Theoretical Methods in Chemistry

Problem Class 2 : Autumn 2004

nicholas.harrison@imperial.ac.uk

- 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;

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

- The Taylor expansion about x=a is;

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

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. ?

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=4.79eV, a = 0.074 nm and α=19.3 nm^{-1}

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

Calculate $\frac{dE}{dr}$ and find the equilibrium bond length of H_2.

What value does E(r) approach far from equilibrium ? what do you deduce from this about the binding energy of H_2 ?

3. Compute $\frac{d^2E}{dr^2}$ 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.

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 = 1.672×10^{-27}kg
   The electronic charge is: 1.602×10^{-19} C
   h-bar (h/2pi) is: $6.6\text{x}10^{-16}$ eVs

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