Chem 3322 homework #8 solutions

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 equations (4 and (5). What law is this?

solution: Define $x = x_1 - x_2$. Then we can write

$$f_1 = -\frac{\partial V}{\partial x_1} = -\frac{\partial V}{\partial x}\frac{\partial x}{\partial x_1} = -\frac{\partial V}{\partial x} \tag{1}$$

and

$$f_2 = -\frac{\partial V}{\partial x_2} = -\frac{\partial V}{\partial x}\frac{\partial x}{\partial x_2} = \frac{\partial V}{\partial x} \tag{2}$$

since $(\partial(x_1 - x_2)/\partial x_1) = 1$ and $(\partial(x_1 - x_2)/\partial x_2) = -1$.

This is Newton's third law: For every action, there is an equal and opposite reaction.

b)

Newton's equations for the two particles are

$$m_1\frac{d^2x_1}{dt^2} = -\frac{\partial V}{\partial x_1} \quad \text{and} \quad m_2\frac{d^2x_2}{dt^2} = -\frac{\partial V}{\partial x_2} \tag{3}$$

Now introduce center of mass and relative coordinates by

$$X \equiv \frac{m_1x_1 + m_2x_2}{M} \tag{4}$$

$$x \equiv x_1 - x_2 \tag{5}$$

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

$$x_1 = X + \frac{m_2}{M}x \quad \text{and} \quad x_2 = X - \frac{m_1}{M}x \tag{6}$$

Show that Newton's equations in these coordinates are

$$m_1\frac{d^2X}{dt^2} + \frac{m_1m_2}{M}\frac{d^2x}{dt^2} = -\frac{\partial V}{\partial x} \tag{7}$$

and

$$m_2 \frac{d^2X}{dt^2} - \frac{m_1 m_2}{M} \frac{d^2x}{dt^2} = +\frac{\partial V}{\partial x} \tag{8}$$

solution: To solve for x_1 and x_2, we multiply Eq. (4) by M and Eq. (5) by m_2 and add them to get x_1, and then we multiply Eq. (4) by M and Eq. (5) by m_1 and substract them to get x_2. The only tricky thing here is to show that

$$\frac{\partial V}{\partial x} = \frac{\partial V}{\partial x_1} \tag{9}$$

and

$$\frac{\partial V}{\partial x} = -\frac{\partial V}{\partial x_2} \tag{10}$$

but we actually did this in Eqs. (1) and (2).

c)

Now add these two equations to find

$$M \frac{d^2X}{dt^2} = 0 \tag{11}$$

Interpret this result.

solution: This result says that the center of mass experiences zero force. Hence the center of mass moves at constant velocity, which we can remove from the problem by taking our origin as the center of mass. Strictly speaking, we have proved that the center of mass reference frame is an inertial reference frame, which allows us to use it without any complications.

d)

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

$$\frac{d^2x}{dt^2} = -\left(\frac{1}{m_1} + \frac{1}{m_2}\right) \frac{\partial V}{\partial x} \tag{12}$$

or

$$\mu \frac{d^2x}{dt^2} = -\frac{\partial V}{\partial x} \tag{13}$$

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.

solution: We have arrived at Eq.(11) which allows us to take the origin of the coordinate system to be the center of mass. Then, Eq. (13) only depends on x, the relative separation, so if we take the center of mass as the origin, we are down to a one-body problem, which was the goal. So we have actually reduced the problem down to one variable x, assuming we don't care where the center of mass is (ie. we are sitting on it, moving with it so we don't notice it is moving).

e)

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

$$r_{12} = \left[(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2\right]^{1/2} \tag{14}$$

solution: The solution here is almost identical to (a-d). We can treat each of x, y, and z separately, and we eventually get

$$\mu \frac{d^2 x}{dt^2} = -\frac{\partial V}{\partial x}\,, \quad \mu \frac{d^2 y}{dt^2} = -\frac{\partial V}{\partial y}\,, \quad \mu \frac{d^2 z}{dt^2} = -\frac{\partial V}{\partial z} \tag{15}$$

or

$$\mu \frac{d^2 r}{dt^2} - \nabla V \tag{16}$$

where $r = (x, y, z)$.

<u>Problem 2</u> – rigid rotor energy term

The TISE for the harmonic oscillator is

$$-\frac{\hbar^2}{2\mu} \frac{\partial^2 \psi(x)}{\partial x^2} + \frac{1}{2} \mu \omega^2 x^2 \psi(x) = E\psi(x) \tag{17}$$

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

$$\psi(x) = e^{-\alpha x^2} \tag{18}$$

with

$$\alpha = \frac{\mu\omega}{2\hbar} \tag{19}$$

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

Solution:

we know this is the ground state because it has zero nodes, and it solves the TISE. To show it solves the TISE, let us first evaluate

$$\frac{\partial^2\psi(x)}{\partial x^2} = \frac{d}{dx}\left(-2\alpha x e^{-\alpha x^2}\right) = (4\alpha^2 x^2 - 2\alpha)\psi(x) \tag{20}$$

Putting this in Eq. (17) gives

$$-\frac{\hbar^2}{2\mu}(4\alpha^2 x^2 - 2\alpha)\psi(x) + \frac{1}{2}\mu\omega^2 x^2\psi(x) = E\psi(x) \tag{21}$$

Canceling $\psi(x)$ on both sides gives

$$x^2\left(-\frac{2\alpha^2\hbar^2}{\mu} + \frac{\mu\omega^2}{2}\right) + \frac{\hbar^2\alpha}{\mu} = E \tag{22}$$

This can only work if

$$\frac{2\alpha^2\hbar^2}{\mu} = \frac{\mu\omega^2}{2} \tag{23}$$

and if

$$\frac{\hbar^2\alpha}{\mu} = E \tag{24}$$

The first condition yields

$$\alpha = \frac{\mu\omega}{2\hbar} \tag{25}$$

which we already, in fact, know from Eq. (19). The second condition yields

$$E = \frac{\hbar^2\alpha}{\mu} = \frac{1}{2}\hbar\omega = E_0 \tag{26}$$

b) Now we will modify the TISE to read

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2\psi(x)}{\partial x^2} + c\,\psi(x) + \frac{1}{2}\mu\omega^2 x^2\psi(x) = E\psi(x) \tag{27}$$

with

$$c = \frac{\hbar^2\ell(\ell+1)}{2\mu r_{eq}^2} \tag{28}$$

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.

Solution: picking up from Eq. (21) but with the new TISE, and canceling $\psi(x)$ on both sides gives

$$-\frac{\hbar^2}{2\mu}(4\alpha^2x^2 - 2\alpha)\psi(x) + c + \frac{1}{2}\mu\omega^2x^2\psi(x) = E\psi(x) \tag{29}$$

As before, the x^2 terms cancel, leaving

$$\frac{\hbar^2\alpha}{\mu} + c = E \tag{30}$$

Putting in $\alpha = \mu\omega/2\hbar$ yields

$$E = \frac{1}{2}\hbar\omega + c = \frac{1}{2}\hbar\omega + \frac{\hbar^2\ell(\ell+1)}{2\mu r_{eq}^2} \tag{31}$$

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.

Solution:

The fundamental vibrational frequency is given by $\omega = (k/\mu)^{1/2}$ where $\omega = 2\pi\nu$. The zero-point energy is $\hbar\omega/2 = h\nu/2$. You need to compute the reduced masses (some of you used 79 for Br, and some people used 79.9, so the answers vary a bit), and then you obtain:

HBr: $\nu = 7.96 \times 10^{13}\mathrm{s}^{-1}$ and $E_0 = 2.63 \times 10^{-20}\mathrm{J}$

Br_2: $\nu = 9.57 \times 10^{12}\mathrm{s}^{-1}$ and $E_0 = 3.17 \times 10^{-21}\mathrm{J}$

CO: $\nu = 6.43 \times 10^{13}\mathrm{s}^{-1}$ and $E_0 = 2.13 \times 10^{-20}\mathrm{J}$

NO: $\nu = 5.59 \times 10^{13}\mathrm{s}^{-1}$ and $E_0 = 1.85 \times 10^{-20}\mathrm{J}$

In general, heavier atoms give lower zero point energies.

Problem 4

Given that the spacing of lines in the pure rotational spectrum of $^{27}\mathrm{Al}^1\mathrm{H}$ 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.

Solution:

The spacing between lines corresponds to the difference in the change of energy between sequential transitions, since each line individually represents a *transition* between two energy levels in the molecule. Let us work it out in general:

$$\Delta E_1 = E_{\ell+1} - E_\ell = \frac{(\ell+1)(\ell+2)\hbar^2}{2\mu r_0^2} - \frac{\ell(\ell+1)\hbar^2}{2\mu r_0^2} = \frac{(2\ell+2)\hbar^2}{2\mu r_0^2} \tag{32}$$

$$\Delta E_2 = E_{\ell+2} - E_{\ell+1} = \frac{(\ell+2)(\ell+3)\hbar^2}{2\mu r_0^2} - \frac{(\ell+1)(\ell+2)\hbar^2}{2\mu r_0^2} = \frac{(2\ell+4)\hbar^2}{2\mu r_0^2} \tag{33}$$

The spacing between lines is then

$$\Delta E_2 - \Delta E_1 = \frac{2\hbar^2}{2\mu r_0^2} = \frac{\hbar^2}{\mu r_0^2} \tag{34}$$

This yields a bond length of 1.665 Å.