量子化学作业　　第十一章（2017-2018 学期）

1. Discuss the bond properties of F_2 and F_2^+ using molecular orbital theory.

2. Predict the relative stabilities of the species N_2, N_2^+, and N_2^-.

3. In Section 11.2, we constructed molecular orbitals for homonuclear diatomic molecules using the $n=2$ atomic orbitals on each of the bonded atoms. In this problem, we will consider the molecular orbitals that can be constructed from the $n=3$ atomic orbitals. These orbitals are important in describing diatomic molecules of the first row of the transition metals. Once again we choose the z axis to lie along the molecular bond. What are the designations for the $3s_A \pm 3s_B$ and $3p_A \pm 3p_B$ molecular orbitals? The $n=3$ shell also contains a set of five $3d$ orbitals. (The shapes of the $3d$ atomic orbitals are shown in Figure 7.8.)(Page 339 of the textbook) Given that molecular orbitals with two nodal planes that contain the internuclear axis are called δ orbitals, show that ten $3d_A \pm 3d_B$ molecular orbitals consist of a bonding σ orbital, a pair of bonding π orbitals, a pair of bonding δ orbitals, and their corresponding antibonding orbitals.

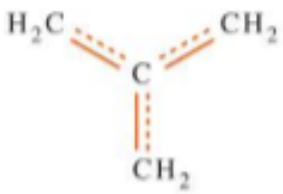
4. Determine the largest bond order for a first-row transition-metal homonuclear diatomic molecule. (See the previous problem.)

5. Show that filled orbitals can be ignored in the determination of molecular term symbols.

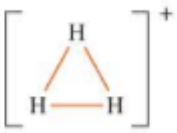
6. Generalize our Hückel molecular orbital treatment of ethene to include overlap of $2p_{z1}$ and $2p_{z2}$. Determine the energies and the orbitals in terms of the overlap integral, S.

7. Show that the four π molecular orbitals for butadiene are given by Equations 11.15.(Page 587 of the textbook.)

8. Calculate the Hückel π-electronic energy of trimethylenemethane:



9. Using Hückel molecular orbital theory, determine whether the linear state $(H\text{-}H\text{-}H)^+$ or the triangular state



of H_3^+ is the more stable state. Repeat the calculation for H_3 and H_3^-.

10. The problem of a linear conjugated polyene of N carbon atoms can be solved in general. The energies E_j and the coefficients of the atomic orbitals in the jth molecular orbital are given by

$$E_j = \alpha + 2\beta \cos\frac{j\pi}{N+1} \qquad j = 1, 2, 3, \ldots, N$$

And

$$c_{jk} = \left(\frac{2}{N+1}\right)^{1/2} \sin\frac{jk\pi}{N+1} \qquad k = 1, 2, 3, \ldots, N$$

Determine the energy levels and the wave functions for butadiene using these formulas.