Chemistry 331 **Tutorial #5**

1. **a)** Use the definitions of the center of mass X_{CM} and the internuclear separation distance r

$$X_{CM} = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}$$

$$r = x_2 - x_1$$

to derive the kinetic energy expression

$$T = \frac{1}{2}(m_1 + m_2)\left(\frac{\mathrm{d}X_{CM}}{\mathrm{d}t}\right)^2 + \frac{1}{2}\frac{m_1 m_2}{m_1 + m_2}\left(\frac{\mathrm{d}r}{\mathrm{d}t}\right)^2$$

for a diatomic harmonic oscillator.

b) Why can the first term in expression for T be ignored if only vibrational kinetic energy is considered?

2. **a)** The motion of a classical harmonic oscillator with amplitude A and angular frequency ω is described by

$$x(t) = A\sin(\omega t)$$

Show that the equation for $x(t)$ obeys the second-order differential equation

$$\mu \frac{\mathrm{d}^2 x}{\mathrm{d}t^2} = -kx$$

k is the force constant k, μ is the reduced mass, and $\omega = (k/\mu)^{1/2}$.

b) Derive expressions for the kinetic energy $T(t)$ and potential energy $V(t)$ of the oscillator. $V(t)$ reaches its maximum value when $T(t)$ is at a minimum, and *vice versa*. Where? Why?

c) Show that the total energy of the oscillator is conserved and equal to $E = kA^2/2$.

d) Show that the average values of T and V are each one half of the total energy.

$$\langle T \rangle = E/2 \qquad \langle V \rangle = E/2.$$

3. **a)** The fundamental vibration frequency of the H_2 molecule, in units of wavenumbers, is 4159 cm^{-1}. Calculate the force constant k for the H–H bond.

b) A one-pound force (4.54 N) extends the spring in a fish-weighing scale by 2.00 cm. Which has a larger force constant, the fish scale or the H–H bond? Does this result seem reasonable?

c) To illustrate an important isotope effect, calculate the fundamental vibration frequency for the D_2 molecule. Assume that D atoms have twice the mass of H atoms. It is an excellent approximation to assume that H_2 and D_2 molecules have identical force constants. Why?

4. Use the definite integrals

$$\int_0^\infty \exp(-bx^2)\mathrm{d}x = \sqrt{\frac{\pi}{4b}} \qquad \int_0^\infty x^2\exp(-bx^2)\mathrm{d}x = \frac{1}{4b}\sqrt{\frac{\pi}{b}}$$

to verify that the wave functions $\psi_0(x)$ and $\psi_1(x)$ for the harmonic oscillator

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4}\exp\left(-\frac{\alpha x^2}{2}\right) \qquad \psi_1(x) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x\exp\left(-\frac{\alpha x^2}{2}\right)$$

are orthogonal and normalized.

5. Prove that $<x>$ and $<p_x>$ are both zero for a harmonic oscillator. Does this make sense?

6. **a)** The average values of $<x^2>$ for an oscillator with $n = 0$ and $n = 1$ are

$$<x^2> = \int_{-\infty}^{\infty}\psi_0^*(x)x^2\psi(x)\mathrm{d}x = \frac{1}{2\alpha} = \frac{1}{2}\frac{h}{2\pi\sqrt{\mu k}} \qquad n = 0$$

$$<x^2> = \int_{-\infty}^{\infty}\psi_1^*(x)x^2\psi_1(x)\mathrm{d}x = \frac{3}{2\alpha} = \frac{3}{2}\frac{h}{2\pi\sqrt{\mu k}} \qquad n = 1$$

Use this information to conjecture the expression for $<x^2>$ for arbitrary values of n.

b) The average values of $<p_x^2>$ for an oscillator with $n = 0$ and $n = 1$ are

$$<p_x^2> = \int_{-\infty}^{\infty}\psi_0^*(x)p_x^2\psi(x)\mathrm{d}x = \frac{1}{2}\frac{h^2\alpha}{4\pi^2} = \frac{1}{2}\frac{h\sqrt{\mu k}}{2\pi} \qquad n = 0$$

$$< p_x^2 >= \int_{-\infty}^{\infty} \psi_1^*(x) p_x^2 \psi_1(x) \mathrm{d}x = \frac{3}{2} \frac{h^2 \alpha}{4\pi^2} = \frac{3}{2} \frac{h\sqrt{\mu k}}{2\pi} \qquad n = 1$$

Use this information to conjecture the correct expression for $<p_x^2>$ for arbitrary values of n.

c) Use the results from parts **a** and **b** to show that the harmonic oscillator obeys the uncertainty principle

$$\sigma_x \sigma_{px} \geq h/4\pi$$

(Recall that $\sigma_a^2 = <a^2> - <a>^2$.)

7. To learn about the typical vibrational amplitudes of diatomic molecules, calculate the standard deviation σ_x for H_2 in its ground state. For comparison, the H_2 bond length is about 0.1 nm.

8. The energy of a harmonic oscillator in its ground state is $(h/2\pi)(k/\mu)^{1/2}$. The greatest displacement a classical harmonic oscillator can have is its amplitude A, where all of its energy is potential energy, and therefore

$$\frac{kA^2}{2} = \frac{h}{4\pi}\sqrt{\frac{k}{\mu}}$$

The classical turning points are therefore

$$A = \sqrt{\frac{h}{\sqrt{k\mu}}}$$

Show that there is a nonzero probability that a quantum mechanical oscillator in its ground state can exceed the classical amplitude of vibration. Is this barrier tunneling or barrier penetration?

9. **a)** A compact and useful definition of the Hermite polynomials is

$$H_n(\xi) = (-1)^n \exp(\xi^2) \frac{\mathrm{d}^n}{\mathrm{d}\xi^n} \exp(-\xi^2)$$

Generate the expressions for $H_0(\zeta)$, $H_1(\zeta)$, and $H_2(\zeta)$

b) Use this definition to prove the recursion relation

$$H_{n+1}(\xi) = 2\xi H_n(\xi) - \frac{\mathrm{d}H_n(\xi)}{\mathrm{d}\xi})$$

which can be used to generate one Hermite polynomial from another.

10. **a)** Show that the commuter between the linear momentum and position is

$$[\hat{p}_x, \hat{x}] = -i\frac{h}{2\pi}$$

which becomes

$$[\hat{p}, \hat{q}] = -i$$

in terms of the dimensionless momentum and position defined as

$$\hat{p} = -i\frac{\mathrm{d}}{\mathrm{d}q} \qquad \hat{q} = \sqrt{\frac{\mu\omega}{h/2\pi}}\,\hat{x}$$

11. For the dimensionless operators defined as

$$\hat{a} = \frac{1}{\sqrt{2}}(\hat{q} + i\hat{p}) \qquad \hat{a}^+ = \frac{1}{\sqrt{2}}(\hat{q} - i\hat{p}) \qquad \hat{H} = \frac{\hat{p}^2 + \hat{q}^2}{2}$$

prove the following relations

$$[\hat{a}, \hat{a}^+] = 1 \qquad \hat{a}\hat{a}^+ = \hat{H} + \frac{1}{2}$$

$$\hat{a}^+\hat{a} = \hat{H} - \frac{1}{2} \qquad \hat{H} = \frac{1}{2}(\hat{a}\hat{a}^+ + \hat{a}^+\hat{a})$$

$$[\hat{a}, \hat{H}] = \hat{a} \qquad [\hat{a}^+, \hat{H}] = -\hat{a}^+$$

12. {*Optional!*}Place the 16 letters of the alphabet listed below into the 4 by 4 array, obeying the following requirements:

A is not next to P.

B is immediately below P.

C touches L.

D is in the lowest row.

E touches N.

F is immediately to the left of D.

G is the only letter above E.

H is in the lowest row.

I forms a 2 by 2 square with 3 other vowels.

J is in the top row.

K is between L and F.

L is immediately to the right of A.

M is in a corner, under O.

N is immediately to the left of J.

O is in the leftmost column.

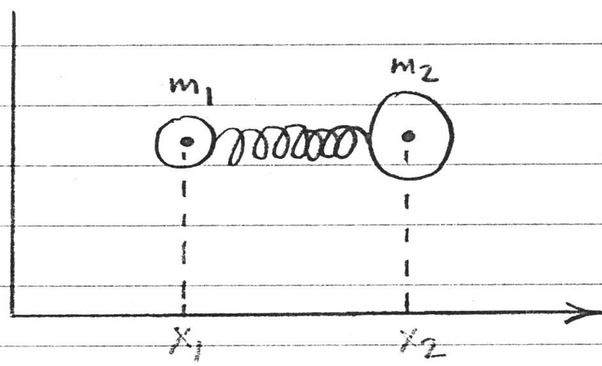
P is in a corner.

Chemistry 331 Tutorial #5

(1.) a) The differential equations describing a classical diatomic harmonic oscillator are

$$m_1 \frac{d^2 x_1}{dt^2} = k(x_2 - x_1 - R_0) \qquad (\mathrm{I})$$

$$m_2 \frac{d^2 x_2}{dt^2} = -k(x_2 - x_1 - R_0) \qquad (\mathrm{II})$$



If $x_2 - x_1 > R_0$, the spring is stretched beyond the equilibrium distance R_0, so the force on m_1 is to the right and the force on m_2 is to the left.

Adding the two equations $(\mathrm{I} + \mathrm{II})$

$$m_1 \frac{d^2 x_1}{dt^2} + m_2 \frac{d^2 x_2}{dt^2} = 0 \quad \text{or} \quad \frac{d^2}{dt^2}(m_1 x_1 + m_2 x_2) = 0$$

which suggests we introduce the center-of-mass coordinate

$$X_{CM} = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}$$

and therefore $$\frac{d^2 X_{cm}}{dt^2} = 0$$

This result tells us that the center of mass moves uniformly with time (no acceleration!) with constant velocity $\frac{dX_m}{dt}$ and the corresponding kinetic energy $T_{CM} = \frac{m_1 + m_2}{2}\left(\frac{dX_{cm}}{dt}\right)$

(1 a) cont.)

Subtracting equation I from II:

$$m_2 \frac{d^2x_2}{dt^2} - m_1 \frac{d^2x_1}{dt^2} = -k(x_2 - x_1 - R_0) - k(x_1 - x_2 - R_0)$$

or

$$\frac{d^2x_2}{dt^2} - \frac{d^2x_1}{dt^2} = -\frac{k}{m_2}(x_2 - x_1 - R_0) - \frac{k}{m_1}(x_1 - x_2 - R_0)$$

$$\frac{d^2}{dt^2}(x_2 - x_1) = -k\left(\frac{1}{m_2} + \frac{1}{m_1}\right)(x_2 - x_1 - R_0)$$

Notice $\frac{1}{m_1} + \frac{1}{m_2} = \frac{m_2 + m_1}{m_1 m_2} = \frac{1}{\mu}$ (μ is the reduced mass)

Defining $r(t) = x_2 - x_1$ (internuclear distance)

gives $\frac{d^2r}{dt^2} = -\frac{k}{\mu}(r - R_0)$ for the vibration of reduced mass μ

Important: We have reduced a two-body problem (eqs. I + II for the motion of masses m_1 and m_2) to a one-body problem (equivalent to the vibration of reduced mass μ.

The total kinetic energy of the harmonic oscillator is

$$T = \underbrace{\frac{1}{2}(m_1 + m_2)\left(\frac{dX_{cm}}{dt}\right)^2}_{\text{(from the motion of the center of mass)}} + \underbrace{\frac{1}{2}\mu\left(\frac{dr}{dt}\right)^2}_{\text{(from vibration of } \mu)}$$

b) the first term is the kinetic energy from the uniform motion of the center of mass of the oscillator → nothing to do with vibration

2. a) $x(t) = A\sin(\omega t)$ $\qquad \mu \dfrac{d^2x}{dt^2} = \mu \dfrac{d}{dt}\left[\dfrac{d}{dt} A\sin(\omega t)\right]$

$$\mu \frac{d^2x}{dt^2} = \mu \frac{d}{dt}\left[A\omega\cos(\omega t)\right] = -\mu A\omega^2 \sin(\omega t) = -\mu\omega^2 x$$

$$= -kx$$

$$\omega^2 = \frac{k}{\mu} \qquad \omega = \sqrt{\frac{k}{\mu}}$$

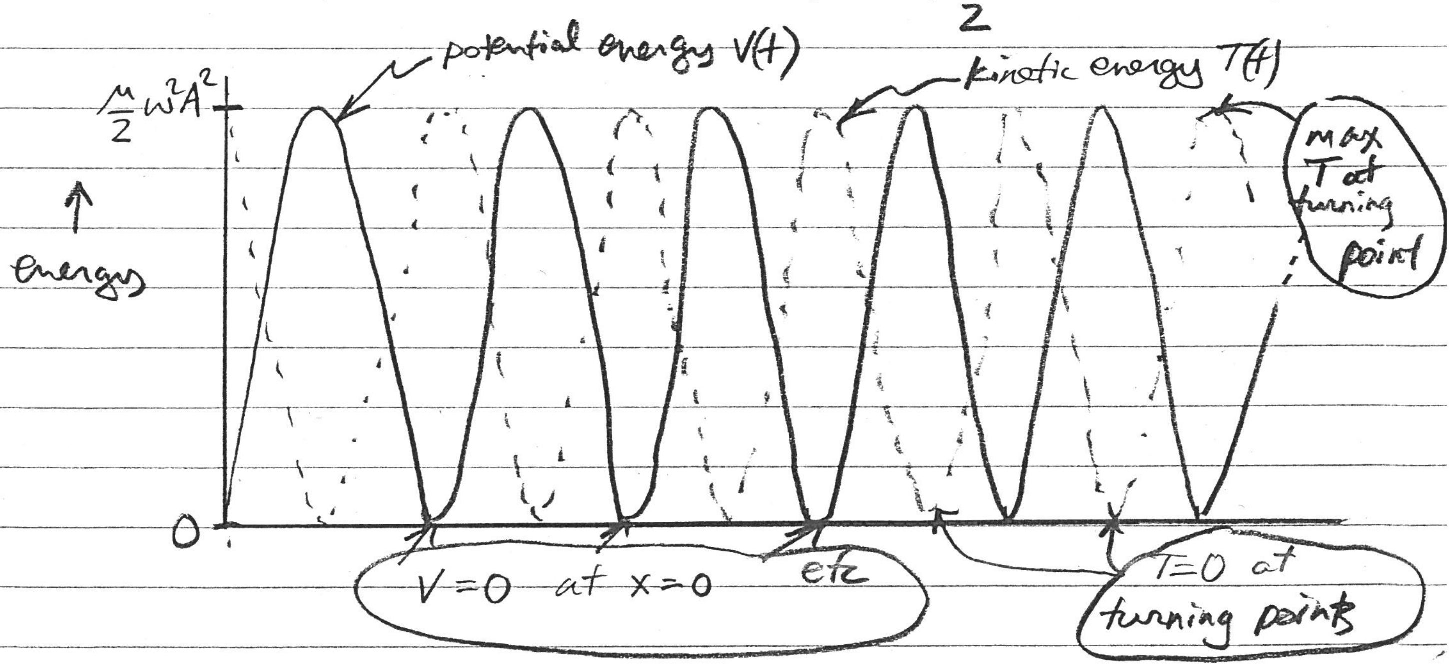
b) kinetic energy $T = \frac{1}{2}\mu\left(\frac{dx}{dt}\right)^2 = \frac{\mu}{2}\left[\frac{d}{dt} A\sin(\omega t)\right]^2$

$$T(t) = \frac{\mu}{2}\left[\omega A\cos(\omega t)\right]^2 = \frac{\mu}{2}\omega^2 A^2 \cos^2(\omega t)$$

The potential energy of the oscillator is the negative integral of the force $-kx$ over the distance x (force $= 0$ at $x = 0$)

$$V(t) = -\int_0^x (-kx)\,dx = \frac{kx^2}{2} = \frac{k}{2}A^2\sin^2(\omega t)$$

but $k = \mu\omega^2$ so $\quad V(t) = \frac{\mu}{2}\omega^2 A^2 \sin^2(\omega t)$



(2 cont.)

c) from trigonometry, $\sin^2\theta + \cos^2\theta = 1$

total energy $E(t) = T(t) + V(t) = \frac{\mu}{2}\omega^2 A^2 \cos^2(\omega t) + \frac{\mu}{2}\omega^2 A s \sin^2(\omega t)$

$$E(t) = \frac{\mu}{2}\omega^2 A^2 \qquad \text{but } \mu\omega^2 = k$$

$$\boxed{E(t) = \frac{k}{2}A^2}$$ constant vibrational energy

d) To find the average potential energy, average $V(t)$ over one cycle, e.g., from $\omega t = 0$ to $\omega t = 2\pi$

$$\langle V(t)\rangle = \frac{1}{2\pi}\int_{\omega t=0}^{\omega t=2\pi} V(t)\, d(\omega t) = \frac{1}{2\pi}\int_0^{2\pi} \frac{kA^2}{2}\sin^2(\omega t)\, d(\omega t)$$

from a Table of integrals $\int_0^a \sin^2\left(\frac{n\pi y}{a}\right) dy = \frac{a}{2}$

use $n=1$ $y=\omega t$ $a=\pi$

so $$\langle V(t)\rangle = \frac{kA^2/2}{2\pi}\,\frac{\pi}{2} = \frac{1}{2}\frac{kA^2}{2}$$

$$\langle V(t)\rangle = \langle E(t)\rangle / 2$$

$$\langle V(t)\rangle + \langle T(t)\rangle = kA^2/2 \qquad \text{so } \langle T(t)\rangle = \frac{1}{2}\frac{kA^2}{2}$$

3.) The fundamental vibration frequency for the H_2 molecule is $\nu = 4159\ \text{cm}^{-1} = \frac{\omega}{2\pi}$ $\quad \mu = \frac{m_1 m_2}{m_1 + m_2}$

$m_1 = m_2 =$ proton mass

(3 cont.)

$\lambda \nu = c \qquad \frac{1}{\lambda} = \frac{\nu}{c} \qquad \nu = \frac{c}{\lambda}$

use

$$\omega = \sqrt{\frac{k}{\mu}} \quad \text{or} \quad \nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad k = \mu(2\pi\nu)^2$$

$$k = \frac{m_p m_p}{m_p + m_p}(2\pi\nu)^2 = \frac{m_p}{2}(2\pi\nu)^2 = \frac{m_p}{2}\left(2\pi\frac{c}{\lambda}\right)^2$$

$$k = \frac{1.673\times10^{-27}\,kg}{2}\left(2\pi\ 2.998\times10^{8}\,\frac{m}{s}\ 4159\ cm^{-1}\ 100\,\frac{cm}{m}\right)^2$$

$$k = 513.4\ \frac{N}{m}$$

b) For the fish-scale spring $k = \frac{4.54\ N}{0.02\ m} = 227\ \frac{N}{m}$

The hydrogen bond is approximately twice as "stiff" as the fish-scale spring!

c) Adding a neutron to each nucleus approximately doubles the nuclear masses of D_2 relative to H_2, but has almost no effect on the electronic structure (neutrons have no charge). The D–D bond is therefore ~~just~~ about exactly as "stiff" as the H_2 bond, and the same force constant applies.
$(k_{D_2} \cong k_{H_2})$

$$\mu_{D_2} = \frac{(2m_p)(2m_p)}{(2m_p)+(2m_p)} = 2\,\frac{m_p m_p}{m_p + m_p} = 2\mu_{H_2}$$

$$\frac{\nu_{D_2}}{\nu_{H_2}} = \frac{\frac{1}{2\pi}\sqrt{\frac{k_{D_2}}{\mu_{D_2}}}}{\frac{1}{2\pi}\sqrt{\frac{k_{H_2}}{\mu_{H_2}}}} = \sqrt{\frac{\mu_{H_2}}{\mu_{D_2}}}\ \sqrt{\cancelto{1}{\frac{k_{D_2}}{k_{H_2}}}} = \sqrt{\frac{1}{2}}$$

$$\boxed{\nu_{D_2} = \frac{\nu_{H_2}}{\sqrt{2}} = 2941\ cm^{-1}}$$

ψ_0, ψ_1 are real, so $\psi_0^* = \psi_0$ and $\psi_1^* = \psi_1$

4. $$\int_{-\infty}^{\infty} \psi_0^*(x)\,\psi_0(x)\,dx = \left(\frac{\alpha}{\pi}\right)^{1/4}\left(\frac{\alpha}{\pi}\right)^{1/4}\int_{-\infty}^{\infty} \exp\left(-\frac{\alpha x^2}{2}\right)\exp\left(-\frac{\alpha x^2}{2}\right)dx$$

even function

$$= \sqrt{\frac{\alpha}{\pi}}\int_{-\infty}^{\infty} \exp(-\alpha x^2)\,dx = 2\sqrt{\frac{\alpha}{\pi}}\int_{0}^{\infty}\exp(-\alpha x^2)\,dx = 2\sqrt{\frac{\alpha}{\pi}}\sqrt{\frac{\pi}{4\alpha}} = 1$$

$$\int_{-\infty}^{\infty} \psi_1^*(x)\,\psi_1(x)\,dx = \left(\frac{4\alpha^3}{\pi}\right)^{1/4}\left(\frac{4\alpha^3}{\pi}\right)^{1/4}\int_{-\infty}^{\infty} x\exp\left(-\frac{\alpha x^2}{2}\right)x\exp\left(-\frac{\alpha x^2}{2}\right)dx$$

even

$$= \sqrt{\frac{4\alpha^3}{\pi}}\int_{-\infty}^{\infty} x^2\exp(-\alpha x^2)\,dx = 2\sqrt{\frac{4\alpha^3}{\pi}}\int_{0}^{\infty} x^2\exp(-\alpha x^2)\,dx$$

$$= 2\sqrt{\frac{4\alpha^3}{\pi}}\;\frac{1}{4\alpha}\sqrt{\frac{\pi}{\alpha}} = 1$$

ψ_0 and ψ_1 are normalized

orthogonal?

$$\int_{-\infty}^{\infty} \psi_0^*\psi_1\,dx = \int_{-\infty}^{\infty}\left(\frac{\alpha}{\pi}\right)^{1/4}\exp\left(-\frac{\alpha x^2}{2}\right)\left(\frac{4\alpha^3}{\pi}\right)^{1/4} x\exp\left(-\frac{\alpha x^2}{2}\right)dx$$

even

$$= \text{constant}\int_{-\infty}^{\infty} x\exp(-\alpha x^2)\,dx$$

odd

$$= \text{constant}\int_{-\infty}^{\infty}(\text{odd function})(\text{even function})\,dx$$

$$= 0$$

$\psi^*(x) = \psi(x)$ ($\psi(x)$ is real)

5. $$\langle x \rangle = \int_{-\infty}^{\infty} \psi_n^*(x)\,\hat{x}\,\psi_n(x)\,dx = \int_{-\infty}^{\infty} \underbrace{x}_{\text{odd}} \overbrace{\psi_n(x)\,\psi_n(x)}^{\text{even}}\,dx$$

whether $\psi_n(x)$ is even or odd, $\psi_n(x)\,\psi_n(x)$ is always <u>even</u>
(Why? odd odd → even, even · even → even)

$$\langle x \rangle = \int_{-\infty}^{\infty} (\text{odd function})(\text{even function})\,dx = 0$$

$$\langle p_x \rangle = \int_{-\infty}^{\infty} \psi_n^*(x)\,\hat{P}_x\,\psi_n(x)\,dx = \int_{-\infty}^{\infty} \psi_n(x)\left(\frac{-ih}{2\pi}\right)\frac{d}{dx}\psi_n(x)\,dx$$

(if ψ_n is even, then $\frac{d\psi_n}{dx}$ is odd
if ψ_n is odd, then $\frac{d\psi_n}{dx}$ is even)

e.g. $\frac{d\cos x}{dx} = -\sin x$ (even → odd)

$\frac{d\sin x}{dx} = \cos x$

$$\therefore \langle p_x \rangle = \int_{-\infty}^{\infty} \text{odd} \cdot \text{even}\,dx \text{ or } \int_{-\infty}^{\infty} \text{even} \cdot \text{odd}\,dx$$

$$\langle p_x \rangle = 0$$

The oscillator vibrates to the left and right, symmetrically, centered on $x = 0$, and the momentum alternates positive and negative, ⇒ $\langle x \rangle = 0$ and $\langle p_x \rangle = 0$ required

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6. a) $\langle x^2 \rangle_{n=0} = \frac{1}{2}\frac{1}{\alpha}$

$\langle x^2 \rangle_{n=1} = \frac{3}{2}\frac{1}{\alpha}$

b) $\langle p_x^2 \rangle_{n=0} = \frac{1}{2}\frac{h^2\alpha}{4\pi^2}$

$\langle p_x^2 \rangle_{n=1} = \frac{3}{2}\frac{h^2\alpha}{4\pi^2}$

suggests: $\langle x^2 \rangle_n = \left(n+\frac{1}{2}\right)\frac{1}{\alpha}$ $\qquad \langle p_x^2 \rangle_n = \left(n+\frac{1}{2}\right)\frac{h^2\alpha}{4\pi^2}$

(6 cont.)

c) $$\sigma_x \sigma_{p_x} = \sqrt{\sigma_x^2 \sigma_{p_x}^2} = \sqrt{\left(n+\tfrac{1}{2}\right)\tfrac{1}{\alpha}\left(n+\tfrac{1}{2}\right)\tfrac{h^2\alpha}{4\pi^2}}$$

$$\sigma_x \sigma_{p_x} = \left(n+\tfrac{1}{2}\right)\frac{h}{2\pi} \qquad n = 0, 1, 2, 3, \ldots$$

$$\sigma_x \sigma_{p_x} \geq \left(0+\tfrac{1}{2}\right)\frac{h}{2\pi} \qquad \boxed{\sigma_x \sigma_{p_x} \geq \frac{h}{4\pi}}$$

(7.) $$\sigma_x = \sqrt{\sigma_x^2} = \sqrt{\langle x^2\rangle - \langle x\rangle^2} = \sqrt{\left(n+\tfrac{1}{2}\right)\tfrac{1}{\alpha} - 0}$$

for $n=0$, $\sigma_x = \sqrt{\dfrac{1}{2\alpha}}$ $\qquad \alpha = \dfrac{\sqrt{k\mu}}{h/2\pi}$

$$\sigma_x = \frac{1}{\sqrt{2}}\frac{1}{\sqrt{\alpha}} = \frac{1}{\sqrt{2}}\frac{\sqrt{h/2\pi}}{(k\mu)^{1/4}} = \frac{1}{\sqrt{2}}\frac{\sqrt{6.634\times10^{-34}/2\pi}}{\left(513.4 \quad \frac{1.673\times10^{-27}}{2}\right)^{1/4}}$$

from problem #3

$$\sigma_x = 8.97\times10^{-12}\ \text{m}$$
$$= 0.00897\ \text{nm}$$

(about 1% of the bond length)

(8.) classical turning points at $x = \pm A = \pm\sqrt{\dfrac{h}{\sqrt{k\mu}}}$

ground state:

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

at the turning points: $\psi_0(\pm A) = \left(\dfrac{\alpha}{\pi}\right)^{1/4} e^{-\frac{\alpha h}{2\sqrt{k\mu}}}$

$\alpha = \dfrac{\sqrt{k\mu}}{h/2\pi}$ $\qquad \psi_0(\pm A) = \left(\dfrac{\alpha}{\pi}\right)^{1/4} e^{-\pi} \neq 0\,!$

$\dfrac{\alpha h}{\sqrt{k\mu}} = 2\pi$ $\qquad$ so $\psi_0^*(\pm A)\psi(\pm A) \neq 0$

take no derivative (0)

9. a) $H_0(\xi) = (-1)^0 e^{\xi^2} \frac{d^0}{d\xi^0} e^{-\xi^2} = (-1)^0 e^{\xi^2 - \xi^2} = 1$

$H_1(\xi) = -1^1 e^{\xi^2} \frac{d}{d\xi} e^{-\xi^2} = -1\, e^{\xi^2} (-2\xi) e^{-\xi^2} = 2\xi$

$H_2(\xi) = (-1)^2 e^{\xi^2} \frac{d^2}{d\xi^2} e^{-\xi^2} = e^{\xi^2} \frac{d}{d\xi}\left(-2\xi e^{-\xi^2}\right)$

$= e^{-\xi^2}\left[(-2\xi)(-2\xi)e^{-\xi^2} + (-2)e^{-\xi^2}\right]$

$H_2(\xi) = 4\xi^2 - 2$

b) take the derivative of

$H_n(\xi) = (-1)^n \exp(\xi^2) \frac{d^n}{d\xi^n} \exp(-\xi^2)$

$\frac{dH_n}{d\xi} = (-1)^n \frac{d}{d\xi}\left[\exp \xi^2 \frac{d^n}{d\xi^n} \exp(-\xi^2)\right]$

$= (-1)^n \left[\exp \xi^2 \frac{d^{n+1}}{d\xi^{n+1}} \exp(-\xi^2) + 2\xi \exp(\xi^2) \frac{d^n}{d\xi^n} \exp(-\xi^2)\right]$

$= \underbrace{\overbrace{(-1)(-1)^n}^{(-1)^{n+1}}}_{(-1)} \exp(\xi^2) \frac{d^{n+1}}{d\xi^{n+1}} \exp(-\xi^2) + 2\xi (-1)^n \exp(\xi^2) \frac{d^2}{d\xi^2} \exp(-\xi^2)$

$\frac{dH_n}{d\xi} = -H_{n+1}(\xi) + 2\xi H_n(\xi) \Rightarrow H_{n+1}(\xi) = -\frac{dH_n(\xi)}{d\xi} + 2H_n(\xi)$

$\hat{x} = x$

(10.) $[\hat{P}_x, \hat{x}] = \hat{P}_x x - x\hat{P}_x$

$$\hat{P}_x(x)xf(x) - x\hat{P}_x f(x) = -\frac{ih}{2\pi}\frac{d}{dx}(xf(x)) - (-x)\frac{ih}{2\pi}\frac{df(x)}{dx}$$

$$= -\frac{ih}{2\pi}\left[\cancel{x\frac{df(x)}{dx}} + f(x)\right] + \cancel{x\frac{ih}{2\pi}\frac{df(x)}{dx}} = -i\frac{h}{2\pi}f(x)$$

$$[\hat{P}, \hat{q}] = \hat{P}\hat{q} - \hat{q}\hat{P}$$

$$\hat{p}\hat{q}f(q) - \hat{q}\hat{p}f(q) = -i\frac{d}{dq}(qf(q)) - q\left(-\frac{i\,df(q)}{dq}\right)$$

$$= -i\left(q\frac{df(q)}{dq} + f(q)\right) + qi\frac{df(q)}{dq} = -if(q)$$

(11.) $[\hat{a}\,\hat{a}^+] = \hat{a}\hat{a}^+ - \hat{a}^+\hat{a}$

$$\hat{a}\hat{a}^+ f(q) - \hat{a}^+\hat{a}f(q) = \hat{a}\frac{1}{\sqrt{2}}(\hat{q} - i\hat{P})f(q) - \hat{a}^+\frac{1}{\sqrt{2}}(\hat{q} + i\hat{P})f(q)$$

$$= \frac{\hat{q} + i\hat{P}}{\sqrt{2}}\frac{\hat{q} - i\hat{P}}{\sqrt{2}}f(q) - \frac{\hat{q} - i\hat{P}}{\sqrt{2}}\frac{\hat{q} + i\hat{P}}{\sqrt{2}}f(q)$$

$$= \frac{\cancel{\hat{q}^2} - \hat{q}i\hat{P} + i\hat{P}\hat{q} - \cancel{i^2\hat{P}^2}}{2}f - \frac{\cancel{\hat{q}^2} + \hat{q}i\hat{P} - i\hat{P}\hat{q} - \cancel{i\hat{P}^2}}{2}f$$

$$= i(\hat{P}\hat{q} - \hat{q}\hat{P})f(q) = i[\hat{P}, \hat{q}]f(q) = i(-i)f(q) = f(q)$$

$$\hat{a}\hat{a}^+ f(q) = f(q) \qquad \hat{a}\hat{a}^+ = 1$$

(11 cont.)

$$\hat{a}\hat{a}^{+} = \frac{1}{\sqrt{2}}(\hat{q}+i\hat{p})\frac{1}{\sqrt{2}}(\hat{q}-i\hat{p}) = \frac{1}{2}(\hat{q}^2 - i\hat{q}\hat{p} + i\hat{p}\hat{q} - i^2\hat{p}^2)$$

$$= \frac{1}{2}(\hat{q}^2 + i[p,q] + \hat{p}^2) = \frac{\hat{q}^2+\hat{p}^2}{2} + \frac{i}{2}(-i)$$

$$= \hat{H} + \frac{1}{2}$$

$$\hat{a}^{+}\hat{a} = \frac{1}{\sqrt{2}}(\hat{q}-i\hat{p})\frac{1}{\sqrt{2}}(\hat{q}+i\hat{p}) = \frac{1}{2}(\hat{q}^2 + i\hat{q}\hat{p} - i\hat{p}\hat{q} - i^2p^2)$$

$$= \frac{1}{2}(q^2+p^2) - \frac{i(\hat{p}\hat{q}-\hat{q}\hat{p})}{2} = H - \frac{i[\hat{p},\hat{q}]}{2}$$

$$= H - \frac{i(-i)}{2} = H - \frac{1}{2}$$

$$\frac{1}{2}(\hat{a}\hat{a}^{+} + \hat{a}^{+}\hat{a}) = \frac{1}{2}\left(\hat{H} + \frac{1}{2} + \hat{H} - \frac{1}{2}\right) = \hat{H}$$

$$[\hat{a},\hat{H}] = \hat{a}\hat{H} - \hat{H}\hat{a} = \hat{a}\,\frac{1}{2}(\hat{a}\hat{a}^{+} + \hat{a}^{+}\hat{a}) - \frac{1}{2}(\hat{a}\hat{a}^{+} + \hat{a}^{+}\hat{a})\,\hat{a}$$

$$= \frac{\hat{a}\hat{a}\hat{a}^{+} + \hat{a}\hat{a}^{+}\hat{a} - \hat{a}\hat{a}^{+}\hat{a} - \hat{a}^{+}\hat{a}\hat{a}}{2}$$

$$= \frac{\hat{a}(\hat{a}\hat{a}^{+} - \hat{a}^{+}\hat{a}) + (\hat{a}\hat{a}^{+} - \hat{a}^{+}\hat{a})\hat{a}}{2}$$

but $[a,a^{+}] = 1$!

$$= \frac{\hat{a}[\hat{a},\hat{a}^{+}] + [\hat{a},\hat{a}^{+}]\hat{a}}{2} = \frac{\hat{a}+\hat{a}}{2} = \hat{a}$$

(11 cont.)

$$[\hat{a}^+, \hat{H}] = \hat{a}^+ \hat{H} - \hat{H} \hat{a}^+$$

$$= \hat{a}^+ \frac{1}{2}(\hat{a}\hat{a}^+ + \hat{a}^+\hat{a}) - \frac{1}{2}(\hat{a}\hat{a}^+ + \hat{a}^+\hat{a})\hat{a}^+$$

$$= \frac{\hat{a}^+\hat{a}\hat{a}^+ + \hat{a}^+\hat{a}^+\hat{a} - \hat{a}\hat{a}^+\hat{a}^+ - \hat{a}^+\hat{a}\hat{a}^+}{2}$$

$$= \frac{(\hat{a}^+\hat{a}\hat{a}^+ - \hat{a}\hat{a}^+\hat{a}^+) + (\hat{a}^+\hat{a}^+\hat{a} - \hat{a}^+\hat{a}\hat{a}^+)}{2}$$

$$= \frac{(\hat{a}^+\hat{a} - \hat{a}\hat{a}^+)\hat{a}^+ + \hat{a}^+(\hat{a}^+\hat{a} - \hat{a}^+\hat{a})}{2}$$

$$= \frac{(-1)\hat{a}^+ + \hat{a}(-1)}{2}$$

$$[a^+, \hat{H}] = -\hat{a}^+$$