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 \(\beta\) 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 \(\text{CH}_2=\text{C}=\text{CH}_2\) 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: \(\text{H}_2\text{S}, \text{SF}_6, \text{XeF}_4, \text{SF}_4, \text{IF}_5\).
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)

![Graph of E(R) vs R]

(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

$$x = R - R_e \quad \text{and} \quad k = 2D\beta^2$$
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 \( \sigma \)-bonds. Each \( p \) orbitals then bonds to a terminal carbon to form a \( \pi \)-bond, as shown below

![Diagram of CH₂ groups in perpendicular planes]

Note that the two CH₂ groups are in perpendicular planes.

3. \( \text{H}_2\text{S} \): S has 6 valence electrons, 2 form bonds to H leaving 4 electrons or 2 unshared pairs. \( \text{SH}_2\text{E}_2 \) approximately tetrahedral configuration giving two S–H bonds for bent H–S–H molecule. Just like \( \text{H}_2\text{O} \)!

\( \text{SF}_6 \): 6 S–F bonds, octahedral molecule.

\( \text{XeF}_4 \): Xe has 8 valence electrons, 4 bonds to F, leaving 2 pairs. \( \text{XeF}_4\text{E}_2 \) octahedral with the two E’s on opposite sides to minimize repulsion, so \( \text{XeF}_4 \) molecule is square planar.

\( \text{SF}_4 \): 4 S–F bonds, leaving 2 electrons or 1 lone pair. \( \text{SF}_4\text{E} \) trigonal bipyramid with E in one equatorial position. The 4 S–F bonds bend away from the E giving a see-saw shaped molecule.

\( \text{IF}_5 \): I has 7 valence electrons, 5 I–F bonds plus 1 lone pair. \( \text{IF}_5\text{E} \) octahedral configuration gives geometry of square pyramid.