

Chemistry 2000 Fall 2013 Test 1

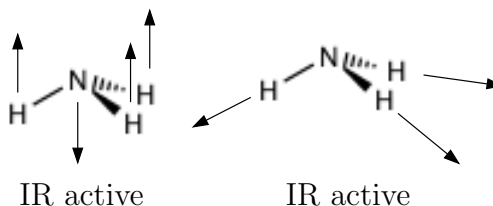
Version A SOLUTIONS

- See figure 1.
 - See figure 1. I think that the next orbital up may also be nonbonding, but I'm less sure about that.
 - The lowest three orbitals are bonding orbitals. We have three pairs of electrons in bonding orbitals, and three N-H bonds, so there is one pair of bonding electrons per N-H bond, i.e. the bond order is 1.
 - A Lewis base is an electron pair donor, so the HOMO is the orbital associated with this property of ammonia. Here, the HOMO is the non-bonding orbital labeled in figure 1. This orbital has a lot of electron density protruding out of the top of the nitrogen atom, which is the basic site in ammonia, so the shape of the HOMO is consistent with ammonia's basicity.
 - No. Only planar molecules can have π orbitals.
 - The nitrogen atom is sp^3 hybridized, so the N-H bond arises from the overlap $N(sp^3)$ - $H(1s)$.
 - Bond dipole moments depend on (a) the amount of charge separation between the two atoms and (b) the length of the bond. The molecular dipole moment is the vector sum of the bond dipole moments. In order for a vibrational mode to be IR active, the dipole moment of the molecule must change during the motion.

Ammonia has a non-zero permanent dipole moment due to its trigonal pyramidal structure. The "vertical" components of the bond dipoles add, resulting in a net dipole moment along the central axis of the molecule (through the nitrogen atom).

In the case of the "umbrella" mode, the molecular dipole moment changes because the angles between the bond dipoles change, which affects the vector sum.

In the case of the symmetric stretch, the bond dipoles change because of the change in the lengths of the bonds, which also affects their sum.



- Figure 2 shows a band diagram for an LED. The diagram shows the LED with a battery connected to it. The negative pole of the battery (represented by a short line) is connected to the n-type side of the diode. Thus, the battery will push electrons in

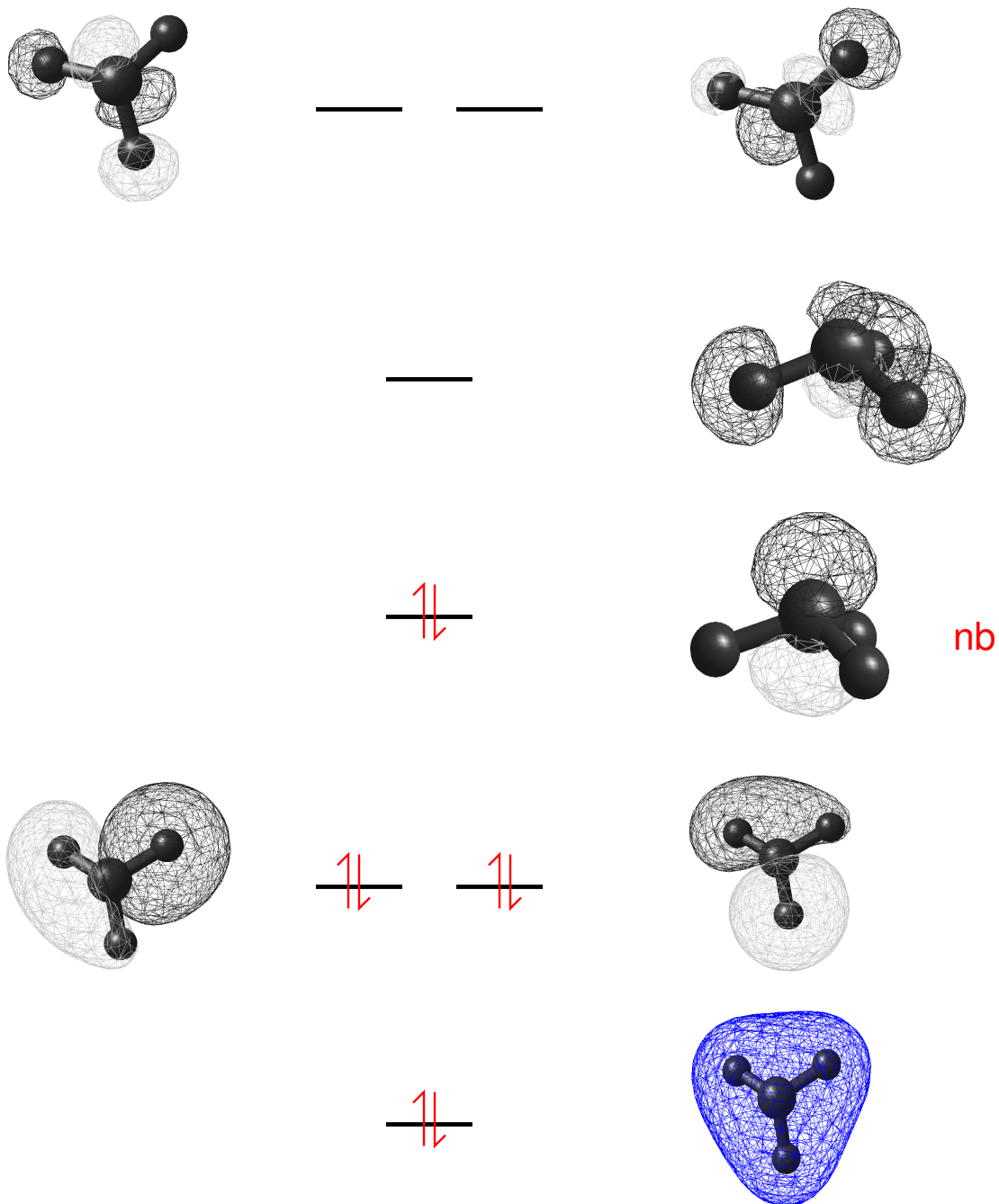


Figure 1: MO diagram of NH_3 .

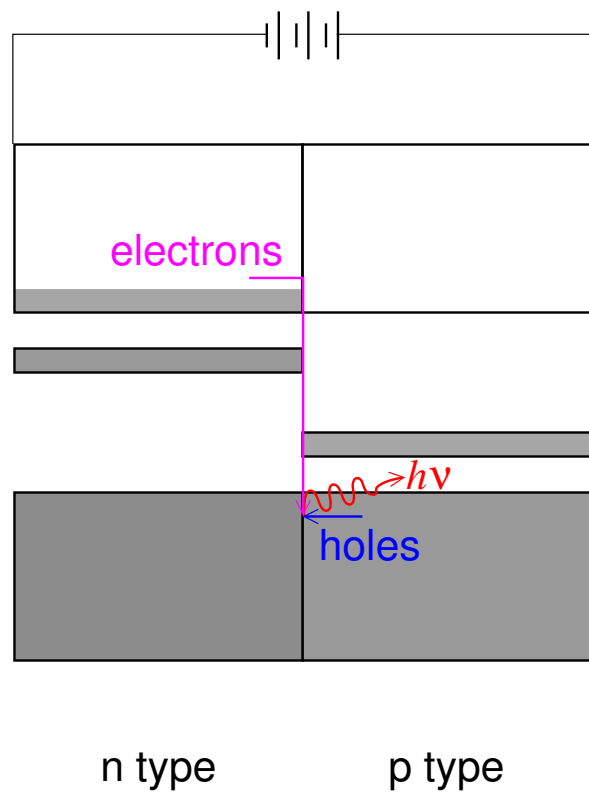


Figure 2: Band diagram for an LED

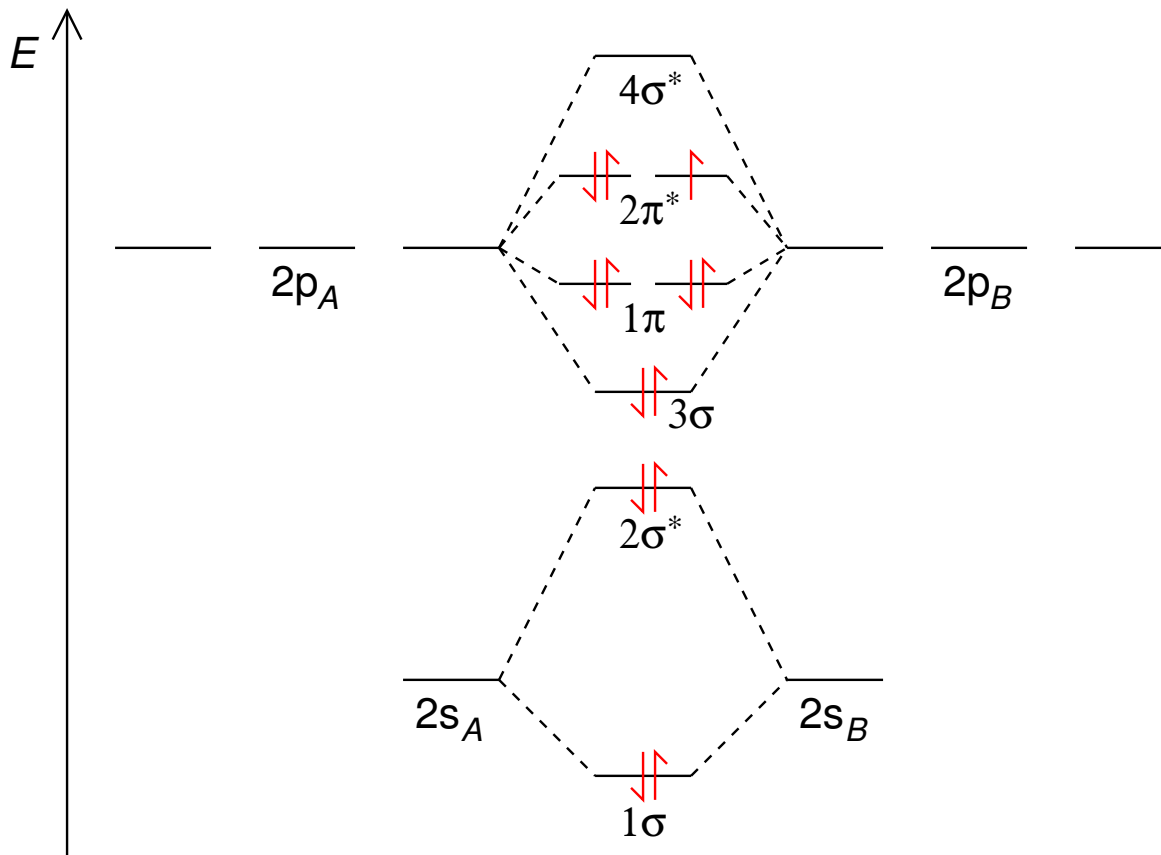


Figure 3: MO diagram for the superoxide ion

the direction in which a diode naturally conducts current. In an LED, electrons fall from the conduction band to the valence band and recombine with holes as they pass through the n-p interface. This process is associated with the emission of a photon whose energy matches the energy lost by the electron when it falls to the valence band. The color of the light emitted is controlled by the size of the band gap.



3. (a)

The bond order is 1.

(b) See figure 3.

(c)

$$\begin{aligned}\text{Bond order} &= \frac{1}{2} [\text{bonding} - \text{antibonding}] \\ &= \frac{1}{2} [8 - 5] = \frac{3}{2}\end{aligned}$$

This is different from the bond order obtained from the Lewis diagram. Experimentally, the bond length in superoxide is consistent with the MO bond order.

4. (a) Orbital energies are obtained using photoelectron spectroscopy. The atoms (in this case) are ionized using a photon of known energy $h\nu$. The kinetic energies of the ejected electrons are given by

$$K = h\nu - I_i$$

where I_i is the ionization energy of an electron in orbital i . If we measure K , we can calculate I_i . By Koopmans' theorem, ϵ_i , the orbital energy, is (approximately) $-I_i$. Thus,

$$\epsilon_i = K - h\nu.$$

(b) Number of σ orbitals: 3

Number of π orbitals: 2

(c) See figure 4.

(d) Number of unpaired electrons: 1

Number of electrons in nonbonding orbitals: 1

The Lewis diagram suggests three unpaired electrons in nonbonding orbitals. This is a vastly different picture than emerges from the MO treatment.

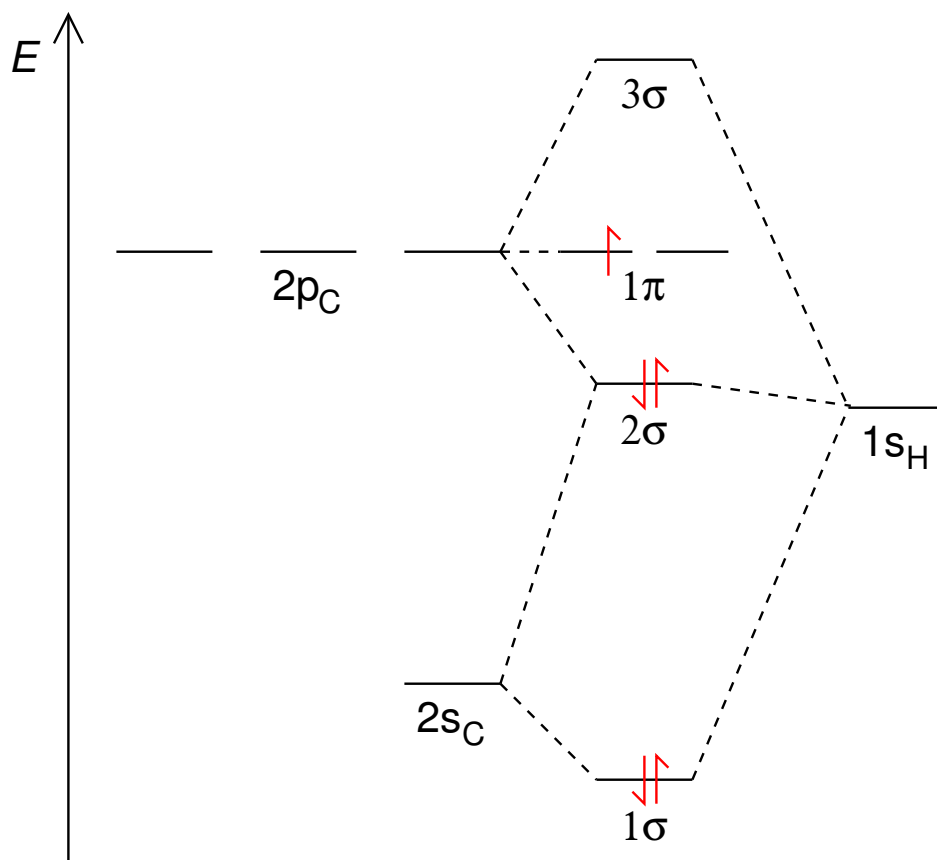


Figure 4: MO diagram for the carbyne radical