Semi-emprical Molecular Orbital Calculation on XeF_2

The bonding in XeF_2 can be interpreted in terms the three-center four-electron bond. In linear XeF_2 the molecular orbital can be considered to be a linear combination of the flourine 2p orbitals and the central xenon 5p.

$$\Psi = C_{F1}\cdot\Psi_{F1} + C_{Xe}\cdot\Psi_{Xe} + C_{F2}\cdot\Psi_{F2}$$

Minimization of the variational integral

$$E = \frac{\int \left(C_{F1}\cdot\Psi_{F1} + C_{Xe}\cdot\Psi_{Xe} + C_{F2}\cdot\Psi_{F2}\right)\cdot H\cdot\left(C_{F1}\cdot\Psi_{F1} + C_{Xe}\cdot\Psi_{Xe} + C_{F2}\cdot\Psi_{F2}\right) d\tau}{\int \left(C_{F1}\cdot\Psi_{F1} + C_{Xe}\cdot\Psi_{Xe} + C_{F2}\cdot\Psi_{F2}\right)^2 d\tau}$$

yields the following 3 x 3 Huckel matrix

$$H = \begin{pmatrix} \alpha_F & \beta & 0 \\ \beta & \alpha_{Xe} & \beta \\ 0 & \beta & \alpha_F \end{pmatrix}$$

All overlap integrals are zero. The Coulomb integrals are parameterized as the negative of the valence orbital ionization energies (-12.13 eV for the Xe 5p orbital, -17.42 eV for the F 2p). The non-zero resonance integral is given a value of -2.0 eV.

$$\alpha_{F1} = \alpha_F = \int \Psi_{F1}\cdot H\cdot\Psi_{F1}\, d\tau = -17.42 \qquad \alpha_{F2} = \alpha_F = \int \Psi_{F2}\cdot H\cdot\Psi_{F2}\, d\tau = -17.42$$

$$\alpha_{Xe} = \int \Psi_{Xe}\cdot H\cdot\Psi_{Xe}\, d\tau = -12.13 \qquad \beta = \int \Psi_{Xe}\cdot H\cdot\Psi_F\, d\tau = -2$$

Mathcad can now be used to find the eigenvalues and eigenvectors of H. First we must give it the values for all the parameters.

$$\alpha_F := -17.42 \qquad \alpha_{Xe} := -12.13 \qquad \beta := -2.00$$

Define the variational matrix shown on the left side of equation (6):

$$H := \begin{pmatrix} \alpha_F & \beta & 0 \\ \beta & \alpha_{Xe} & \beta \\ 0 & \beta & \alpha_F \end{pmatrix}$$

Find the eigenvalues: $E := \mathrm{sort}(\mathrm{eigenvals}(H))$ $\quad E_0 = -18.647 \quad E_1 = -17.42 \quad E_2 = -10.903$

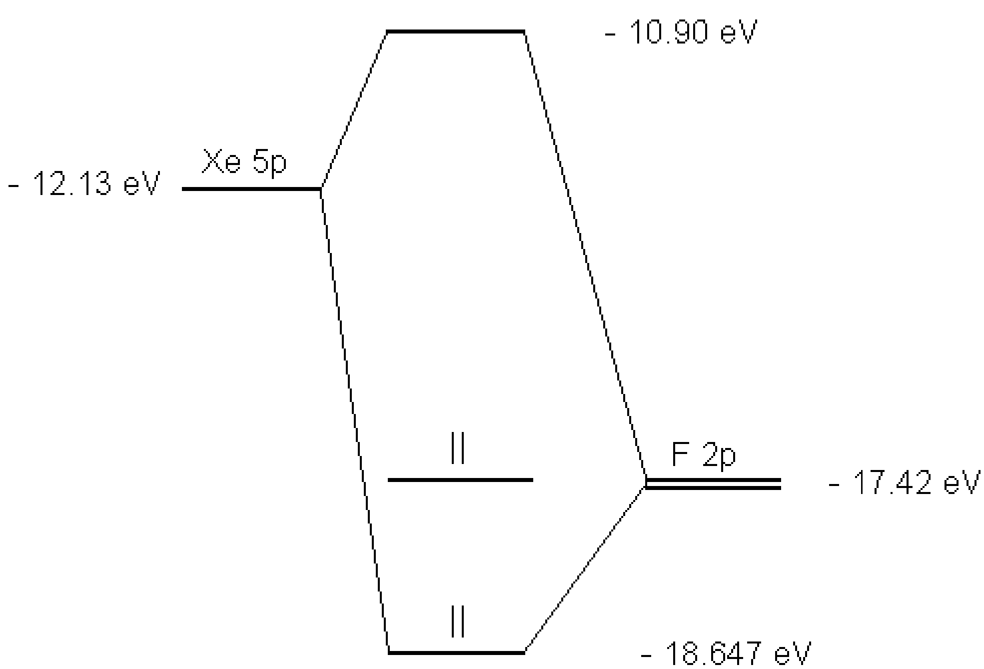
Now find the eigenvectors:

The bonding MO is: $\Psi_b := \text{eigenvec}(H, E_0)$ $\Psi_b = \begin{pmatrix} 0.649 \\ 0.398 \\ 0.649 \end{pmatrix}$ $\overrightarrow{\left(\Psi_b^{\,2}\right)} = \begin{pmatrix} 0.421 \\ 0.158 \\ 0.421 \end{pmatrix}$

The non-bonding MO is: $\Psi_{nb} := \text{eigenvec}(H, E_1)$ $\Psi_{nb} = \begin{pmatrix} -0.707 \\ 0 \\ 0.707 \end{pmatrix}$ $\overrightarrow{\left(\Psi_{nb}^{\,2}\right)} = \begin{pmatrix} 0.5 \\ 0 \\ 0.5 \end{pmatrix}$

The anti-bonding MO is: $\Psi_a := \text{eigenvec}(H, E_2)$ $\Psi_a = \begin{pmatrix} -0.282 \\ 0.917 \\ -0.282 \end{pmatrix}$ $\overrightarrow{\left(\Psi_a^{\,2}\right)} = \begin{pmatrix} 0.079 \\ 0.842 \\ 0.079 \end{pmatrix}$

The molecular orbital diagram for this system is shown below.



Is the molecule stable? The diagram shows two electrons each in the bonding and non-bonding orbitals for a total energy of -72.14 eV. The energy of the isolated atoms is 2(-12.13 eV) + 2(-17.42 eV) = - 59.1 eV. Thus, the molecule is more stable than the isolated atoms according to this crude semi-empirical model.

The partial charges are calculated next. The fluorine atoms have a kernel charge of +7. They get credit for 6 non-bonding atomic electrons, 42.1% of the two electrons in the bonding MO, and 50% of the two electrons in the non-bonding MO. This gives a partial charge of (7 - 6 - 2(.421) - 2(.50)) -0.842.

The xenon atom has a kernel charge of +8. It gets credit for 6 non-bonding atomic electrons, 15.8% of the two electrons in the bonding MO, and no credit for the two electrons in non-bonding MO. This yields a partial charge of (8 - 6 - 2(.158)) +1.684. This value is reasonable because xenon is bonded to the most electronegative element in the periodic table.