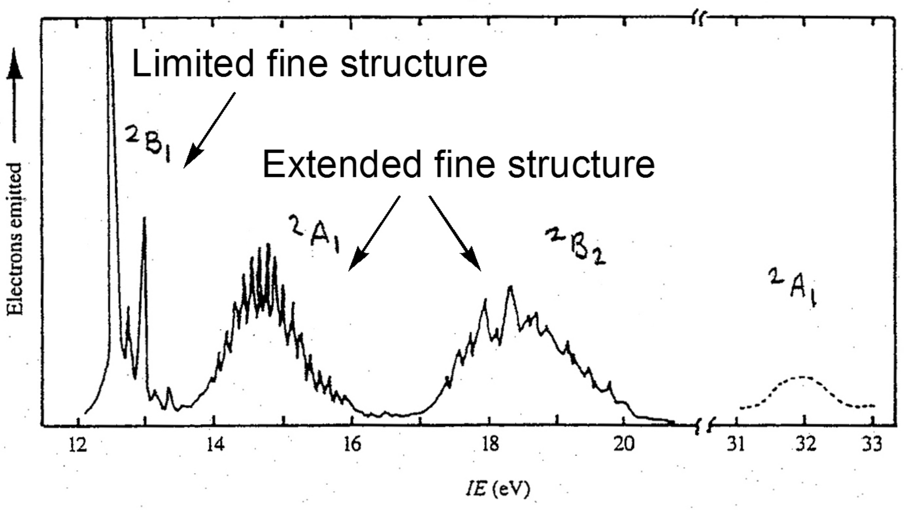
higher band
most intense

narrow band

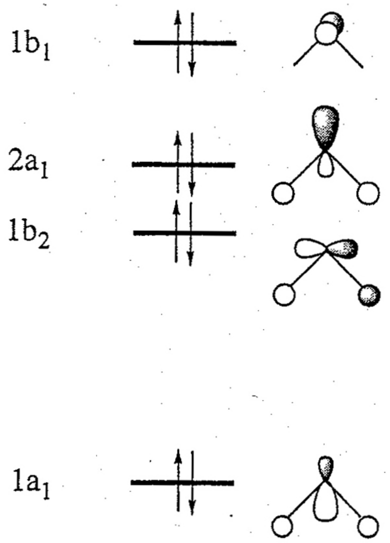


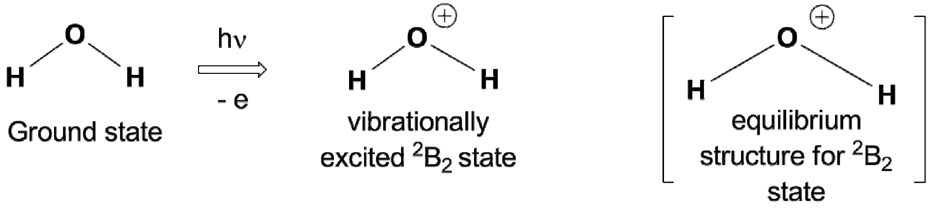
PES revisited: H_2O

(0,0) band
most intense


Limited fine structure

Extended fine structure

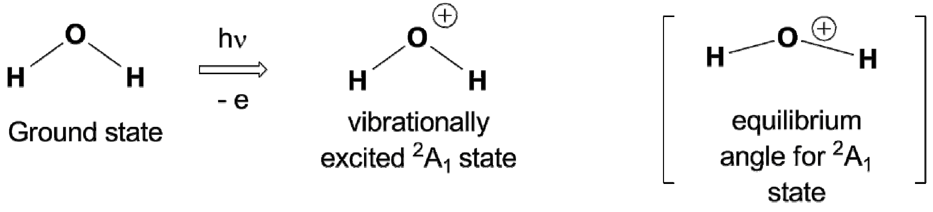




Ground state

vibrationally excited $^2B_2$ state

equilibrium structure for $^2B_2$ state



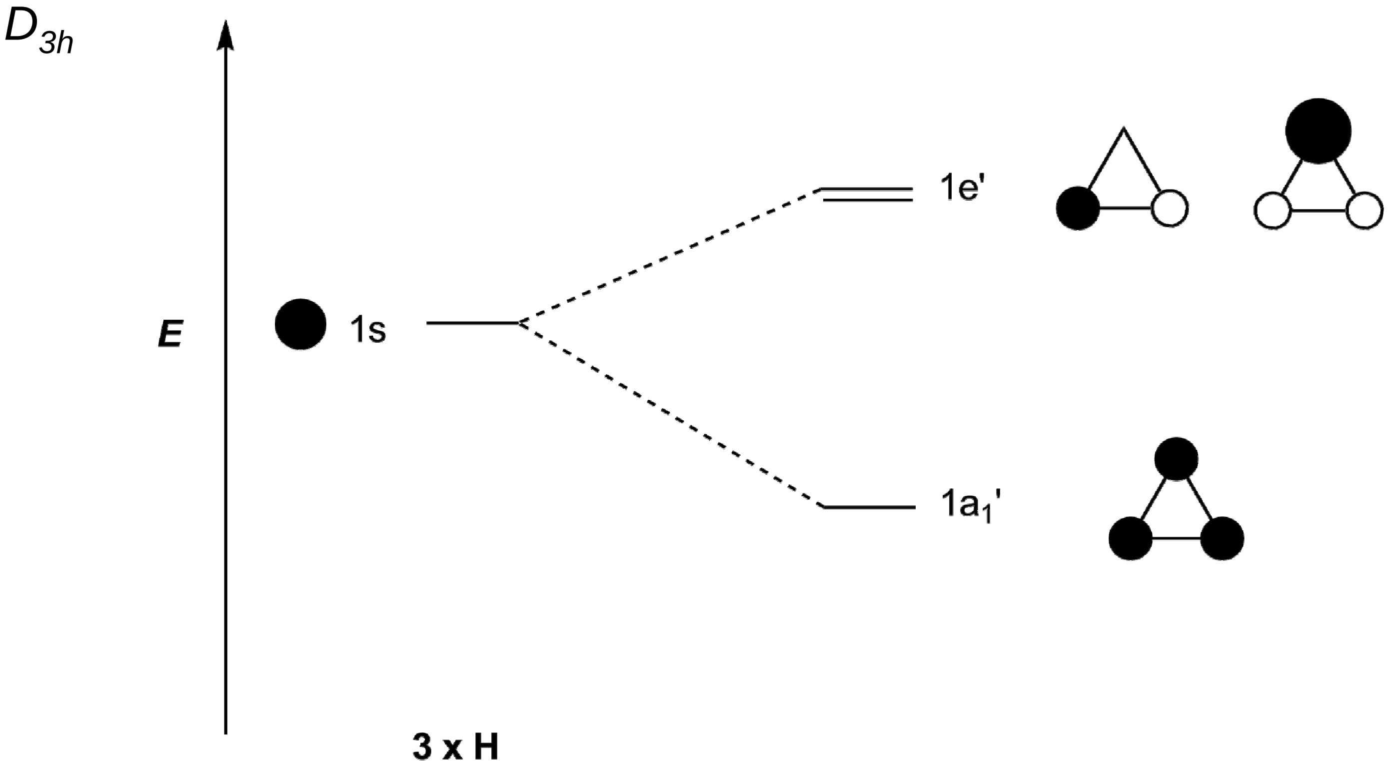
Ground state

vibrationally excited $^2A_1$ state

equilibrium angle for $^2A_1$ state

The shapes of H_3^+ and H_3^-:
1st order JT effects, 3-centre-4-electron and 3-centre-2-electron bonds

Consider MOs for the 2 limiting shapes for a 3-atom system:
linear ($D_{\infty h}$) and triangular (D_{3h})



(using the SALCS given in the handout)

The shapes of H_3^+ and H_3^-:
1st order JT effects, 3-centre-4-electron and 3-centre-2-electron bonds

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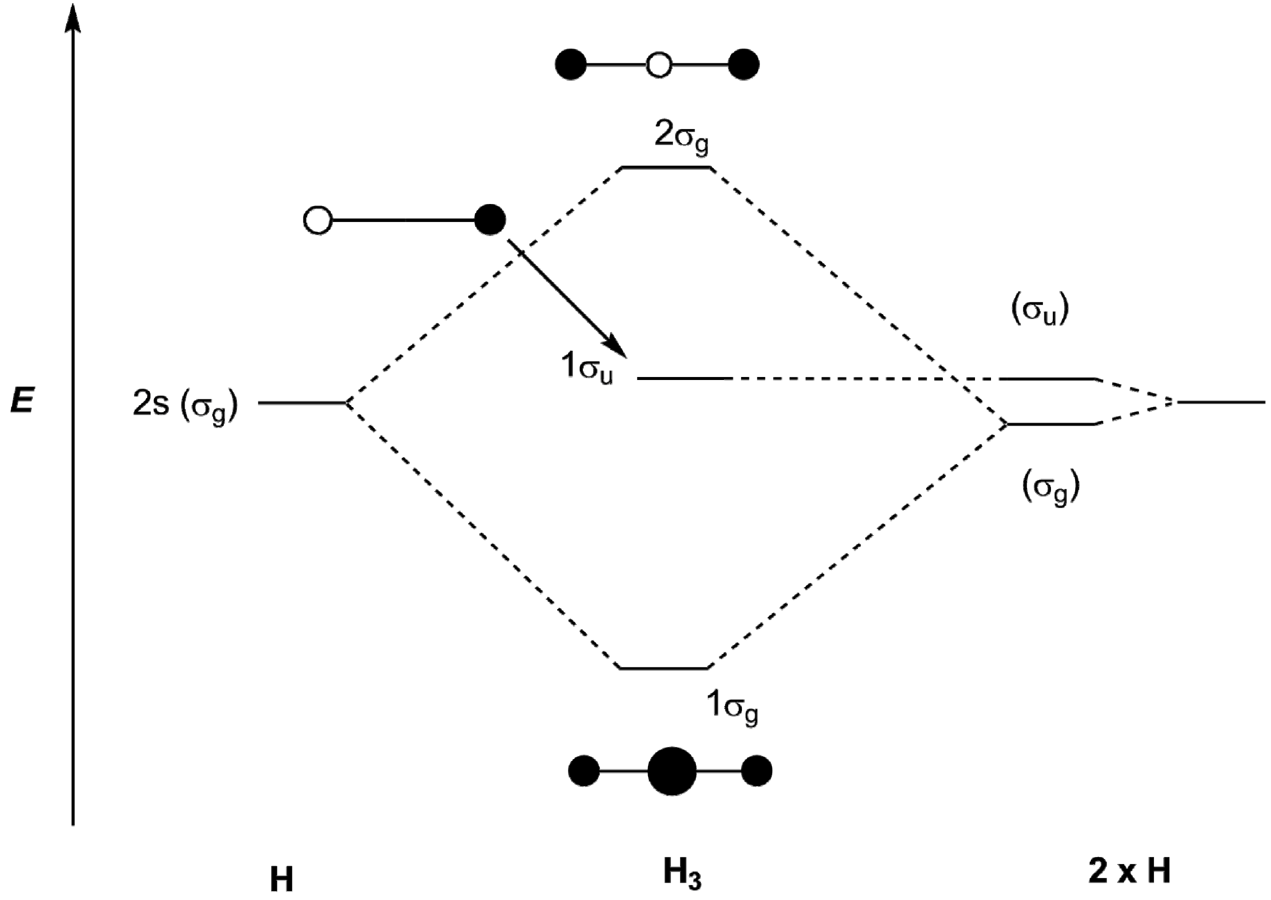
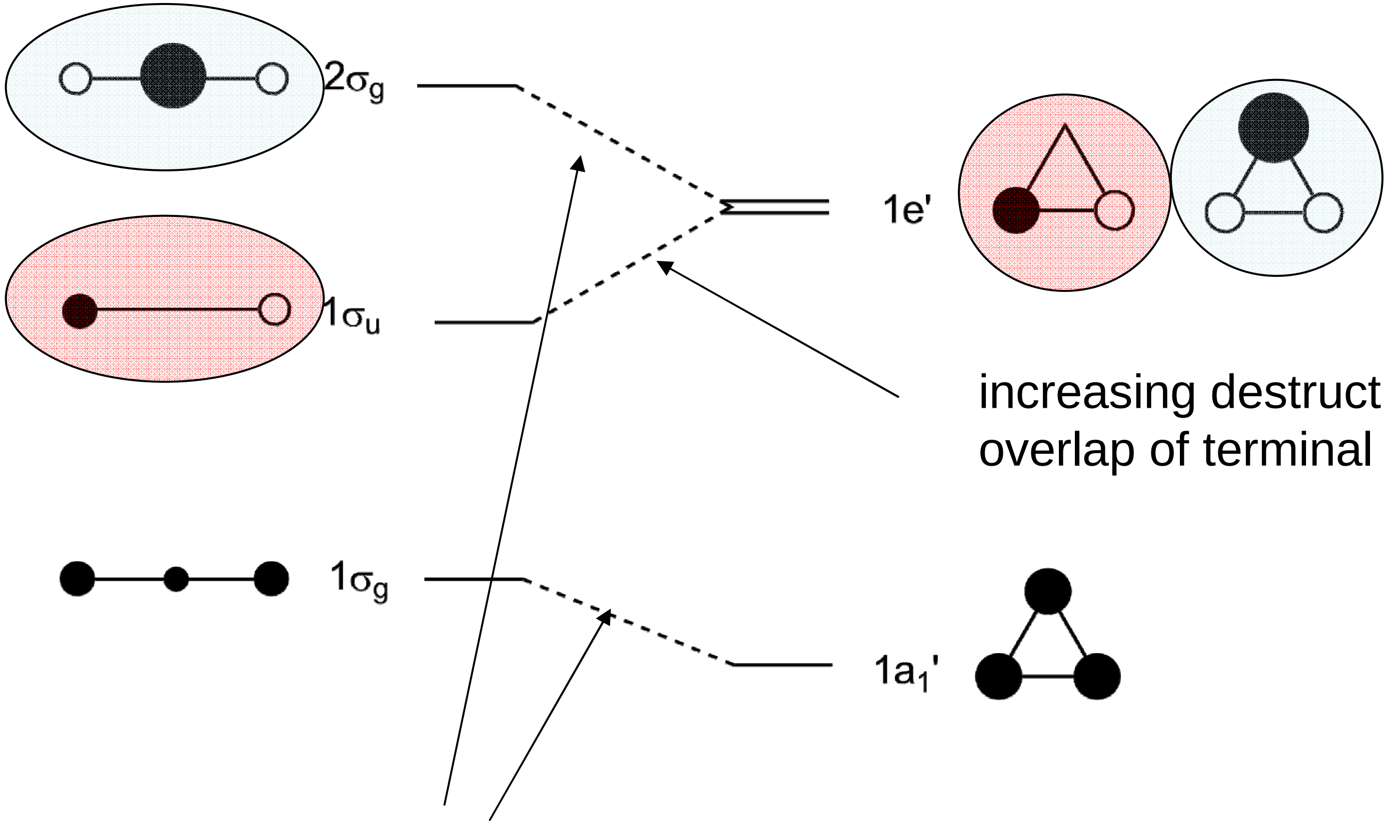
linear ($D_{\infty h}$) and triangular (D_{3h})

$D_{\infty h}$



Walsh diagram

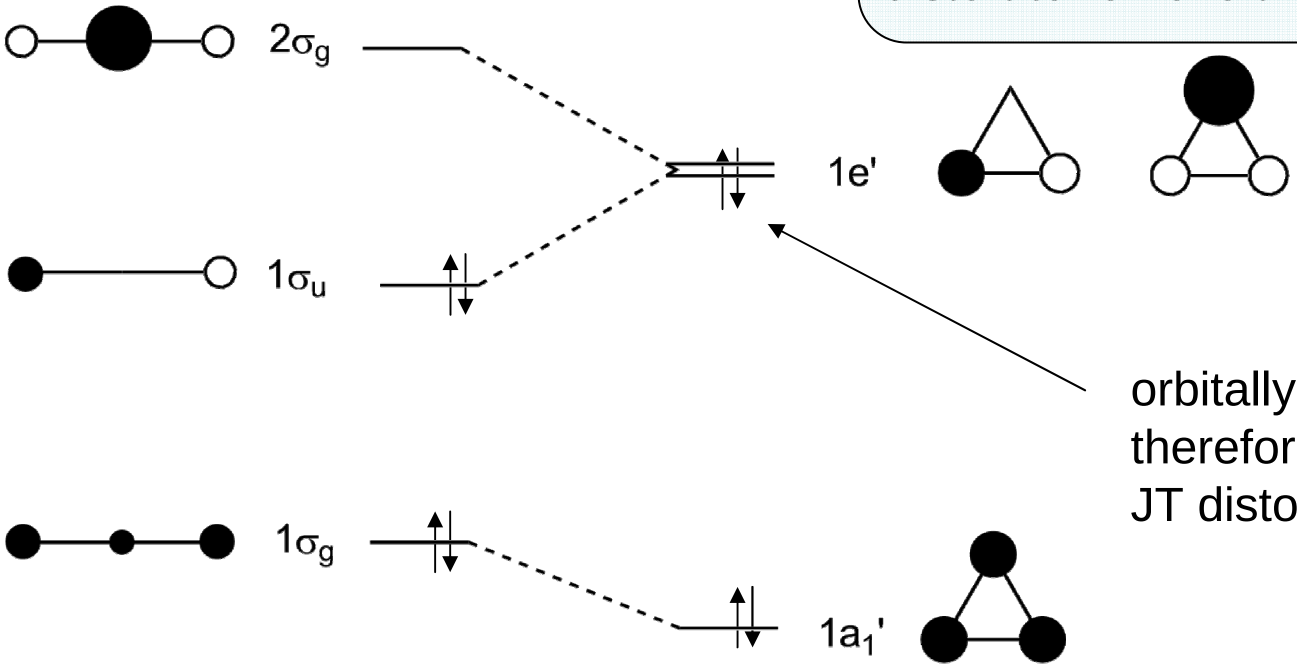


increasing destructive
overlap of terminal H 1s

increasing constructive
overlap of terminal H 1s

Walsh diagram

(1st order) Jahn-Teller theorem
If a non-linear molecule is in an orbitally degenerate state, it will distort to remove the degeneracy



orbitally degenerate therefore a *first-order* JT distortion

H_3^-
(a 3-centre-4-electron bond)
c.f. hypervalent species
such as HF_2^-, XeF_2

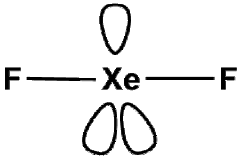
H_3^+
(a 3-centre-2-electron bond)
c.f. electron deficient species
such as boranes

Bonding in Hypervalent Molecules

XeF_2 (‘hypervalent’ = 10 electrons on Xe)

Possible explanations?

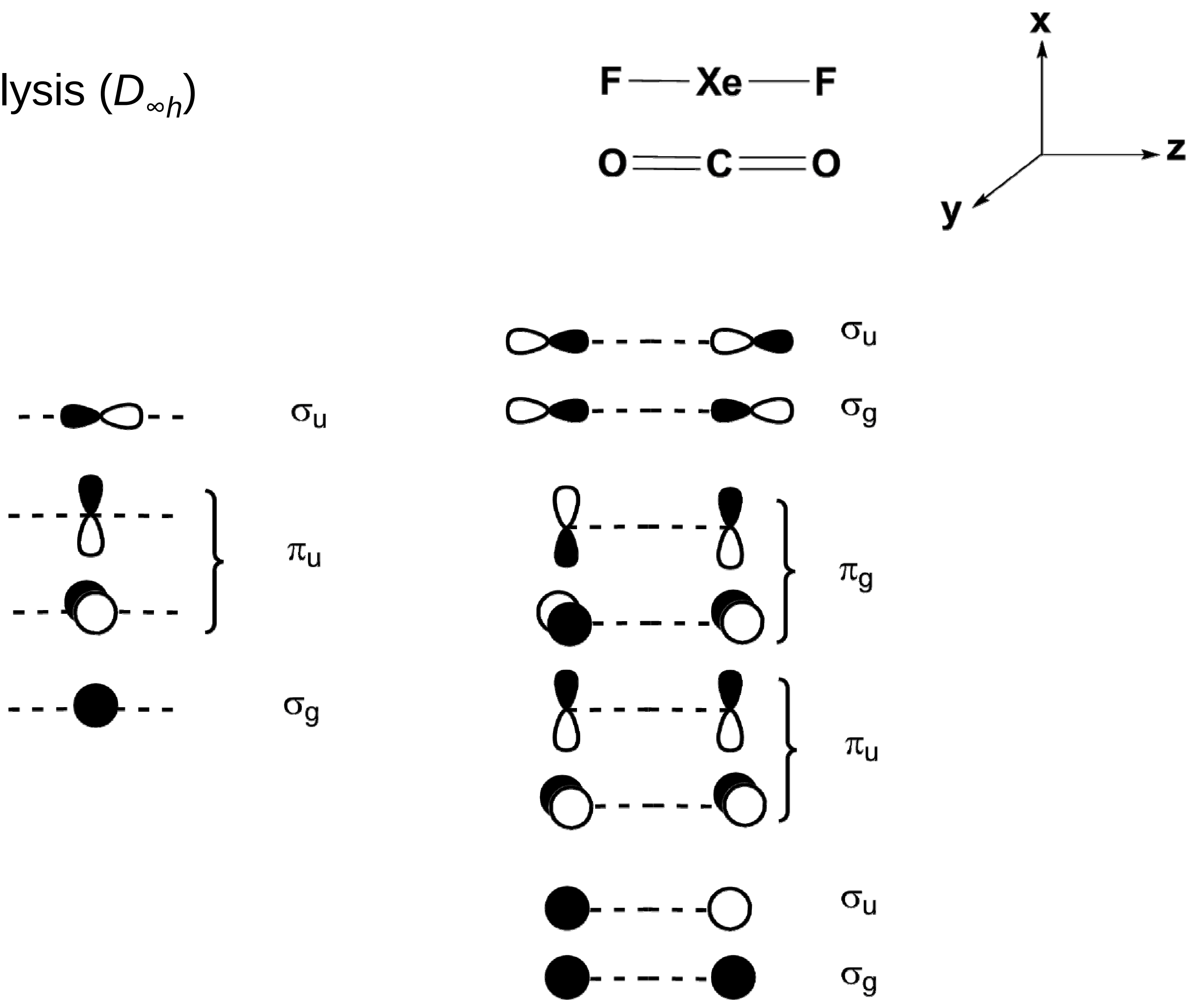
sp^3d hybridisation?

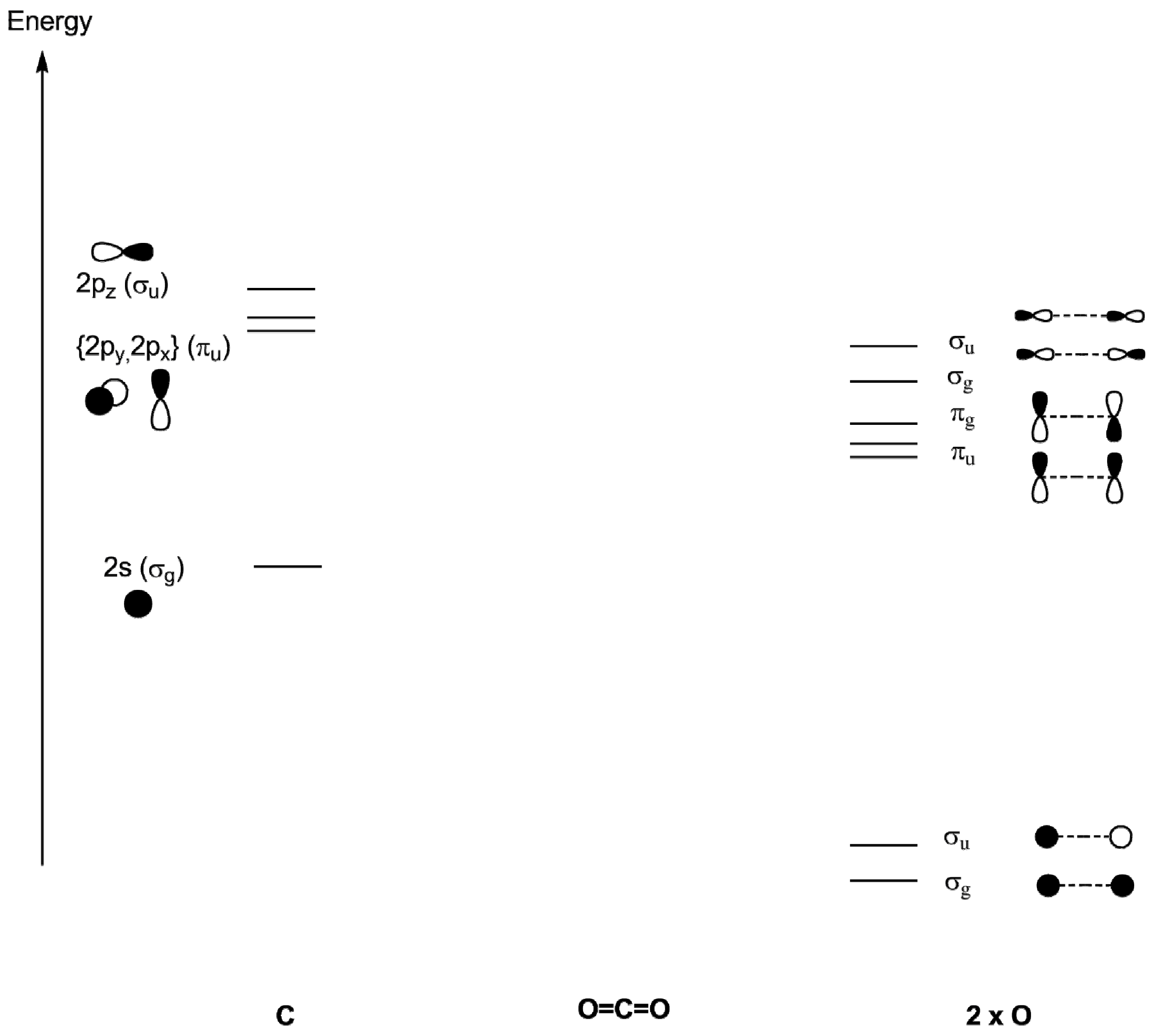


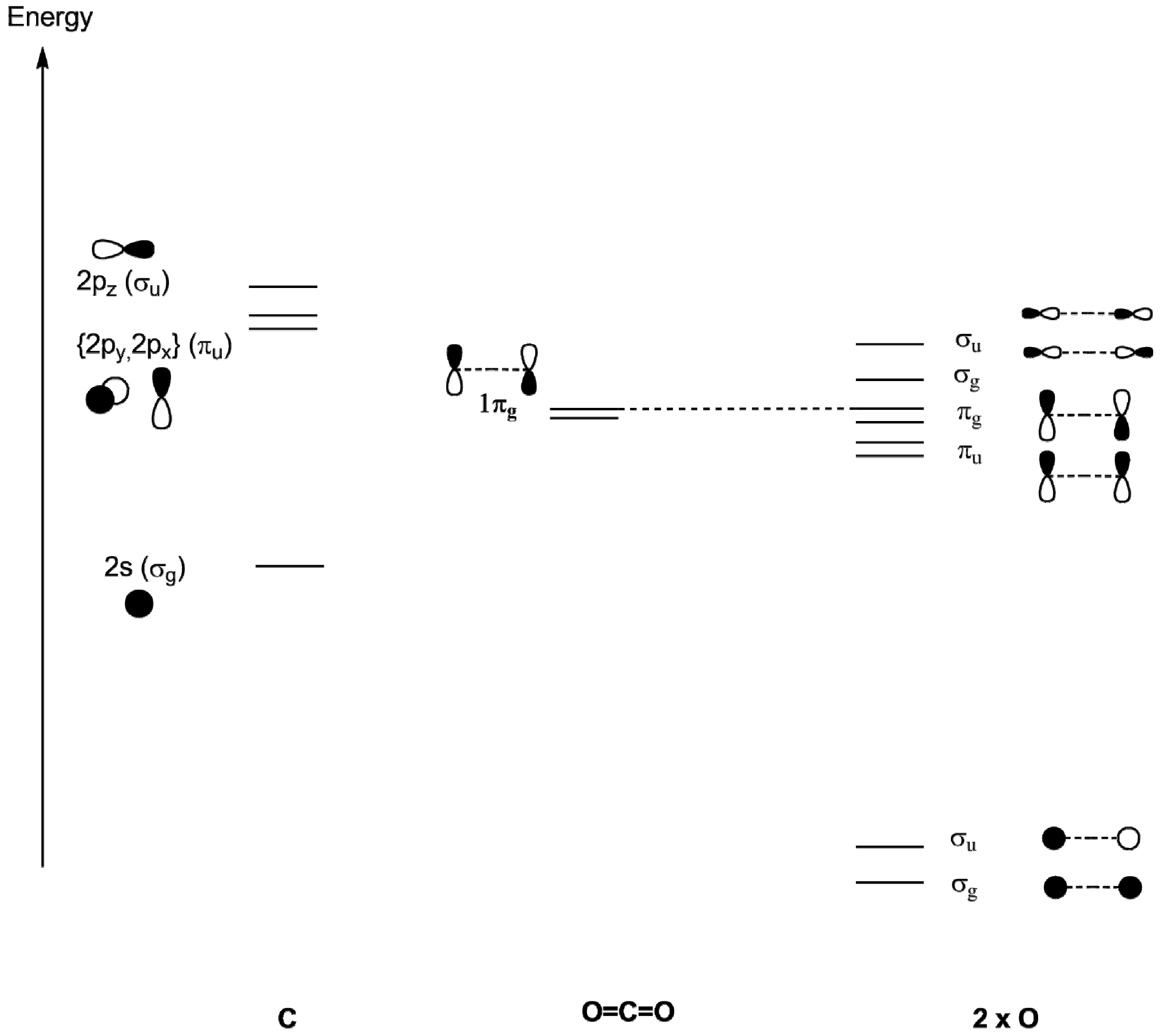
Ionic resonance forms?

order 0.5

Symmetry analysis ($D_{\infty h}$)




Energy
2p$_z$ (σ_u)
{2p$_y$,2p$_x$} (π_u)
2s (σ_g)
σ_u
σ_g
π_g
π_u
σ_u
σ_g
C
O=C=O
2 x O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$1\pi_g$
σ_u
σ_g
π_g
π_u
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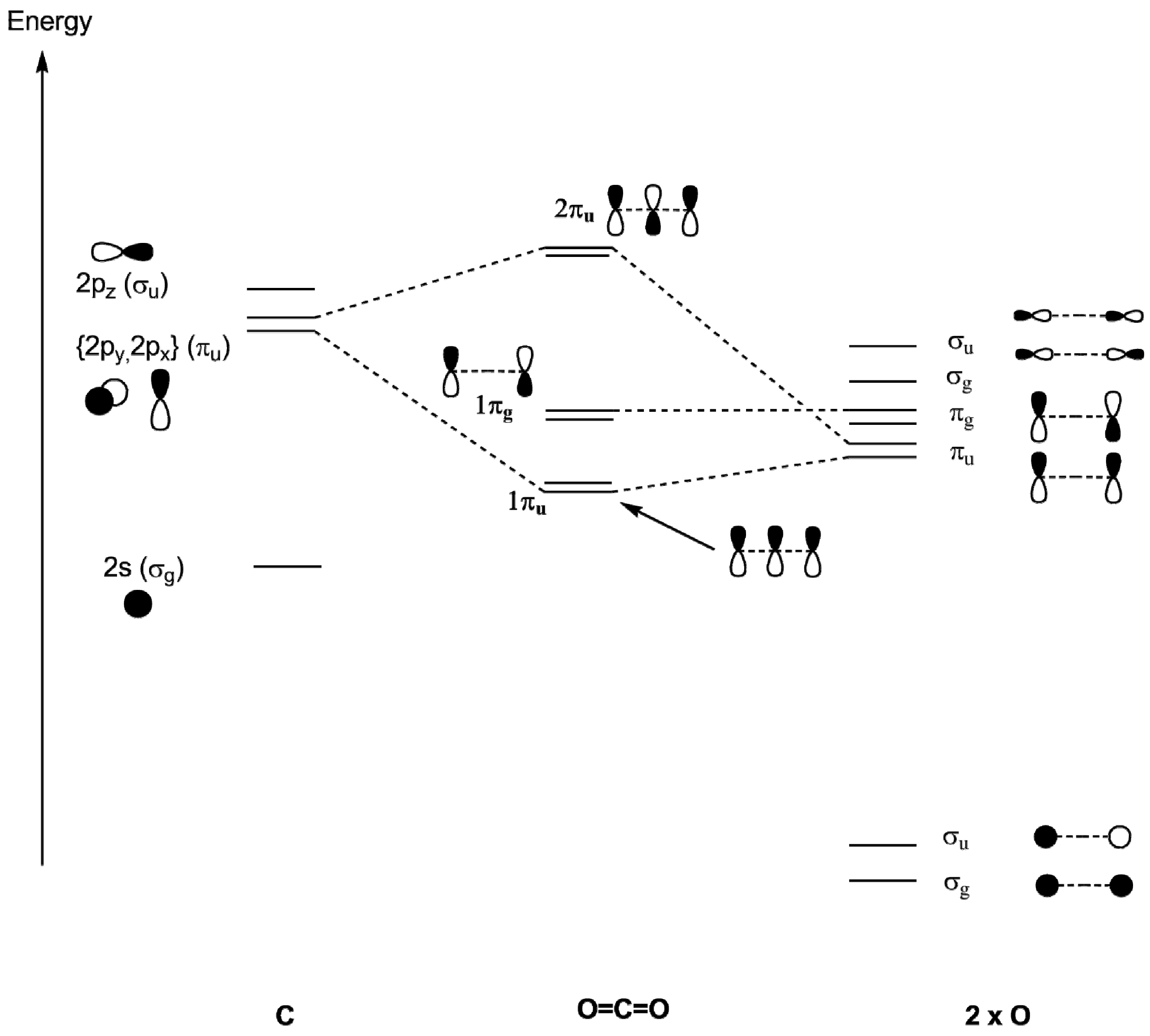
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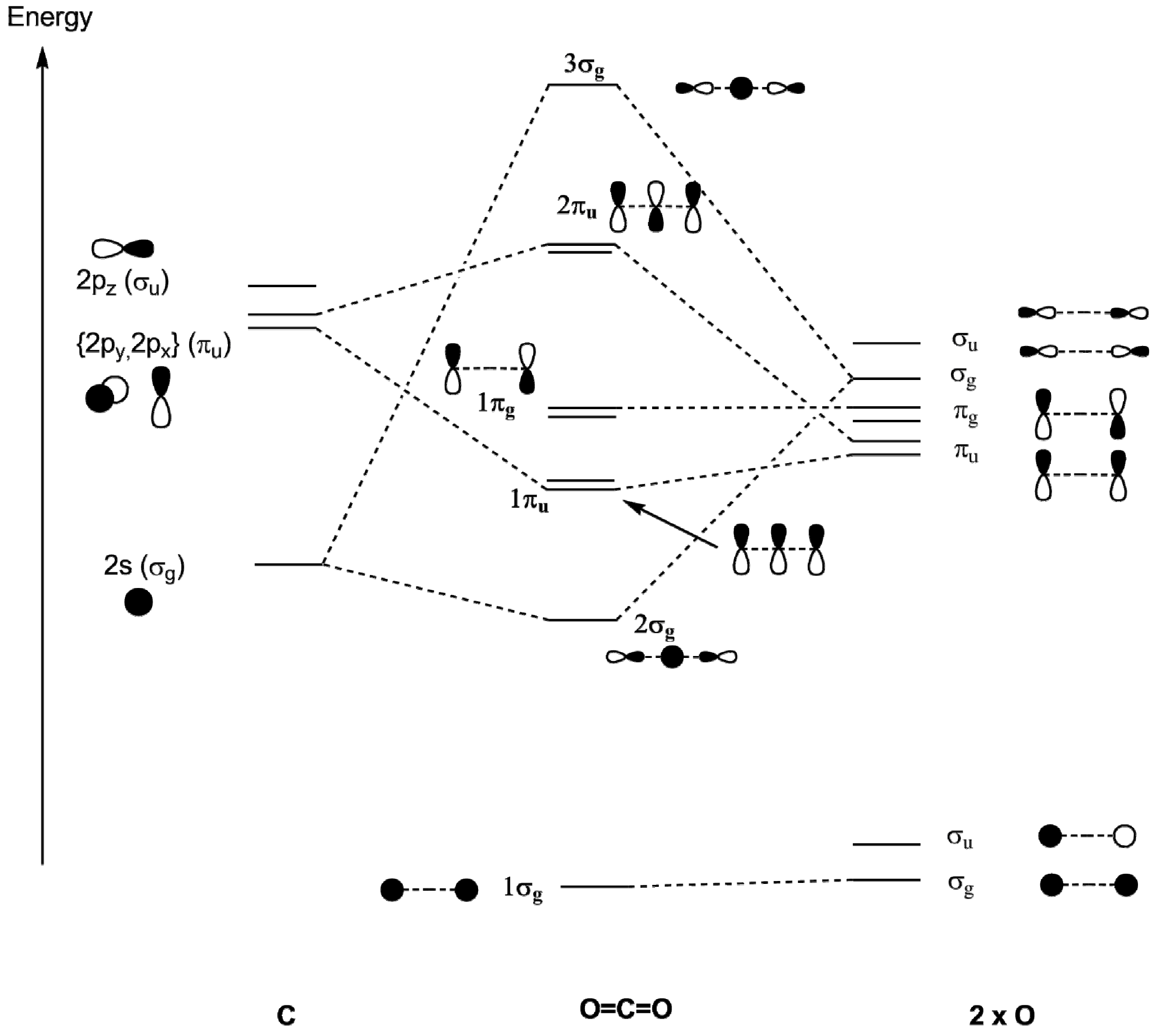
Energy
3σ_g
2π_u
2p_z (σ_u)
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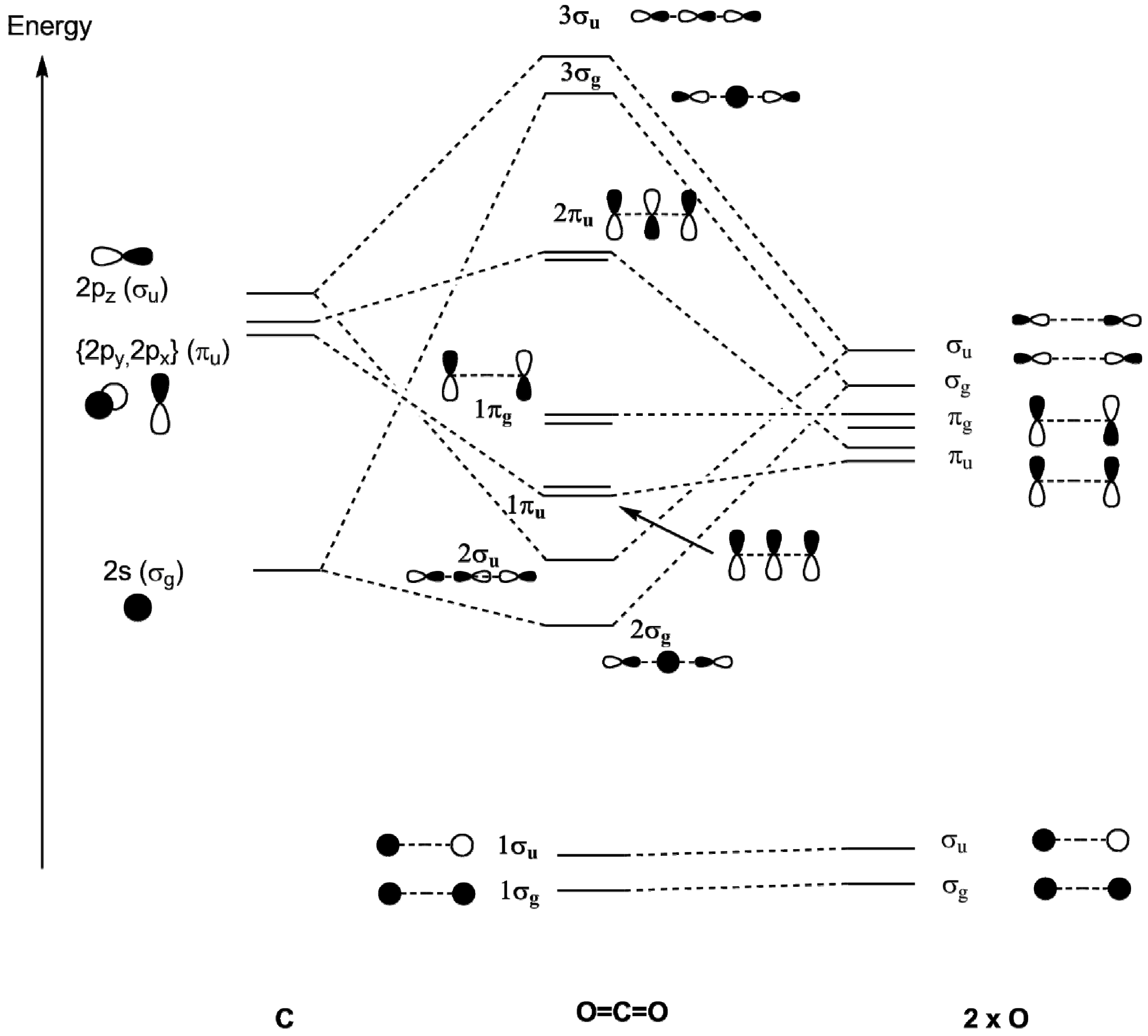
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π_u
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σ_u
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