

# Theoretical Methods in Chemistry

## Problem Class 2 : Autumn 2004

### Tutors Sheet

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- Knowledge of the derivatives of a well behaved function at a point is enough to define the function over all space !! – through a polynomial expansion.
- The Maclaurin expansion about  $x=0$  is;

$$f(x) = f(0) + \left. \frac{df}{dx} \right|_{x=0} x + \frac{1}{2!} \left. \frac{d^2 f}{dx^2} \right|_{x=0} x^2 + \frac{1}{3!} \left. \frac{d^3 f}{dx^3} \right|_{x=0} x^3 + \dots$$

- The Taylor expansion about  $x=a$  is;

$$f(x) = f(a) + \left. \frac{df}{dx} \right|_{x=a} (x-a) + \frac{1}{2!} \left. \frac{d^2 f}{dx^2} \right|_{x=a} (x-a)^2 + \frac{1}{3!} \left. \frac{d^3 f}{dx^3} \right|_{x=a} (x-a)^3 + \dots$$

1. Make a Maclaurin expansion of  $e^x$ .

Note:

The exponential function is *defined* such that  $\frac{de^x}{dx} = e^x$ .

How many terms are required to compute  $e^2$  to 3 decimal places, 4 d.p. and 5 d.p. ?  
Sketch  $e^x$  and these polynomial approximations to it.

Make a Taylor expansion about  $x=1$ , using this expansion how many terms are required to compute  $e^2$  to 5 d.p. ?

**Tutors Note:**

Straightforward ☺

2. The potential energy of interaction between the H-atoms in the hydrogen molecule can be approximated by the Morse form;

$$E(r) = D_e \left\{ 1 - e^{-\alpha(r-a)} \right\}^2$$

with,  $D_e = 4.79 \text{ eV}$ ,  $a = 0.074 \text{ nm}$  and  $\alpha = 19.3 \text{ nm}^{-1}$

Sketch this potential energy surface – mark  $D_e$  on your sketch, what role do  $a$  and  $\alpha$  play ?

Calculate  $\frac{dE}{dr}$  and find the equilibrium bond length of  $\text{H}_2$ .

What value does  $E(r)$  approach far from equilibrium ? what do you deduce from this about the binding energy of  $\text{H}_2$  ?

**Tutor Note:**

$$\frac{dE}{dr} = 2\alpha D_e \left( 1 - e^{-\alpha(r-a)} \right)$$

At equilibrium;

$$2\alpha D_e \left( 1 - e^{-\alpha(r-a)} \right) = 0$$

$$\left( 1 - e^{-\alpha(r-a)} \right) = 0$$

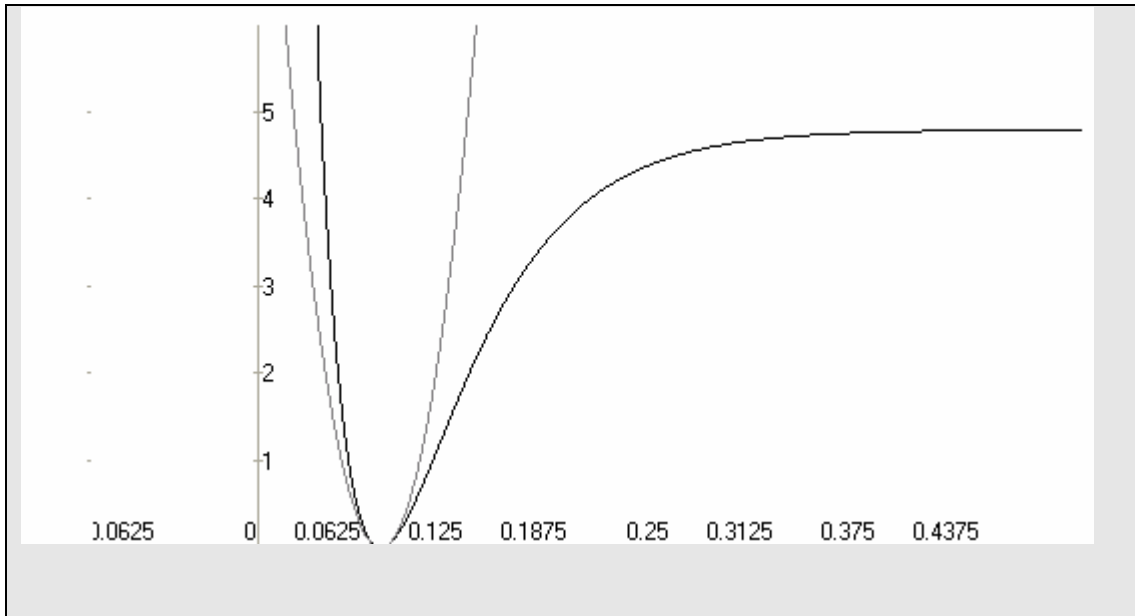
$$e^{-\alpha(r-a)} = 1$$

$$\alpha(r-a) = 0$$

$$r = a$$

So  $a$  is the equilibrium bond length,  $1/\alpha$  is a measure of the length scale on which the potential decays to 0 with distance (prove it ?).  $D_e$  is the binding energy if one ignores zero point vibration.

The sketch should look like; ( $E(r)$  eV :  $r$  (nm))



3. Compute  $\frac{d^2 E}{dr^2}$  make a Taylor expansion of  $E(r)$  about  $r=a$  and thus show that near equilibrium ( $r \approx a$ ) the Morse potential is harmonic with force constant  $k = m\omega^2 = 2D_e\alpha^2$ . Add this harmonic approximation to your sketch.

**Tutor Note:**

$$\frac{d^2 E}{dr^2} = \frac{d}{dr} (2\alpha D_e (1 - e^{-\alpha(r-a)})) = 2\alpha^2 D_e e^{-\alpha(r-a)}$$

Taylor expansion about  $r=a$ ,

Note:

$$E(r) \Big|_{r=a} = D_e \{1 - e^{-\alpha(r-a)}\}^2 \Big|_{r=a} = D_e \{1 - 1\}^2 = 0$$

$$\frac{dE}{dr} \Big|_{r=a} = 2\alpha D_e (1 - e^{-\alpha(r-a)}) \Big|_{r=a} = 2\alpha D_e (1 - e^{-\alpha(r-a)}) = 2\alpha D_e (1 - 1) = 0$$

as expected for the minimum, and,

$$\frac{d^2 E}{dr^2} \Big|_{r=a} = 2\alpha^2 D_e e^{-\alpha(r-a)} \Big|_{r=a} = 2\alpha^2 D_e$$

Thus the Taylor expansion to second order is;

$$\begin{aligned}
 E(r) &= E(a) + \left. \frac{dE}{dr} \right|_{r=a} (r-a) + \frac{1}{2} \left. \frac{d^2E}{dr^2} \right|_{r=a} (r-a)^2 \\
 &= 0 + 0 + \alpha^2 D_e (r-a)^2 \\
 &= \alpha^2 D_e (r-a)^2
 \end{aligned}$$

Comparing this to the harmonic oscillator of form  $E = \frac{1}{2} k(r-a)^2$  it is an harmonic potential with spring constant  $2D_e\alpha^2$  as required (this harmonic potential is indicated on the plot above).

4. The energy of the lowest vibrational mode of  $H_2$  is approximately  $\frac{1}{2} \hbar \omega$

Find the energy of the lowest vibrational mode and use it to estimate the dissociation energy of  $H_2$ .

Note:

The mass of a proton =  $1.672 \times 10^{-27} \text{ kg}$

The electronic charge is:  $1.602 \times 10^{-19} \text{ C}$

$\hbar$  ( $h/2\pi$ ) is:  $6.6 \times 10^{-16} \text{ eVs}$

### Tutor Note:

As stated in the question  $k = m\omega^2 = 2D_e\alpha^2$ . The mass used should be the reduced mass of  $H_2$  ie:  $m_p m_p / (m_p + m_p) = m_p / 2$  where;

$$\omega = \sqrt{\frac{k}{(m_p / 2)}}$$

so – using SU units as much as is bearable,

$$\begin{aligned}
 \omega^2 &= (2 \times 2 \times 4.79 \times 1.602 \times 10^{-19} \times (19.3)^2 \times 10^{18}) / 1.672 \times 10^{-27} \text{ Jm}^{-2}\text{kg}^{-1} \\
 &= 6838 \times 10^{26}
 \end{aligned}$$

$$\omega = 82.69 \times 10^{13} \text{ s}^{-1}$$

$$E_{\text{vib}} = \frac{1}{2} \hbar \omega = \frac{1}{2} \times 6.6 \times 10^{-16} \times 82.69 \times 10^{13} = 0.273 \text{ eV}$$

So the ground state vibrational energy is 0.273 eV.

From the potential energy curve and part i) it is clear that the potential energy of dissociation of  $\text{H}_2$  is  $D_e = 4.79\text{eV}$ , but the zero point vibrational energy is  $0.273\text{eV}$  so measured dissociation energy will be  $4.79 - 0.273 = 4.517\text{eV}$ .

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