

Q1. Use the properties of **even and odd wave functions** to prove:

- [2] a) the average momentum of a harmonic oscillator is zero ( $\langle p_x \rangle = 0$ );  
 b) the average squared momentum of a harmonic oscillator is not zero ( $\langle p_x^2 \rangle \neq 0$ ).

Q2. For a quantum mechanical harmonic oscillator

$$\langle x \rangle = 0 \qquad \langle x^2 \rangle = \frac{\hbar}{\sqrt{\mu k}} \left( n + \frac{1}{2} \right) \qquad \langle p_x \rangle = 0 \qquad \langle p_x^2 \rangle = \hbar \sqrt{\mu k} \left( n + \frac{1}{2} \right)$$

Use this information to prove: a) the Uncertainty Principle is obeyed;

- [3] b) the average kinetic energy of the oscillator is one half of its total energy ( $\langle T \rangle = E_n/2$ );  
 c) the average potential energy of the oscillator is one half of its total energy ( $\langle V \rangle = E_n/2$ ).

*Hint:* the energy of the oscillator is  $E_n = \hbar \sqrt{\frac{k}{\mu}} \left( n + \frac{1}{2} \right) \qquad n = 0, 1, 2, 3, \dots$

Q3. a) A scale for weighing fish consists of a spring attached to a pointer. A fish hung on the spring stretches the spring. The position of the pointer indicates the weight of the fish. A 15-pound striped bass stretches the spring by 1.60 inches. Calculate the spring constant  $k$  in  $\text{N m}^{-1}$ . *Data:*  $g = 9.81 \text{ m s}^{-2}$ .

[3] b) The fundamental vibration frequency  $\nu$  of  $\text{H}_2$  molecules is  $4330 \text{ cm}^{-1}$ . Calculate the force constant of the H-H bond. How does it compare to the spring constant of the fish scale?

Q4. a) Why would you expect  $\text{H}_2$  and  $\text{D}_2$  molecules to have nearly identical force constants?

[2] b) Use the fundamental vibration frequency of  $\text{H}_2$  ( $\nu = 4330 \text{ cm}^{-1}$ ) to predict  $\nu$  for  $\text{D}_2$ .

Q5. a) *But wait!*  $\text{H}_2$  molecules mentioned in Q2 are *not IR active*. Why?

b) Does this mean  $\text{H}_2$  molecules do not vibrate at IR frequencies? Explain.

[3] c) If  $\text{H}_2$  molecules are not IR active, how can their vibration frequencies be measured?

Q6. a) Molecules, unlike classical oscillators, do not have definite vibration amplitudes. Why?

b)  $\sigma_x$  can be used to estimate vibration amplitudes. Calculate  $\sigma_x$  for ground-state  $\text{H}_2$  molecules.

[3] c) Compare the standard deviation of the vibration displacement to the  $\text{H}_2$  bond length (0.097 nm).

- Q7.** The IR spectrum for CO shows a strong absorption at  $2143\text{ cm}^{-1}$  and a weak absorption at  $4260\text{ cm}^{-1}$ .
- a)** About 1% of naturally-occurring carbon is the  $^{13}\text{C}$  isotope. Is the weak absorption at  $4260\text{ cm}^{-1}$  caused by  $^{13}\text{CO}$ ? Justify your answer.
  - b)** The treatment of IR spectra developed in class predicts one IR absorption for  $^{12}\text{CO}$ . Why are two absorptions observed?
- [4] **c)** Why is the absorption at  $4260\text{ cm}^{-1}$  relatively weak?
- d)** The frequency of the weak absorption is about twice that of the stronger absorption. Explain.

(Q1) a) average oscillator momentum:

$$\langle P_x \rangle = \int_{-\infty}^{\infty} \Psi_n^*(x) \hat{P}_x \Psi_n(x) dx$$

( $\Psi_n$  is real,  
so  $\Psi_n^* = \Psi_n$ )

$$= \int_{-\infty}^{\infty} \Psi_n(x) \left(-i\hbar \frac{\partial}{\partial x}\right) \Psi_n(x) dx$$

(if  $\Psi_n$  is even  
then  $\partial\Psi_n/\partial x$  is odd,  
and vice versa)

$$= -i\hbar \int_{-\infty}^{\infty} \Psi_n(x) \frac{\partial \Psi_n(x)}{\partial x} dx$$

$$= i\hbar \int_{-\infty}^{\infty} (\text{even})(\text{odd}) dx \quad \text{or} \quad i\hbar \int_{-\infty}^{\infty} (\text{odd})(\text{even}) dx$$

$$= 0$$

b) average squared momentum

$$\langle P_x^2 \rangle = \int_{-\infty}^{\infty} \Psi_n^*(x) \hat{P}_x^2 \Psi_n(x) dx$$

$$= -\hbar^2 \int_{-\infty}^{\infty} \Psi_n(x) \frac{\partial}{\partial x} \frac{\partial}{\partial x} \Psi_n(x) dx$$

$$= -\hbar^2 \int_{-\infty}^{\infty} (\text{even})(\text{even}) dx$$

$$= -\hbar^2 \int_{-\infty}^{\infty} (\text{odd})(\text{odd}) dx$$

$$\neq 0$$

$$\left( \begin{aligned} \hat{P}_x^2 &= \hat{P}_x \hat{P}_x \\ &= \left(i\hbar \frac{\partial}{\partial x}\right) \left(-i\hbar \frac{\partial}{\partial x}\right) \\ &= i^2 \hbar^2 \frac{\partial}{\partial x} \frac{\partial}{\partial x} \\ &= -\hbar^2 \frac{\partial}{\partial x} \frac{\partial}{\partial x} \end{aligned} \right)$$

(Q1 b cont)

Why? If  $\psi_n$  is even =

$$\frac{\partial}{\partial x} \left( \frac{\partial}{\partial x} \text{even} \right) = \frac{\partial}{\partial x} (\text{odd}) = \text{even}$$

if  $\psi_n$  is odd :

$$\frac{\partial}{\partial x} \left( \frac{\partial}{\partial x} \text{odd} \right) = \frac{\partial}{\partial x} (\text{even}) = \text{odd}$$

$\frac{\partial}{\partial x} \frac{\partial}{\partial x}$  shifts  
the symmetry  
of  $\psi_n$  twice,  
returning the  
original  
symmetry

(Q2) a)  $\sigma_x = \sqrt{\langle x^2 \rangle - \cancel{\langle x \rangle^2} \rightarrow 0}$

$$= \sqrt{\frac{\hbar}{\mu k} \left( n + \frac{1}{2} \right)}$$

$$\sigma_{p_x} = \sqrt{\langle p_x^2 \rangle - \cancel{\langle p_x \rangle^2} \rightarrow 0}$$
$$= \sqrt{\hbar \mu k \left( n + \frac{1}{2} \right)}$$

$$\sigma_x \sigma_{p_x} = \sqrt{\frac{\hbar}{\mu k} \left( n + \frac{1}{2} \right)} \sqrt{\hbar \mu k \left( n + \frac{1}{2} \right)}$$

$$\sigma_{p_x} \sigma_x = \hbar \left( n + \frac{1}{2} \right)$$

$$n = 0, 1, 2, \dots$$

$$\sigma_x \sigma_{p_x} \geq \frac{\hbar}{2}$$

Uncertainty Principle obeyed

(Q2 cont.)

b) average kinetic energy of the oscillator:  $\langle T \rangle$

classically  $T = \frac{1}{2} \mu v_x^2 = \frac{1}{2} \frac{(\mu v_x)^2}{\mu} = \frac{P_x^2}{2\mu}$

quantum mechanically  $\hat{T} = \frac{\hat{P}_x^2}{2\mu}$

$$\begin{aligned}\langle T \rangle &= \int \psi_n^* \hat{T} \psi_n dx = \int \psi_n^* \frac{\hat{P}_x^2}{2\mu} \psi_n dx \\ &= \frac{1}{2\mu} \int \psi_n^* \hat{P}_x^2 \psi_n dx = \frac{1}{2\mu} \langle P_x^2 \rangle \\ &= \frac{1}{2\mu} \hbar \sqrt{\mu k} \left(n + \frac{1}{2}\right) = \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \left(n + \frac{1}{2}\right) \\ &= \frac{1}{2} E_n \quad (\text{same result for classical oscillators})\end{aligned}$$

c) average potential energy  $\langle V \rangle$

$$\begin{aligned}\langle V \rangle &= \int \psi_n^* \hat{V} \psi_n dx \quad (\hat{V} = V = \frac{k}{2} x^2) \\ &= \int \psi_n^* V \psi_n dx = \int \psi_n^* \frac{1}{2} k x^2 \psi_n dx \\ &= \frac{1}{2} k \int \psi_n^* x^2 \psi_n dx = \frac{1}{2} k \langle x^2 \rangle \\ &= \frac{1}{2} k \frac{\hbar}{\sqrt{\mu k}} \left(n + \frac{1}{2}\right) = \frac{1}{2} E_n\end{aligned}$$

(Q3) a) A 15 lb fish stretched the spring by  $x = 1.60$  inches

conversion factors: 1 lb = weight of 0.454 kg

1 inch = 0.0254 m

Hooke's law Force =  $-kx$

$$\text{force constant } k = \frac{|\text{Force}|}{|\text{displacement}|} = \frac{mg}{x}$$

$$= \frac{15 (0.454 \text{ kg}) (9.81 \text{ m s}^{-2})}{(1.60 \text{ in}) (0.0254 \text{ m in}^{-1})}$$

$$k = 1650 \text{ N m}^{-1}$$

b) fundamental vibration frequency of  $\text{H}_2$

$$\tilde{\nu} = 4330 \text{ cm}^{-1} = \frac{\nu}{c}$$

$$\nu = c \tilde{\nu} = (2.998 \times 10^{10} \text{ cm s}^{-1}) (4330 \text{ cm}^{-1})$$

$$\nu = 1.298 \times 10^{14} \text{ s}^{-1}$$

$$\text{reduced mass } \mu = \frac{m_p m_p}{m_p + m_p} = \frac{m_p}{2} = 0.8363 \times 10^{-27} \text{ kg}$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \Rightarrow k = (2\pi\nu)^2 \mu = 556.2 \text{ N m}^{-1}$$

c) The force constant of a tiny  $\text{H}_2$  molecule is  $\approx \frac{1}{3}$  as large as that of the macroscopic fish scale!

(Q4) a) Adding neutrons (zero electric charge) to the nuclei of  $H_2$  molecules produces almost no change in the electron density of  $D_2$  molecules, and therefore almost no change in the bond strength or length.

$$\text{So } k_{H_2} \approx k_{D_2}$$

$$\begin{aligned}
 \text{b) } \frac{\nu_{D_2}}{\nu_{H_2}} &= \frac{\frac{1}{2\pi} \sqrt{\frac{k_{D_2}}{\mu_{D_2}}}}{\frac{1}{2\pi} \sqrt{\frac{k_{H_2}}{\mu_{H_2}}}} = \sqrt{\frac{\mu_{H_2}}{\mu_{D_2}}} \\
 &= \sqrt{\frac{\frac{m_p m_p}{m_p + m_p}}{\frac{m_D m_D}{m_D + m_D}}} = \frac{m_p}{m_D} \sqrt{\frac{m_D}{m_p}} = \sqrt{\frac{m_p}{m_D}}
 \end{aligned}$$

$$\nu_{D_2} = \sqrt{\frac{m_p}{m_D}} \nu_{H_2}$$

$$\tilde{\nu}_{D_2} = \sqrt{\frac{m_p}{m_D}} \tilde{\nu}_H$$

$$\tilde{\nu}_{D_2} = \sqrt{\frac{1.673 \times 10^{-27} \text{ kg}}{3.344 \times 10^{-27} \text{ kg}}} 4330 \text{ cm}^{-1}$$

$$\boxed{\tilde{\nu}_{D_2} = 3063 \text{ cm}^{-1}}$$

(Q5)

a)  $H_2$  molecules are not IR active because the vibration of  $H_2$  produces no electric dipole moment to interact with the oscillating electric field of IR radiation

b)  $H_2$  molecules are not IR active, but they do vibrate at IR frequencies!

$$\nu_{H_2} = 4330 \text{ cm}^{-1} \text{ (in the IR region)}$$

see Q4

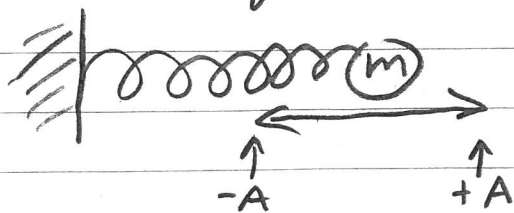
c)  $H_2$  molecules do not absorb IR radiation (why?  $H_2$  vibration produces no dipole moment to interact with electromagnetic radiation)

but  $H_2$  vibrations can be measured by using Raman Spectroscopy

or by "exciting"  $H_2$  molecules with ultraviolet radiation, or with electron- $H_2$  molecule collisions in an electric discharge, and measuring the emitted IR radiation

(Q6)

a) a macroscopic classically-vibrating mass has a definite amplitude of vibration  $A$



A microscopic quantum oscillating mass is a spread-out probability wave  $\Rightarrow$  no fixed vibration amplitude



(Q6 cont.)

b) the amplitude of vibrating  $H_2$  molecules is not defined, but the standard deviation of the displacement can be calculated

for ground-state ( $n=0$ ) vibrating  $H_2$  :  
see Q2

$$\sigma_x = \sqrt{\frac{\hbar}{\sqrt{\mu k}} \left(n + \frac{1}{2}\right)} \quad n=0$$

$$= \sqrt{\frac{\hbar}{\sqrt{\mu k}} \frac{1}{2}} = \sqrt{\frac{h}{2\pi} \frac{1}{\sqrt{\mu k}} \frac{1}{2}}$$

using  $\mu = \frac{m_p}{2} = 0.8363 \times 10^{-27} \text{ kg}$  } see Q3  
and  $k = 556 \text{ N m}^{-1}$

$$\sigma_x = \sqrt{\frac{6.626 \times 10^{-34}}{2\pi} \frac{1}{\sqrt{(0.8363 \times 10^{-27})(556)}} \frac{1}{2}} \quad \left. \vphantom{\frac{6.626 \times 10^{-34}}{2\pi}} \right\} \begin{array}{l} \text{all} \\ \text{SI} \\ \text{units} \end{array}$$

$$\sigma_x = 0.879 \times 10^{-12} \text{ m} = 0.00879 \text{ nm}$$

c)  $\sigma_x$ , the standard deviation of the displacement of vibrating ground-state  $H_2$  molecules is  $\frac{0.00879 \text{ nm}}{0.097} 100\%$   
= 9.06% of the  $H_2$  bond length

Q7

CO has a strong IR absorption at  $2143 \text{ cm}^{-1}$ , and a weak absorption at  $4260 \text{ cm}^{-1}$

a) Is the weak absorption for  $^{13}\text{CO}$ ?

No The slightly heavier  $^{13}\text{CO}$  molecule

has a slightly larger reduced mass, that

would decrease its vibrational frequency

b) The analysis of molecular vibrations in class is based on harmonic oscillators. This is a very good approximation for molecules, but not 100% accurate, so some deviation from harmonic oscillation is expected for real molecules.

harmonic oscillator  $\Delta n = \underline{+1}$  only for absorption

real diatomic oscillator (not quite harmonic)  $\Delta n = +1$ , but non-harmonic absorptions for  $\Delta n = +2$ ,  $\Delta n = 3$ , possible

c) The  $4260 \text{ cm}^{-1}$  is weak because its  $\Delta n = +2$  violates the selection rule  $\Delta n = +1$  for harmonic oscillator

d) The  $4260 \text{ cm}^{-1}$  "overtone" absorption for  $n=0$  to  $n=2$  is approximately twice the frequency of the  $n=0$  to  $n=1$  absorption