Homework H33 Solution

1. Write down the electron configuration (= full product wavefunction) for the excited $^3\Pi$ state of hydrogen fluoride with M_S=+1 and M_L=-1. Draw the corresponding orbital energy diagram, labeling each orbital with the one-electron basis function (e.g. 1σ, 2π+, etc) and fill in the correct number of electrons.

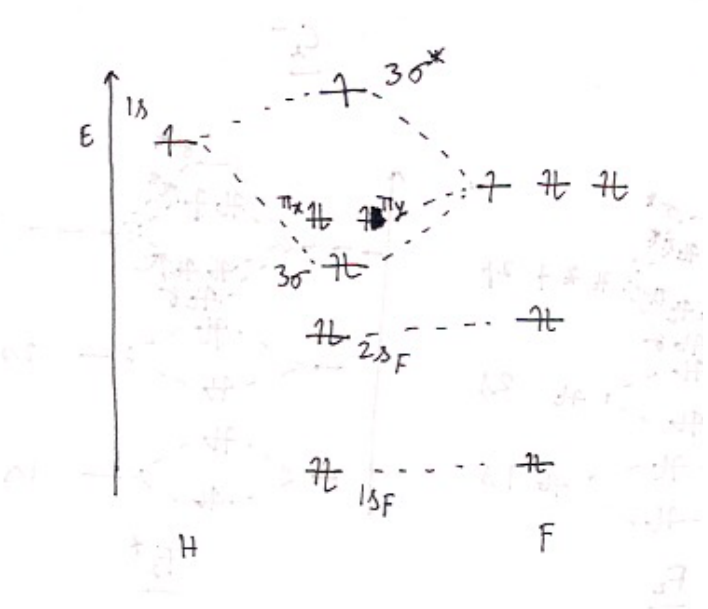
   Solution:
   For the $^3\Pi$ state, clearly $2S + 1 = 3$, or $S = 1$. Thus there are 2 unpaired electrons. This is achieved by exciting one electron from the π_x or π_y level to the $3\sigma^*$ level, and flipping its spin. Thus the electronic configuration for this state is,

$$\hat{\mathcal{A}}_{10} 1s_F^{\,2}\, 2s_F^{\,2}\, 3\sigma^2\, \pi_x^{\,2}\, \pi_y^{\,1}\, 3\sigma^{*1}$$

   or,

$$\hat{\mathcal{A}}_{10} 1s_F^{\,2}\, 2s_F^{\,2}\, 3\sigma^2\, \pi_x^{\,1}\, \pi_y^{\,2}\, 3\sigma^{*1}$$

   The corresponding orbital energy diagram follows.



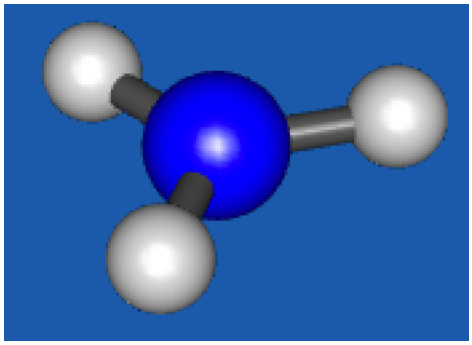
2. If I ionize the HF molecule in the $^3\Pi$ state from problem 3 by removing the highest energy electron to get HF^+, what is its term symbol then? ($^3\Pi$,$^1\Sigma$ etc. are "term symbols").

   Solution:
   When the electron from $3\,\sigma^*$ is removed to get HF^+, we are left with just one unpaired electron in π_x or π_y. Then, $S = \frac{1}{2}$ and $2S + 1 = 2$. Since there is still one electron in a π state, $M_L = \pm 1$. So this is a Π state.
   So, the term symbol is $^2\Pi$.

3. In this homework, we will investigate the application of Hartree-Fock (HF) theory to the inversion reaction of ammonia.

- **Solution:**

A. Geometry of transition state:

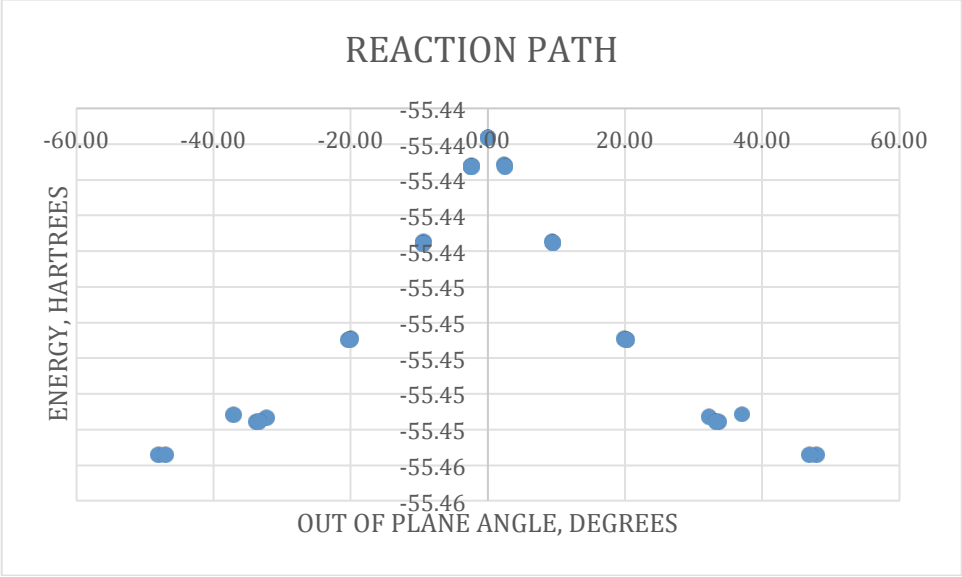


The transition state has a trigonal planar geometry. It is sp^2 hybridized.

B. In the animation, the ammonia molecule flips over, tunneling back and forth between the equilibrium geometries through the sp^2 hybridized (planar) transition state.

C. If you divide the distance b between H1 and H2 in two, you obtain a right triangle with hypotenuse a, side $b/2$, and angle $\theta/2$ (Note that for an equilateral triangle, an angle bisector is also a perpendicular and segment bisector). Thus $\theta/2=\sin^{-1}(b/2a)$. Thus $(360°-3\theta)$*sign yields the desired result.

D. Plot absolute energy *vs.* out-of-plane angle. This is your reaction path:



E. What is the absolute energy of the transition state? Are the energies of the reactant and product different? Should they be different? Why?

$$E_{TS} = -55.4376 \text{ hartrees}$$

$$E_{prod} = -55.4554 \text{ hartrees}$$
$$E_{reactant} = -55.4554\ hartrees$$

The energies of the reactant and product are the same. They should NOT be different because the geometry of the molecule is the same except that the ammonia molecule is pointing in opposite direction in space. Note that computer rounding error can produce a small difference in the 5th or 6th digit after the decimal point.

F. What is the geometry of the stable product/reactant? Intuitively, why do you think this geometry is lower in energy than the transition state?

The stable product/reactant has a trigonal pyramidal geometry, sp^3 hybridized. Intuitively, since ammonia has a non-bonding lone pair of electrons that occupy more space than the bonding counterparts, electron repulsion leads us to expect the N-H bonds to form a pyramid.

G. The difference between the energy of the transition state and the stable reactant (lowest energy) is the reaction barrier. Using the conversion factor: $1\ Ha = 2625.50\ kJ/mol$, calculate the barrier to this reaction in kJ/mol (Hint: subtract the energy of the transition state by the reactant state).

$$\begin{aligned} \Delta E &= E_{TS} - E_{reactant} \\ &= -55.4377\ hartrees - (-55.4554\ hartrees) \\ &= 0.0177\ hartrees \\ &\approx 46.5\ kJ/mol \end{aligned}$$

Compared to the experimental value of $24.2\ kJ/mol$, the HF-SCF with a minimal basis set gives a barrier twice as high as the real reaction barrier. To get a more accurate answer, you would have to use a larger basis set, and for the most accurate answer, diagonalize a matrix with more than one electron configuration.