Chemistry 3405, Spring Semester 2019

1 Potential Energy Surfaces

The energy of a bound diatomic molecule AB as a function of internuclear separation is described by its potential energy surface shown in Fig.1. The existence of a minimum of

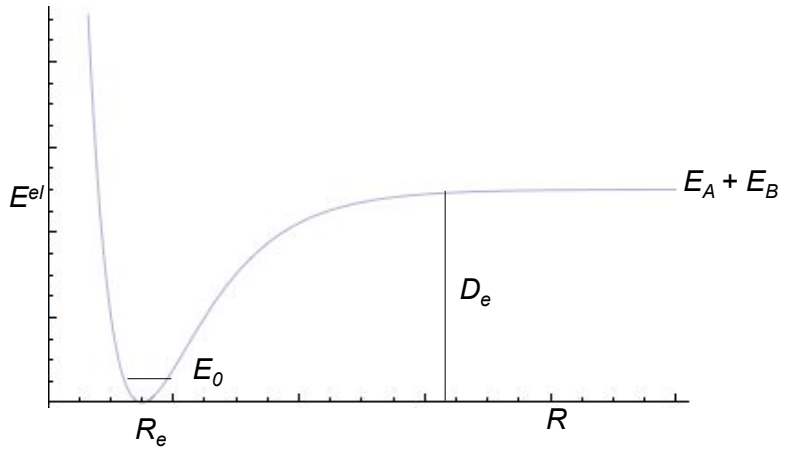

Figure 1: Potential energy surface of a diatomic molecule A-B.

the potential energy surface (PES) implies there is a stable chemical bond between the two atoms. The minimum represents the equilibrium bond length R_e of the molecule. A molecule however is not completely frozen but can vibrate around the minimum with some vibrational frequency ν_e. As the internuclear separation increases at values higher than minimum the energy increases also until the bond breaks and the two atoms are separated and they do not interact with each other any more. The energy at the dissociation limit is equal to the sum of the energies of the two atoms. The energy required to break the bond is the dissociation energy D_e. This potential can be described by a Morse potential

$$E^{el}(R) = D_e\{1 - \exp\left[-\alpha(R - R_e)\right]\}^2 + C \tag{1}$$

where $\alpha = \sqrt{\frac{k}{2D_e}}$. k is the force constant defined as $k = (\frac{d^2E^{el}}{dR^2})_{R=R_e}$. The frequency of vibrational motion is given by:

$$\nu_e = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}. \tag{2}$$

The PES around the minimum can be approximated by a quadratic potential

$$E^{el}(R) = \frac{1}{2}k(R - R_e)^2 + c \tag{3}$$

In this case the vibration of molecules is described by a Harmonic Oscillator.

2 Experimental procedure

1. Step 1: As a first step in the study of the diatomic molecule H_2 you will obtain the equilibrium bond distance. Follow the WebMO instructions to build H_2 and optimize its structure at the CAS(2,2)/6-31G(d) level of theory. Choose optimization +frequency from the menu. After the calculation is finished report the optimized equilibrium geometry R_e and the vibrational frequency ν_e.

   At the minimum of the PES the first derivative of $E^{el}(R)$ with respect to R is zero. The curvature is given by the second derivative $\frac{d^2E^{el}}{dR^2}$ which at a true minimum is positive. The curvature is also related to the force constant and subsequently the vibrational frequency via Eq. 2. The above input will calculate the vibrational frequency after the optimization is finished (keyword: opt freq).

2. Step 2: a) Use WebMO to calculate the potential energy curve of H_2 at the CAS(2,2)/6-31G(d) level. Choose bond lengths starting at 0.5 Å and increasing at an interval of 0.1 Å. (0.5, 0.6, 0.7, ...). The input is shown below.

   #N CAS(2,2)/6-31G(d) Scan

   H2

   0 1
   H
   H 1 B1

   B1 0.5 30 0.1

   Using WebMO, build H_2 and choose a single point calculation at the CAS(2,2)/6-31G(d) level at the job options window. Then go to the preview window and click on generate to generate the input. You will have to edit the input file so that it resembles the one above. Specifically you will have to change the SP keyword to SCAN. Then you will have to change the last line that gives the value of the coordinate B1. This should be (B1 0.5 30 0.1) as shown above. This line means that 30 single point calculations will be done where the bond length of H_2 will be varied. The first value will be 0.5 Å and then it will increase by 0.1 Å for 30 times. After you change the input submit the calculation. When the calculation is done, open the raw output file. Almost at the end of the file the summary of the calculation will be given. It will report:
   Scan completed.

Summary of the potential surface scan:
N B1 SCF
—- ——— ———
1 0.5000 xxxxxx

and all the energies as a function of bond distance will be given. Plot the potential energy curve. Use the energy of the last point on the curve (which is close to the dissociation limit) to obtain the dissociation energy D_e.

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1. Report the equilibrium geometry R_e in Å, vibrational frequency ν_e in wavenumbers, and dissociation energy D_e in eV.

2. Include a plot of the potential energy surface of H_2