Symmetry & Bonding

Answers to the Questions 14-17

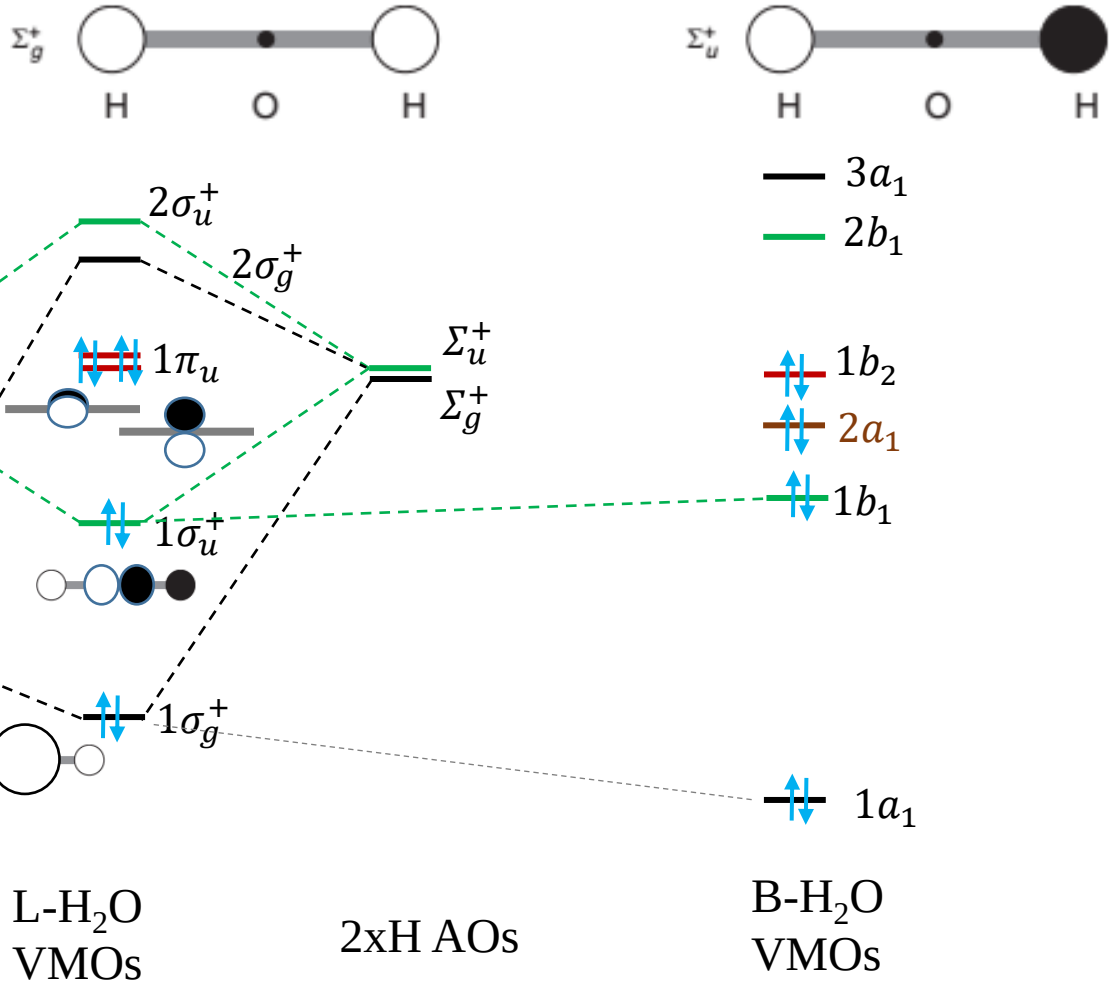
14. This exercise is concerned with a hypothetical linear geometry of the water molecule H–O–H. Such a molecule belongs to the point group $D_{\infty h}$; note that the *z*-axis coincides with the long axis of the molecule. In this group the oxygen 2*s* transforms as the irreducible representation Σ_g^+, the 2*pz* transforms as Σ_u^+, and the $2p_x$ and $2p_y$ AOs transform together as the two-dimensional IR Π_u. The two hydrogen 1*s* AOs form two symmetry orbitals shown below, along with their symmetry labels.

(a) Using the same approach as in Fig. 6.1 on page 50 construct an approximate MO diagram for water in this geometry.

(b) Label each MO with its appropriate symmetry label (remember that lower case letters are used for MOs, so an MO transforming as Σ_g^+ is labelled σ_g^+).

(c) Determine which MOs are occupied and sketch their forms.

(d) Compare your MO diagram to that for water in its bent geometry. Which do you think has the greater degree of bonding overall?



15. This exercise is concerned with constructing an MO diagram for ammonia, NH_3, which has a trigonal pyramidal geometry.

(a) Determine the point group of this molecule.

(b) Classify the valence orbitals (i.e. the 2*s* and 2*p*) on nitrogen according to symmetry.

(c) Determine the characters of the representation generated by the three hydrogen 1*s* AOs, reduce the representation and sketch the form of the resulting symmetry orbitals.

(d) Writing the three hydrogen AO wavefunctions as s_A, s_B an s_C, write down the form of the SOs and normalize them.

(e) Construct an MO diagram, labelling each MO with an appropriate symmetry label.

(f) Sketch the form of the occupied MOs and comment on the extent of bonding shown by each.

C_{3v}	E	$2C_3^z$	$3\sigma_v$	
A_1	1	1	1	z
A_2	1	1	−1	
E	2	−1	0	(x,y)

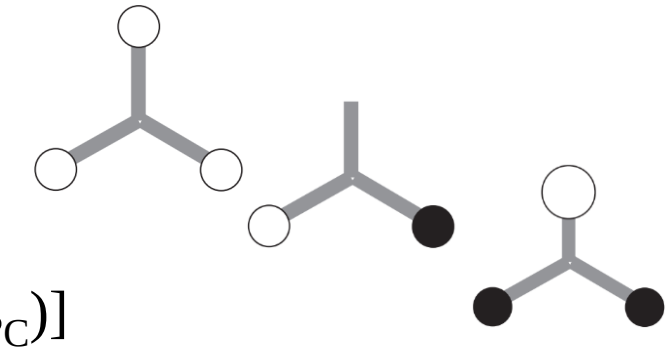
3xH1s: 3 0 1 $A_1 \oplus E$

(b) N 2s, $2p_z \sim A_1$, $(2p_x,2p_y) \sim E$

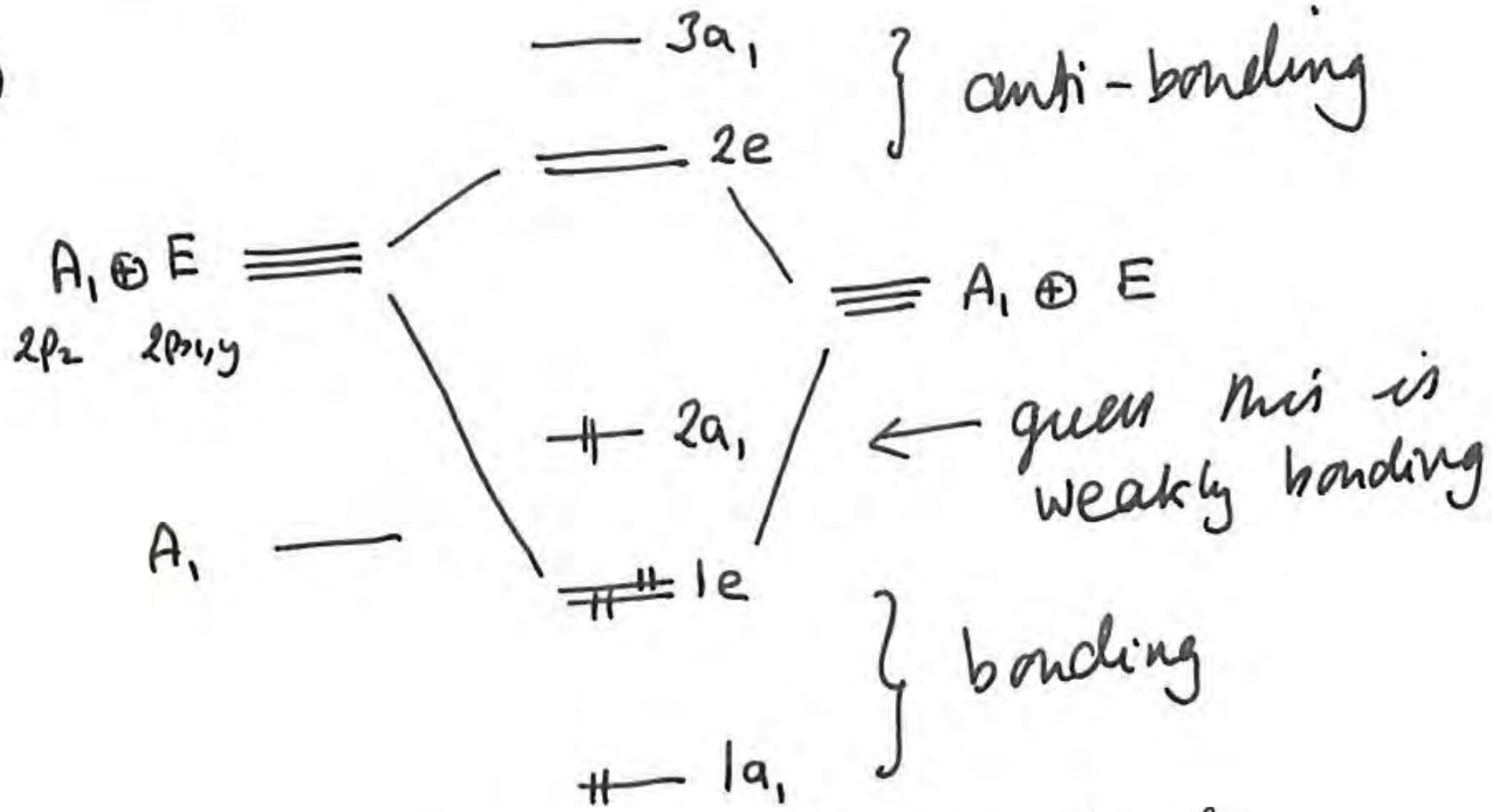
(c) 3xH1s: $\theta(A_1) = 3^{-1/2}(s_A+s_B+s_C)$

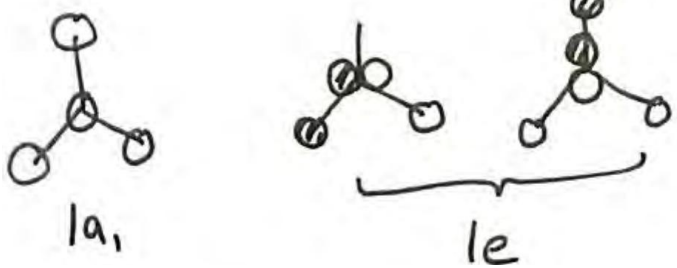
$\theta(E_x) = 2^{-1/2}(s_B - s_C)$

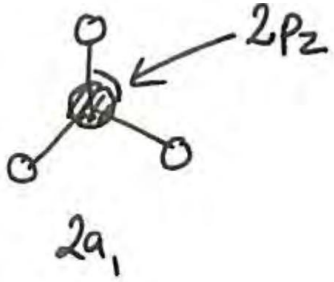
$\theta(E_y) = (2/3)^{1/2}[s_A - 2^{-1}(s_B + s_C)]$



(e)


3a1
2e
anti-bonding
A1 ⊕ E
2pz 2px,y
A1 ⊕ E
2a1
green mo is weakly bonding
A1
1e
bonding
1a1


1a1
1e


2pz
2a1

16 Consider an alternative geometry for NH_3 in which the molecule is flat i.e. point group D_{3h}. The MO diagram for BH_3, shown in Fig. 6.4 on page 56, can be used to describe the bonding in trigonal planar NH_3. Determine which MOs are occupied, compare the overall degree of bonding between the trigonal planar and trigonal pyramidal geometries, and hence rationalize the known geometry of NH_3.
Speculate about how the molecular geometry might change along the series NH_3^q (q=0, +1,+2) .

A: NH_3基态电子组态

平面三角形 $(1a_1')^2\,(1e')^4(1a_2'')^2$ HOMO为非键轨道(N $2p_z$)

三角锥 $(1a_1)^2\,(1e)^4(2a_1)^2$ HOMO为弱成键轨道

后者总体上成键要强于前者， 故中性分子取三角锥形。

分子的最高占据轨道上有电子占据时，倾向于采取三角锥形，故q=0及+1时，分子取三角锥形；

q=+2时，离子与BH_3等电子，变为平面形结构更稳定。

注： 更精准的回答是画出两种构型下分子轨道组成及能量随角度的变化关系图来加以回答！