Chem 3322 homework #8, due April 5, 2024

Problem 1 – reduced mass

Please read the following as background for this question

`https://web1.eng.famu.fsu.edu/~dommelen/quantum/style_a/nt_mred.html`

a) Consider two particles of masses m_1 and m_2 in one dimension, interacting through a potential that depends only upon their relative separation. Given that the force acting upon the jth particle is $f_j = -(\partial V/\partial x_j)$, show that $f_1 = -f_2$. To show this, you must change variables using equation (2). What law is this?

b) Newton's equations for the two particles are

$$m_1 \frac{d^2 x_1}{dt^2} = -\frac{\partial V}{\partial x_1} \quad \text{and} \quad m_2 \frac{d^2 x_2}{dt^2} = -\frac{\partial V}{\partial x_2} \tag{1}$$

Now introduce center of mass and relative coordinates by

$$X \equiv \frac{m_1 x_1 + m_2 x_2}{M} \qquad x \equiv x_1 - x_2 \tag{2}$$

where $M = m_1 + m_2$, and solve for x_1 and x_2 to obtain

$$x_1 = X + \frac{m_2}{M} x \quad \text{and} \quad x_2 = X - \frac{m_1}{M} x \tag{3}$$

Show that Newton's equations in these coordinates are

$$m_1 \frac{d^2 X}{dt^2} + \frac{m_1 m_2}{M} \frac{d^2 x}{dt^2} = -\frac{\partial V}{\partial x} \tag{4}$$

and

$$m_2 \frac{d^2 X}{dt^2} - \frac{m_1 m_2}{M} \frac{d^2 x}{dt^2} = +\frac{\partial V}{\partial x} \tag{5}$$

c) Now add these two equations to find

$$M \frac{d^2 X}{dt^2} = 0 \tag{6}$$

Interpret this result.

d)

Now divide the first equation by m_1 and the second by m_2 and subtract to obtain

$$\frac{d^2 x}{dt^2} = -\left(\frac{1}{m_1} + \frac{1}{m_2}\right) \frac{\partial V}{\partial x} \tag{7}$$

or

$$\mu \frac{d^2 x}{dt^2} = -\frac{\partial V}{\partial x} \tag{8}$$

where $\mu = m_1 m_2/(m_1 + m_2)$ is the reduced mass. Interpret this result, and discuss how the original two-body problem has been reduced to two one-body problems.

e)

Extend the result of (a-d) to three dimensions. Note that in three dimensions the relative separation is given by

$$r_{12} = \left[(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2\right]^{1/2} \tag{9}$$

Problem 2 – rigid rotor energy term

The TISE for the harmonic oscillator is

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{1}{2}\mu\omega^2 x^2 \psi(x) = E\psi(x) \tag{10}$$

a) Show that the ground state solution to this equation is

$$\psi(x) = e^{-\alpha x^2} \tag{11}$$

with

$$\alpha = \frac{\mu\omega}{2\hbar} \tag{12}$$

and find the energy $E = E_0$ as part of your solution. How do you know this is the ground state?

b) Now we will modify the TISE to read

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2 \psi(x)}{\partial x^2} + c\,\psi(x) + \frac{1}{2}\mu\omega^2 x^2 \psi(x) = E\psi(x) \tag{13}$$

with

$$c = \frac{\hbar^2 \ell(\ell+1)}{2\mu r_{eq}^2} \tag{14}$$

Show that your solution to (a), $\psi(x) = e^{-\alpha x^2}$, also solves this modified equation and find the energy corresponding to this solution.

Problem 3

The force constants of some diatomics are: HBr: 410 N/m; Br_2: 240 N/m; CO: 1860 N/m; NO: 1530 N/m Calculate the fundamental vibrational frequency in hertz and the zero-point energy in joules of these molecules.

Problem 4

Given that the spacing of lines in the pure rotational spectrum of $^{27}Al^{1}H$ is constant at 12.604 cm^{-1}, calculate the bond length of this molecule. **Hint:** each *line* in the spectra corresponds to a transition between energy levels in the molecule.