Chemistry 331 **Problem Set #6** *(due Thursday 07 November, in class)*

1. A 0.15 gram mass undergoing classical harmonic vibration is located at position

$$x(t) = A\sin(2\pi\nu t)$$

at time t. The vibration frequency and amplitude are $\nu = 5.2\ s^{-1}$ and $A = 0.24$ cm.

a) Derive expressions for:

i) $F(t)$, the force acting on the mass at time t (*hint*: force = mass × acceleration)

ii) $T(t)$, the kinetic energy at time t

iii) $V(t)$, the potential energy at time t.

[8] **b)** The kinetic energy $T(t)$ and potential energy $V(t)$ are constantly changing, but show the total energy $T(t) + V(t)$ is constant and equal to $kA^2/2$. (*hint*: $\cos^2\theta + \sin^2\theta = 1$)

c) Calculate:

i) the force constant k in units of N m^{-1}

ii) the total energy of the oscillator in units of Joules

iii) the time required for one oscillation

iv) the angular frequency ω.

2. This question refers to the ground vibrational state ($n = 0$) of the N_2 molecule (fundamental frequency $\nu = 2331\ cm^{-1}$). Use 2.32×10^{-26} kg for the mass of the nitrogen nucleus.

a) Calculate:

i) the reduced mass μ of the N_2 molecule

[8] **ii)** the force constant k

iii) the ground-state vibrational energy E_0

iv) the maximum speed of the vibrating nitrogen nuclei

v) the classical amplitude of vibration A (Use $kA^2/2$ for the classical vibration energy. For comparison, the equilibrium bond length of the N_2 molecule is 0.109 nm)

b) Why is it impossible to determine a definite value for the amplitude of the vibration of the N_2 molecule?

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3. **a)** We derived the Schrodinger equation for the harmonic oscillator, but did not solve it.

Verify that the ground-state wave function of the harmonic oscillator given in class

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} \qquad \text{with} \qquad \alpha = \frac{2\pi}{h}\sqrt{k\mu}$$

[4] is a valid solution of the Schrodinger equation.

$$-\frac{h^2}{8\pi^2\mu}\frac{d^2\psi_0(x)}{dx^2} + \frac{1}{2}kx^2\psi_0(x) = E_0\psi_0(x)$$

b) Use the results from **a** to show the ground state energy of the oscillator is

$$E_0 = \frac{h}{4\pi}\sqrt{\frac{k}{\mu}}$$

4. **a)** Explain briefly, in words, why the average momentum of a harmonic oscillator is zero.

[3]

$$\langle p_x \rangle = 0$$

b) Use the concept of even and odd functions to prove $\langle p_x \rangle = 0$ for a harmonic oscillator.

5. The average squared momentum of a harmonic oscillator is not zero:

[2]

$$\langle p_x^2 \rangle = \frac{h}{2\pi}\sqrt{\mu k}\,(n+\frac{1}{2})$$

Use this result to prove the average kinetic energy of the oscillator equals one half of the total oscillator energy: $\langle T_n \rangle = E_n/2$.

Chem 331 **Assignment #5**

Q1 The classical harmonic oscillation of a 0.15 gram mass with amplitude $A = 0.24$ cm and frequency $\nu = 5.2\ s^{-1}$.

Position of the mass at time t:

$$x(t) = A\sin(2\pi\nu t)$$

a) derive expressions for:

i) the force acting on the oscillating mass

$F(t)$ = mass times acceleration

$$= m\frac{dv_x}{dt} = m\frac{d}{dt}\frac{dx}{dt} = m\frac{d^2x}{dt^2}$$

$$= m\frac{d^2}{dt^2}A\sin(2\pi\nu t)$$

$$= m\frac{d}{dt}(2\pi\nu)A\cos(2\pi\nu t)$$

$$= m(2\pi\nu)(-2\pi\nu)A\sin(2\pi\nu t)$$

$$= -m4\pi^2\nu^2 A\sin(2\pi\nu t)$$

$$\boxed{F(t) = -m4\pi^2\nu^2 x(t) = -k\,x(t)}$$

notice force constant $k = 4\pi^2 m\nu^2$

(Q1 a) cont.)

ii) kinetic energy at time t :

$$T(t) = \frac{1}{2} m v_x^2 = \frac{1}{2} m \left(\frac{dx(t)}{dt}\right)^2$$

$$= \frac{1}{2} m \left(\frac{d\, A\sin(2\pi\nu t)}{dt}\right)^2$$

$$= \frac{1}{2} m \left[2\pi\nu A \cos(2\pi\nu t)\right]^2$$

$$\boxed{T(t) = 2\pi^2 m \nu^2 A^2 \cos^2(2\pi\nu t)}$$

iii) potential energy at time t :

$$V(t) = \frac{1}{2} k[x(t)]^2$$

(from part i, the force constant is $k = 4\pi^2 m \nu^2$)

$$= \frac{1}{2} k \left[A \sin(2\pi\nu t)\right]^2$$

$$= \frac{1}{2} 4\pi^2 m \nu^2 A^2 \sin^2(2\pi\nu t)$$

$$\boxed{V(t) = 2\pi^2 m \nu^2 A^2 \sin^2(2\pi\nu t)}$$

(Q1 cont.)

b) Total energy of the oscillator:

$$E = T(t) + V(t) \qquad \text{(kinetic plus potential energy)}$$

$$= 2\pi^2 m \nu^2 A^2 \cos^2(2\pi\nu t) + 2\pi^2 m \nu^2 A \sin^2(2\pi\nu t)$$

$$= 2\pi^2 m \nu^2 A^2 \left(\overbrace{\cancel{\cos^2(2\pi\nu t) + \sin^2(2\pi\nu t)}}^{1} \right)$$

$$= 2\pi^2 m \nu^2 A^2$$

$$= \frac{1}{2}\left(4\pi^2 m \nu^2\right) A^2$$

$$E = \frac{1}{2} k A^2 \qquad (\underline{\text{constant}})$$

c) i) $k = 4\pi^2 m \nu^2 = 4\pi^2 \overbrace{(0.00015\,\text{kg})(5.2\,\text{s}^{-1})^2}^{\text{(SI units)}}$

$$\boxed{k = 0.160\ \text{N m}^{-1}}$$

ii) $E = \frac{1}{2} k A^2 = \frac{1}{2}\left(0.160\,\frac{\text{N}}{\text{m}}\right)(0.0024\,\text{m})^2 = \boxed{4.61 \times 10^{-7}\,\text{J}}$

iii) $\nu = 5.2$ oscillations per second

time for one oscillation $= \frac{1}{\nu} = \boxed{0.192\ \text{s}}$

iv) angular frequency $\omega = 2\pi\nu$

$$= 2\pi(5.2\,\text{s}^{-1})$$

$$= \boxed{32.7\,\text{s}^{-1}}$$

Q2 The quantum mechanical vibration of the N_2 molecule.

a) i) reduced mass $\mu = \dfrac{m_N m_N}{m_N + m_N} = \dfrac{m_N}{2}$

$$\mu = \frac{2.32\times10^{-26}}{2}\ kg = 1.16\times10^{-26}\ kg$$

ii) force constant $k = 4\pi^2\mu\nu^2$

frequency in wave numbers $\tilde{\nu} = \dfrac{\nu}{c}$ in cm s^{-1}

$$\text{frequency } \nu = c\tilde{\nu} = \left(2.998\times10^{10}\ \frac{cm}{s}\right)\left(2331\ cm^{-1}\right)$$

$$\nu = 6.988\times10^{13}\ s^{-1}$$

$$k = 4\pi^2\mu\nu^2 = 4\pi^2\left(1.16\times10^{-26}\ kg\right)\left(6.988\times10^{13}\ s^{-1}\right)^2$$

$$\boxed{k = 2236\ N\ m^{-1}}$$

iii) vibrational energy $E_n = h\nu\left(n+\frac{1}{2}\right)$ $n = 0, 1, 2, \ldots$

ground-state ($n=0$) vibrational energy $= h\nu\frac{1}{2} = \dfrac{\left(6.626\times10^{-34}\ Js\right)6.988\times10^{13}\ s^{-1}}{2}$

$$\boxed{E_0 = 2.315\times10^{-20}\ J \quad (0.1445\ eV)}$$

(Q2 a) cont.)

iv) maximum speed of the vibrating nitrogen nuclei?

max. speed at displacement $x = 0$
where all of the energy is kinetic

the max. kinetic energy of one nucleus

$$= \frac{E_0}{2} = \frac{2.315 \times 10^{-20} \text{ J}}{2} = \frac{1}{2} m_N v_{N\,max}^2$$

$$2.315 \times 10^{-20} \text{ J} = m_N v_{N\,max}^2$$

$$v_{N\,max} = \sqrt{\frac{2.315 \times 10^{-20} \text{ J}}{2.32 \times 10^{-26} \text{ kg}}} = \boxed{999 \ \frac{m}{s}}$$

about 1 km per second!

v) classical amplitude of vibration?

use $E_0 = \frac{1}{2} k A^2$

$$A = \sqrt{2E_0/k}$$

$$= \sqrt{2\,(2.315 \times 10^{-20} \text{ J})\,/\,(2236 \text{ N m}^{-1})}$$

$$= 4.55 \times 10^{-12} \text{ m} = \boxed{0.00455 \text{ nm}}$$

(about 4.1% of the bond length 0.109 nm)

(Q2 cont.)

b) Why is it impossible to have a precise value for the amplitude of vibration of N_2 molecules?

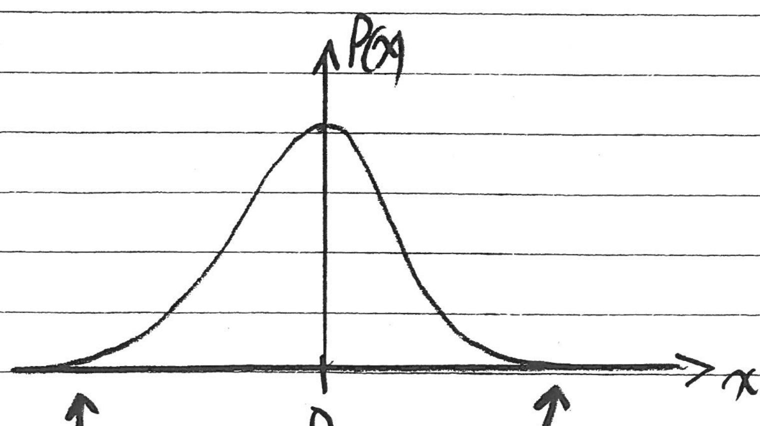
The oscillating reduced mass can penetrate the harmonic potential energy barrier $\frac{1}{2}kx^2$, so the probability distribution

$$P(x) = \psi^*(x)\,\psi(x)$$

$$= \left(\frac{\alpha}{\pi}\right)^{4} e^{-\alpha x^2/2} \left(\frac{\alpha}{\pi}\right)^{4} e^{-\alpha x^2/2}$$

$$= \sqrt{\frac{\alpha}{\pi}}\; e^{-\alpha x^2}$$

gradually decays to zero as the displacement increases, without a sharp cut-off at a definite amplitude of vibration



no sharp cut-off at a definite vibration amplitude

$$\alpha = \frac{2\pi}{h}\sqrt{k\mu}$$

Q3 a) Show the ground-state wave function

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$

is a solution of the Schrodinger equation ($\hat{H}\psi_0 = E_0\psi_0$)

$$-\frac{h^2}{8\pi^2\mu}\frac{d^2\psi_0(x)}{dx^2} + \frac{1}{2}kx^2\psi_0(x) = E_0\psi_0(x)$$

for the harmonic oscillator.

$$LS = \frac{-h^2}{8\pi^2\mu}\frac{d}{dx}\left(\frac{d}{dx}\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}\right) + \frac{1}{2}kx^2\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$

$$= -\frac{h^2}{8\pi^2\mu}\frac{d}{dx}\left(\frac{-2\alpha x}{2}\right)\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} + \frac{1}{2}kx^2\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$

$$= \left(\frac{h^2}{8\pi^2\mu}\right)\left(\frac{\alpha}{\pi}\right)^{1/4}\alpha\left(\frac{d}{dx}x e^{-\alpha x^2/2}\right) + \frac{1}{2}kx^2\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$

$$= \frac{h^2}{8\pi^2\mu}\left(\frac{\alpha}{\pi}\right)^{1/4}\alpha\left(x\left(-\frac{\alpha 2x}{2}\right)+1\right)e^{-\alpha x^2/2} + \frac{1}{2}kx^2\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$

$$= \left[\frac{h^2}{8\pi^2\mu}\left(-\alpha^2x^2+\alpha\right) + \frac{1}{2}kx^2\right]\overbrace{\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}}^{\psi_0(x)}$$

$$= \left[\cancel{\frac{-h^2}{8\pi^2\mu}\frac{4\pi^2}{h^2}k\mu x^2} + \frac{h^2}{8\pi^2\mu}\frac{2\pi}{h}\sqrt{k\mu} \cancel{+\frac{1}{2}kx^2}\right]\psi_0(x)$$

$$LS = \frac{h}{4\pi}\sqrt{\frac{k}{\mu}}\,\psi_0(x)$$

verify $\hat{H}\psi_0 = E_0\psi_0$

b) $LS = \hat{H}\psi_0(x)$ $\qquad\qquad$ $RS = E_0\psi_0(x)$

$$= \underbrace{\frac{h}{4\pi}\sqrt{\frac{k}{\mu}}}_{\substack{\text{eigenvalue} \\ E_0}}\psi_0(x)$$

ground state oscillator energy $E_0 = \frac{h}{4\pi}\sqrt{\frac{k}{\mu}}$

Q4 a) Why is the average linear momentum of a harmonic oscillator zero?

Half the time the displacement is increasing

$v_x > 0$ $\qquad$ $p_x > 0$

but half the time the displacement is decreasing

$v_x < 0$ $\qquad$ $p_x < 0$ $\qquad$ (if ψ is odd, $\frac{d\psi}{dx}$ is even; if ψ is even, $\frac{d\psi}{dx}$ is odd)

averaging to $\langle p_x \rangle = 0$

b) $$\langle p_x \rangle = \int_{-\infty}^{\infty} \psi^*(x)\,\hat{p}_x\,\psi(x)\,dx = \int_{-\infty}^{\infty} \psi(x)\,\frac{-ih}{2\pi}\frac{d}{dx}\psi(x)\,dx$$

$$= \frac{-ih}{2\pi}\int_{-\infty}^{\infty} \psi(x)\frac{d\psi(x)}{dx}\,dx$$

$$= -\frac{ih}{2\pi}\int_{-\infty}^{\infty}(\text{odd})(\text{even})\,dx \quad \text{or} \quad -\frac{ih}{2\pi}\int_{-\infty}^{\infty}\text{even odd}\,dx$$

$$= 0 \qquad\qquad = 0$$

Q5 The average squared momentum of a quantum harmonic oscillator is

$$\langle p_x^2 \rangle = \frac{h}{2\pi}\sqrt{\mu k}\,(n+\tfrac{1}{2})$$

the average kinetic energy

$$\langle T \rangle = \langle \tfrac{1}{2}\mu v_x^2 \rangle = \tfrac{1}{2}\mu\langle v_x^2 \rangle$$

$$= \frac{1}{2}\left\langle \frac{\mu^2 v_x^2}{\mu} \right\rangle$$

$$= \frac{1}{2}\frac{\langle p_x^2 \rangle}{\mu}$$

$$= \frac{1}{2}\,\frac{h}{2\pi}\,\frac{\sqrt{\mu k}\,(n+\frac{1}{2})}{\mu}$$

$$= \frac{1}{2}\,\frac{h}{2\pi}\sqrt{\frac{k}{\mu}}\,(n+\tfrac{1}{2})$$

$$\langle T \rangle = \frac{1}{2}E_n$$

Similarly, the average potential energy is

$$\langle V \rangle = \tfrac{1}{2}k\langle x^2 \rangle = \tfrac{1}{2}E_n$$