Chapter 10. Exercises

1. The electronic energy of a diatomic molecule can be approximated by the Morse function:

$$E(R) = D\left(1 - e^{-\beta(R-R_e)}\right)^2$$

R_e is the equilibrium internuclear separation while D and β are constants.

(i) Find the dissociation energy D_e

(ii) Sketch the Morse function, labelling D_e and R_e.

(iii) Expand the Morse function up to terms quadratic in $(R - R_e)$. Show that this approximates a harmonic oscillator potential and identify the force constant k.

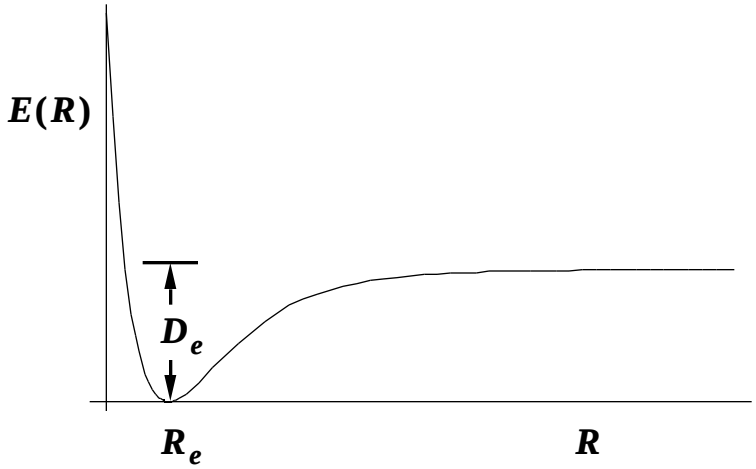
2. The allene molecule CH_2=C=CH_2 is known to have a linear geometry for the three carbon atoms. Rationalize this on the basis of hybridization of carbon AO's.

3. Applying the valence-shell model, predict the shapes of each of the following molecules: H_2S, SF_6, XeF_4, SF_4, IF_5.

Chapter 10. Solutions

1. (i) Minimum value of $E(R)$ can be found by setting $E(R) = 0$. It is easy to see from the formula itself that $E(R)$ will have a minimum value of 0 when $R = R_e$. As $R \to \infty$, $E(R)$ approaches D. Thus $D_e = D$, the dissociation energy.

(ii)



(iii) Remember the expansion for the exponential (In fact, don't ever forget this!)

$$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!} = 1 + x + \frac{x^2}{2} + \frac{x^3}{6} + \ldots$$

Expanding the Morse function up to terms quadratic in $R - R_e$ gives

$$E(R) = 0 + D\beta^2(R - R_e)^2 + \ldots$$

This has the form of a harmonic oscillator potential $V(x) = \frac{1}{2}kx^2$ with

$$x = R - R_e \qquad \text{and} \qquad k = 2D\beta^2$$

2. The central carbon forms two *sp*-hybrids and two unhybridized *p*-orbitals, just like acetylene. The *sp*-hybrids bond to the terminal carbons in a linear arrangement of σ-bonds. Each *p* orbitals then bonds to a terminal carbon to form a π-bond, as shown below

Note that the two CH_2 groups are in perpendicular planes.

3. H_2S: S has 6 valence electrons, 2 form bonds to H leaving 4 electrons or 2 unshared pairs. SH_2E_2 approximately tetrahedral configuration giving two S–H bonds for bent H–S–H molecule. Just like H_2O!

SF_6: 6 S–F bonds, octahedral molecule.

XeF_4: Xe has 8 valence electrons, 4 bonds to F, leaving 2 pairs. XeF_4E_2 octahedral with the two E's on opposite sides to minimize repulsion, so XeF_4 molecule is square planar.

SF_4: 4 S–F bonds, leaving 2 electrons or 1 lone pair. SF_4E trigonal bipyramid with E in one equatorial position. The 4 S–F bonds bend away from the E giving a see-saw shaped molecule.

IF_5: I has 7 valence electrons, 5 I–F bonds plus 1 lone pair. IF_5E octahedral configuration gives geometry of square pyramid.