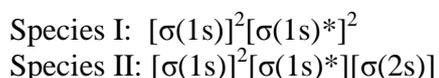


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1) (50 points) This problem deals with two electronic states of diatomic helium, e.g. He<sub>2</sub>. The electronic configuration of each species is given below.



a) Which species is an excited state of He<sub>2</sub>? Provide the basis for your answer.

Species II has a  $\sigma(2s)$  MO which is constructed using atomic orbitals outside the valence shell of ground state helium.

b) Sketch the PES, i.e. a graph of electronic energy versus internuclear separation, of each species.

Species I

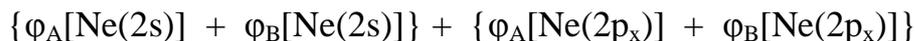
Species II

Refer to Figure 1 at the end for the solution.

c) Both species contain a molecular orbital with a node. Which molecular orbital? What is the location and physical significance of this node?

The  $\sigma(1s)^*$  MO is an antibonding orbital and contains a nodal surface between the two helium atoms and perpendicular to the interatomic axis. It decreases the electron density between the two helium nuclear and thereby increases the internuclear repulsion in the molecule.

d) Simplissimus constructed the following molecular orbital for Ne<sub>2</sub>. His z axis is the line connecting the two Ne atoms.



i) Point out the flaw(s) in his molecular orbital.

In constructing MO's, one must use atomic orbitals of the same symmetry. Simplissimus has a used  $\sigma$ , e.g. Ne(2s), and  $\pi$ , e.g., Ne(2p<sub>x</sub>), atomic orbitals in the same MO.

ii) Modify his orbital and convert it into one that is acceptable.

He could use Ne(2p<sub>z</sub>) atomic orbitals instead of the Ne(2p<sub>x</sub>)'s. In your answer provide a MO, not a configuration which merely indicates which MO's are used.

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2) (60 points) Methyl peroxyxynitrate,  $\text{H}_3\text{C-O-NO}_2$ , is a pungent component of photochemical smog.

a) Draw an acceptable Lewis dot structure of the compound. Include all resonance structures. Provide the formal charge and hybridization of each atom.

Refer to Figure 2a at the end for the electron-dot structure. There is a pair of resonance structures. Unless otherwise indicated below, the atoms have zero formal charge. The N has a formal charge of +1 and one of the terminal oxygen atoms has a formal charge of -1. The hydrogen orbitals are unhybridized. The carbon and the central oxygen have  $\text{sp}^3$  hybridization. The nitrogen and the two terminal oxygen atoms have  $\text{sp}^2$  hybridization.

b) Predict the bond angles of methyl peroxyxynitrate.

$$\angle\text{HCO} = \angle\text{HCH} = \angle\text{CON} \cong 109^\circ \text{ (SN} = 4\text{)}$$

$$\angle\text{ONO} \cong 120^\circ \text{ (N. B. Three, not two atoms, define an angle.)}$$

c) N-O and N=O bond lengths are 1.43 Å and 1.17 Å, respectively. Predict the N,O bond lengths in methyl peroxyxynitrate.

The oxygen atom which is also bonded to the methyl ( $\text{CH}_3$ ) group has a single bond to the nitrogen. A bond length of 1.43 Å is expected. In each of the two resonance structures, the remaining, terminal oxygens bond to the nitrogen with single and double bonds. Resonance leads to a bond with a bond order of 1.5 and a bond length roughly halfway between 1.43 Å and 1.17 Å, i.e. 1.30 Å

d) Provide the Lewis electron dot structure of **one** isomer of methyl peroxyxynitrate.

Refer to Figure 2b at the end for electron-dot structures of possible isomers. There are many correct solutions. The structures shown in the solutions have been reported in the chemical literature.

3) (30 points) Draw an acceptable Lewis dot structure for the phosphite anion,  $\text{HPO}_3^{-2}$ . Is  $\text{HNO}_3^{-2}$ , the corresponding nitrogen analogue, possible. Briefly explain.

The electron-dot formula is given in Figure 3. The phosphite anion requires extended valence and the use of d orbitals to avoid formal charge on the phosphorus atom. The negative formal charge on two of the oxygen atoms is acceptable since the ion has a net charge of -2. N has no d orbitals in its valence shell so  $\text{HNO}_3^{-2}$  is a fictitious species.

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4) (30 points) The government of Iran has recently constructed high-speed centrifuges to separate the isotopes of uranium. The hardware requires a gaseous form of uranium. Discuss the feasibility of generating a gaseous compound of this metallic element.

One requires a compound of uranium with covalent bonding. Preparation of a compound in which uranium has a high positive oxidation number will display covalency. The high energetic cost of the ionization of many electrons in the formation of a highly charged uranium cation makes ionic bonding unlikely. With covalent bonding, weak intermolecular forces between the molecules lead to a high vapor pressure. Fluorine is a highly reactive element that can yield uranium compounds with a high oxidation number for the uranium. In practice, the hexafluoride of uranium is used.

5) (30 points) The compound ethylene,  $\text{H}_2\text{C}=\text{CH}_2$ , is completely planar but two H's in allene,  $\text{H}_2\text{C}=\text{C}=\text{CH}_2$ , do not fall in the same plane defined by the other atoms.

a) Use the valence bond model to explain the differences in 3D structure.

This question is a variant of a problem assigned for homework. Consider first ethylene. Both carbon atoms have a steric number of 3 and a trigonal planar geometry with the result that the carbon and the 3 attached atoms lie in the same plane. There are two such planes. Overlap of the C(2p<sub>z</sub>) unhybridized orbitals forces the two planes to overlap. Hence the molecule is completely planar.

In the case of allene, the two terminal carbons have trigonal planar geometry. The formation of the pi part of the two double bonds is different. The central carbon has a steric number of 2 and sp hybridization. It has two unhybridized p orbitals, e.g. C 2p<sub>x</sub> and C 2p<sub>y</sub>, which are perpendicular to one another. These two orbitals overlap pairwise with the carbon unhybridized orbitals on the two terminal carbons. If one of the two unhybridized orbitals on the central carbon, say the C 2p<sub>x</sub>, overlaps with the hybridized p orbital on the terminal carbon on the left, then the pi part of the double bond for the terminal carbon on the right must be formed the remaining C 2p<sub>y</sub> orbital of the central carbon.

b) Do ethylene and allene have microwave spectra? Provide the basis for your answer.

Both species are symmetric and therefore have a zero dipole moment and no microwave spectrum. Ethylene has a center of symmetry. In the case of allene, the bond dipole from the left side of the molecule is cancelled by that from the right.

c) Suggest a spectroscopic method that would **directly** and **easily** demonstrate the presence of a double bond in these compounds.

Infrared spectroscopy is a good choice. The method measures the frequencies of bond-stretching motions. A double bond will have an infrared frequency much higher than that of a single bond. X-ray crystallography might work but would be very difficult. A good single crystal is required. NMR would also work fine.

Fig 1

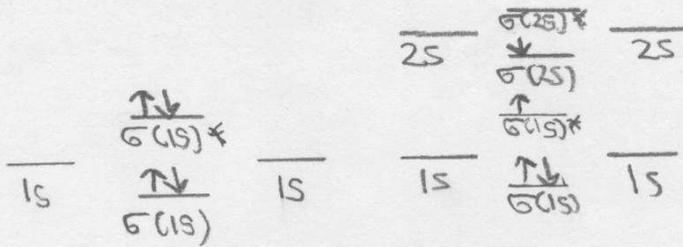
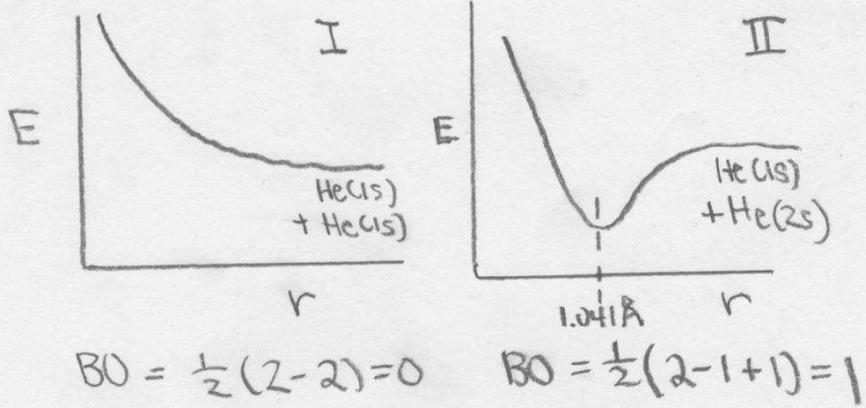


Fig 2

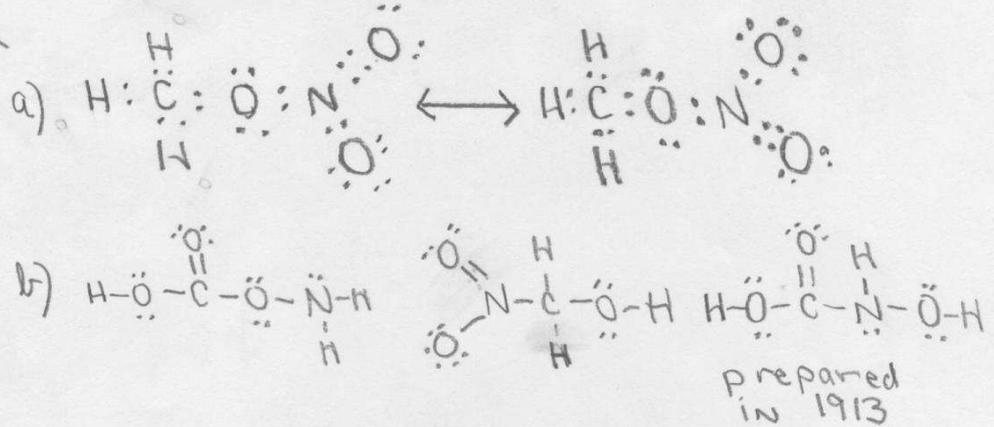


Fig 3  $\text{HPO}_3^{-2}$

