10.E: Theories of Electronic Molecular Structure (Exercises)

Q10.1

1. Plot the amplitude of the atomic and molecular orbitals along the inter-nuclear axis (defined as the z-axis) of the H_2^+ molecule.
   a. Plot the four basis functions for the H_2^+ molecule:

$$\varphi_{1sA}, \varphi_{1sB}, \varphi_{2p_zA}, \varphi_{2p_zB} \tag{10.E.1}$$

   b. Construct and graph a bonding molecular orbital using these basis functions with a parameter λ multiplying the $2p_z$ functions, for a few values of the parameter λ between 0 and 1. Determine the normalization constant N for each value of λ by assuming that the atomic overlap integrals are either 0 or 1.

$$\psi = \frac{1}{N}[\varphi_{1sA} + \varphi_{1sB} + \lambda(\varphi_{2p_zA} + \varphi_{2p_zB})] \tag{10.E.2}$$

   c. Explain why the molecular orbital you graphed is a bonding orbital.
   d. Explain why a value for λ greater than 0 should improve the description of a bonding orbital.

Q10.2

Construct energy level diagrams for B_2 and O_2 that show both the atomic orbitals and the molecular orbitals and use these diagrams to explain why both molecules are paramagnetic. Label the molecular orbitals to reveal both their symmetry and their atomic orbital parentage. Note: one diagram and labeling does not apply to both molecules.

Q10.3

Defend or shoot down the following statement. The Born-Oppenheimer approximation predicts that vibrational frequencies, vibrational force constants, and bond dissociation energies should be independent of isotopic substitution.

Q10.4

Explain in terms of both the electronic charge density and the electronic energy, why chemists describe the overlap of atomic orbitals as being important for bond formation.

Q10.5

Compare the extended Hückel calculation on HF with the SCF calculation reported in B.j. Ransil, Rev. Mod. Phys. 32, 239, 245 (1960) in J.A. Pople and D.L. Beveridge, Approximate Molecular Orbital Theory (McGraw-Hill, 1970) pp. 46-51.

Q10.6

From the following bond lengths and dipole moments, compute the charges on the hydrogen atom and the halide atom. Compare the results with the electronegativities predicted from the order of these elements in the Periodic Table. What do these charges tell you about the contribution of the hydrogen 1s atomic orbital to the molecular orbitals for each molecule? Use the insight you gained from this problem, to define ionic and covalent bonding.

Molecule	R_0 in pm	μ in 10^{-30} C m
HF	91.7	6.37
HCl	127.5	3.44
HBr	141.4	2.64
HI	160.9	1.40