

Oct. 31, 2007
Chem. 1410
Practice Problem for Hour Exam 2

1) For a quantum mechanical diatomic system bound by the central potential $v(r)$, the radial motion is determined, for each value of the angular momentum quantum number l , by the effective radial potential

$$v^{eff}(r) = v(r) + \hbar^2 l(l+1) / 2\mu r^2 \quad , \quad [1]$$

where μ is the usual reduced mass of the system.

In Problem Set 6, we considered the specific case that $v(r)$ is the vibrational potential $v(r) = \frac{1}{2}k(r-r_e)^2$, k being the restoring force constant and r_e the equilibrium bond length. For this system:

a) Calculate the radial position of the minimum of $v^{eff}(r)$ (i.e., the equilibrium separation between the two atoms in the diatomic) in the case that centrifugal distortion introduced by the 2nd term on the r.h.s. of Eq. 1 is small. Specifically, designate the position of the minimum of $v^{eff}(r)$ as $r_m = r_e + x$. Then, if $x/r_e \ll 1$, show that:

$$x \cong \frac{r_e}{\left(3 + \frac{k\mu r_e^4}{\hbar^2 l(l+1)}\right)} \quad (2)$$

[Hint: for $x/r_e \ll 1$, $\frac{1}{r_m^n} \cong \frac{1}{r_e^n} (1 - n \frac{x}{r_e})$ for any positive integer n .]

Note: According to Eq. 2, $x > 0$, implying that $r_m > r_e$ as expected (why)?

b) Using Mathcad (or other software/program), compute a quadratic expansion to $v^{eff}(r)$ valid in the radial region near r_m . That is, numerically calculate

$$v_{quad}(r) = v^{eff}(r_m) + \frac{1}{2} \frac{d^2 v^{eff}(r_m)}{dr^2} (r - r_m)^2 \quad ,$$

and plot this on the same graph with $v^{eff}(r)$ for the parameter choices: $\hbar^2 l(l+1) = 9$, $\mu = 5, k = 1, r_e = 2$. Is $x/r_e \ll 1$? Is the quadratic accurate in the region of $r \approx r_m$?