

Oct. 15, 2007
Chem. 1410
Problem Set 6, due Oct. 22, 2007

Do the following problems; these are *not* to be handed in for grading; solutions will be distributed via .pdf.

Engel Chapter 8: P8.1, P8.7, P8.16

and

(0) Counting the Number of Independent Normal Modes of vibration in a Polyatomic Molecule.

How many vibrational normal modes are there in:

i) ICN ? [Note: this molecule is linear.]

ii) CH₄ ?

The following two problems are to be handing in for grading:

(1) 3D Kinetic energy of a Diatomic Molecule expressed in Center of Mass and Relative Coordinates.

Consider the diatomic molecule shown in Fig. 1: The total classical kinetic energy of the molecule is given by:

$$T = \frac{1}{2}m_1\vec{x}_1^2 + \frac{1}{2}m_2\vec{x}_2^2$$

where $\vec{x}_{1,2}$ is the 3D cartesian coordinate vector that prescribes the location of atom 1,2 with respect to a given lab-fixed coordinate origin. Using the definitions of the center of mass vector \vec{X} and the relative coordinate vector \vec{r} given in class, show that T can be written equivalently as:

$$T = \frac{1}{2}M\vec{X}^2 + \frac{1}{2}\mu\vec{r}^2$$

where M and μ are the usual total system mass and reduced diatomic mass, respectively.

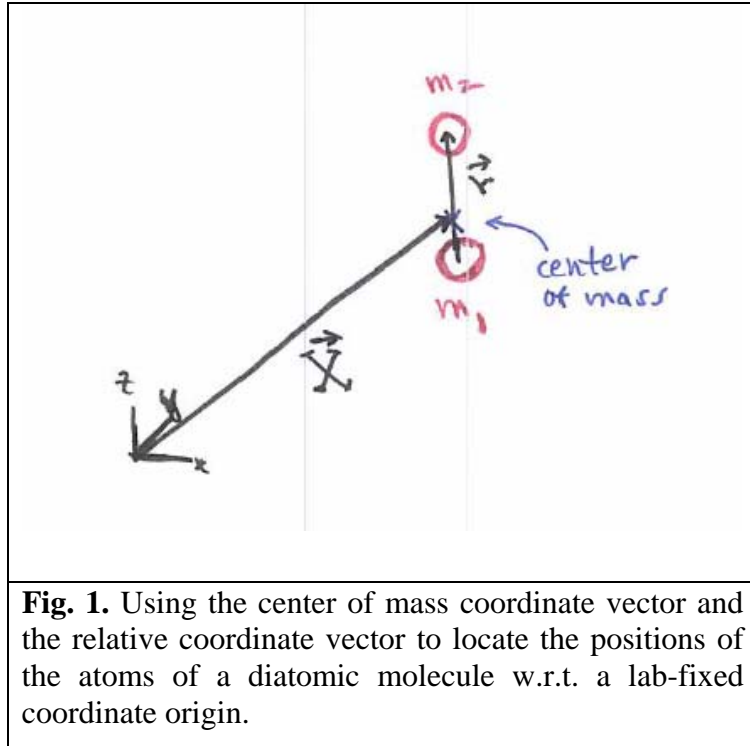


Fig. 1. Using the center of mass coordinate vector and the relative coordinate vector to locate the positions of the atoms of a diatomic molecule w.r.t. a lab-fixed coordinate origin.

(2) Separation of variables in the quantum mechanical motion of a 3D diatomic molecule.

The relative motion of a diatomic molecule [see problem 1 above for the definition of the relative coordinate vector $\vec{r} = (x, y, z)^T$] obeys the 3D Schrödinger Eq.:

$$\left(-\frac{\hbar^2}{2\mu} \nabla^2 + v(r) \right) \psi(\vec{r}) = E\psi(\vec{r}) \quad [1]$$

where μ is the reduced mass of the diatomic and the Laplacian is given by $\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$.

Furthermore, note that the Laplacian can be written in spherical polar coordinates as:

$$\nabla^2 = \frac{1}{r} \frac{\partial^2(r \quad)}{\partial r^2} + \frac{1}{r^2} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial}{\partial \theta}) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right\}$$

a) Show that there is a solution to Eq. [1] having the form $\psi(\vec{r}) = \psi(r, \theta, \phi) = \frac{1}{r} \chi_l(r) Y_{lm}(\theta, \phi)$, where $Y_{lm}(\theta, \phi)$ is the standard spherical harmonic function (with the usual allowed values of l, m) and $\chi_l(r)$ obeys the 1D Schrödinger Eq.:

$$\left(-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} + v_l^{\text{eff}}(r) \right) \chi(\vec{r}) = E \chi(\vec{r}) ,$$

with the effective 1D potential energy function (dependent on the value of l):

$$v_l^{\text{eff}}(r) = v(r) + \hbar^2 l(l+1) / 2\mu r^2$$

b) Let $v(r)$ be the standard vibrational potential $v(r) = \frac{1}{2} \kappa (r - r_{eq})^2$, where κ is the restoring force constant and r_{eq} is the equilibrium bond length. Does the position of mechanical equilibrium of the radial oscillation [determined by the location of the minimum of $v_l^{\text{eff}}(r)$] increase or decrease with increasing values of l ? (Hint: An easy way to determine the answer to this question is to plot $v_l^{\text{eff}}(r)$ for several values of l , for (arbitrary) fixed values of κ, r_{eq} .)