

3.35: Semi-empirical Molecular Orbital Calculation on XeF₂

The bonding in XeF₂ can be interpreted in terms of the three-center four-electron bond. In linear XeF₂ the molecular orbital can be considered to be a linear combination of the fluorine 2p orbitals and the central xenon 5p.

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

Minimization of the variational integral

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

yields the following 3 x 3 Hückel 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.

$$\begin{aligned} \alpha_{F1} = \alpha_F &= \int \Psi_{F1} H \Psi_{F1} d\tau = -17.42 & \alpha_{F2} = \alpha_F &= \int \Psi_{F2} H \Psi_{F2} d\tau = -17.42 \\ \alpha_{Xe} &= \int \Psi_{Xe} H \Psi_{Xe} d\tau = -12.13 & \beta &= \int \Psi_{Xe} H \Psi_F d\tau = -2 \end{aligned}$$

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

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

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

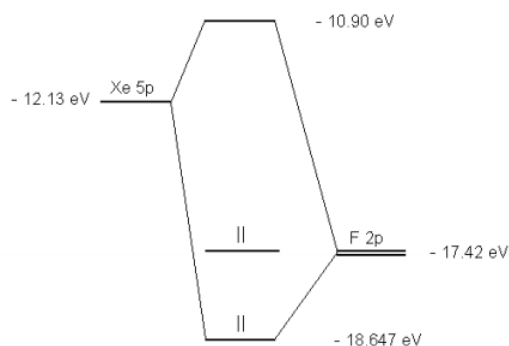
$$H = \begin{pmatrix} \alpha_F & \beta & 0 \\ \beta & \alpha_{Xe} & \beta \\ 0 & \beta & \alpha_F \end{pmatrix}$$

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

Now find the eigenvectors:

$$\begin{aligned} \text{The bonding MO is: } \Psi_b &= \text{eigenvec}(H, E_0) & \Psi_b &= \begin{pmatrix} 0.649 \\ 0.389 \\ 0.649 \end{pmatrix} & \xrightarrow{(\Psi_b)^2} & \begin{pmatrix} 0.421 \\ 0.158 \\ 0.421 \end{pmatrix} \\ \text{The non-bonding MO is: } \Psi_{nb} &= \text{eigenvec}(H, E_1) & \Psi_{nb} &= \begin{pmatrix} -0.707 \\ 0 \\ 0.707 \end{pmatrix} & \xrightarrow{(\Psi_{nb})^2} & \begin{pmatrix} 0.5 \\ 0 \\ 0.5 \end{pmatrix} \\ \text{The anti-bonding MO is: } \Psi_a &= \text{eigenvec}(H, E_2) & \Psi_a &= \begin{pmatrix} -0.282 \\ 0.917 \\ -0.282 \end{pmatrix} & \xrightarrow{(\Psi_a)^2} & \begin{pmatrix} 0.079 \\ 0.842 \\ 0.079 \end{pmatrix} \end{aligned}$$

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 $2(-12.13 \text{ eV}) + 2(-17.42 \text{ eV}) = -59.1 \text{ eV}$. 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.

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