QMS Problem Set 2

W7: The zero-point energy of a harmonic oscillator is $E_0 = \frac{1}{2}\hbar\omega = \frac{1}{2}\hbar\sqrt{\frac{k_f}{\mu}}$

Reduced mass (μ)

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad \Big\| \text{ set } m_1 = m_2 = m_{Cl}$$

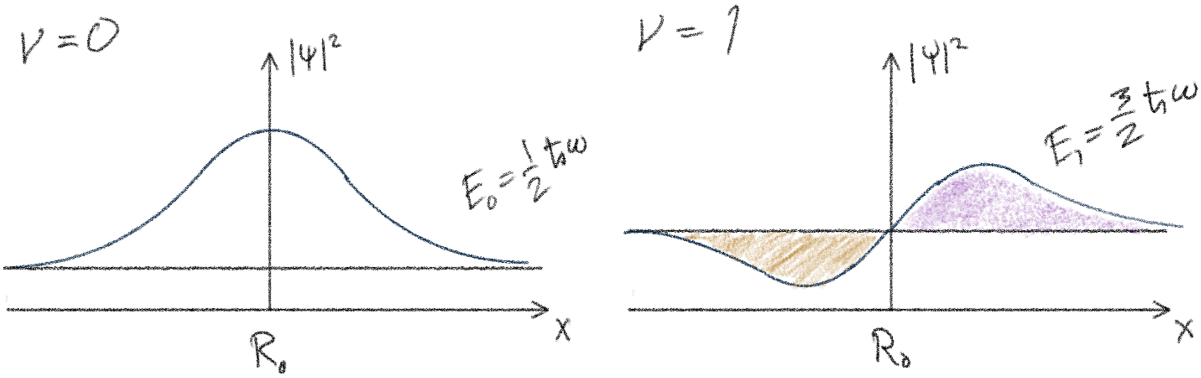
$$\mu = \frac{m_{Cl}^2}{2\,m_{Cl}} = \frac{m_{Cl}}{2} \quad \Big\| \; m_{Cl} = 34.9688 \cdot 1.661 \cdot 10^{-27}\,\text{kg}$$

$$E_0 = \frac{1}{2}\left(1.055 \cdot 10^{-34}\,\text{Js}\right)\sqrt{\frac{2 \cdot 329\,N/m}{34.9688 \cdot 1.661 \cdot 10^{-27}\,\text{kg}}}$$

$$E_0 = 5.614 \ldots \cdot 10^{-21}\,\text{J} \quad \Big\| \cdot N_A$$

$$\Rightarrow E_0 = 3381.045\ldots \approx 3.4\,\frac{\text{kJ}}{\text{mol}}$$

W 2:



The functions corresponding to different eigenvalues of a Hermitian operator are orthogonal.

The product of v=0 and v=1 wavefunctions is similar to v=1 wf but larger amplitude in the middle. The product has equal areas (yellow and purple) on the negative and the positive side and hence the integral $\int_\tau \psi_0^* \psi_1 \, d\tau$ goes to zero.

W3: Transition $v=0 \rightarrow v=1$

a) $\Delta E = E_{photon} = \hbar\omega = \frac{h}{2\pi}\sqrt{\frac{k_f}{\mu}} = h\nu = \frac{hc}{\lambda} = hc\tilde{\nu}$

$\Rightarrow \hbar\omega = \hbar \cdot 2\pi c\tilde{\nu}$

$\omega = 2\pi c\tilde{\nu}$

$\tilde{\nu} = \frac{\omega}{2\pi c}$

b) $\omega_{HCl} = 5.63 \cdot 10^{14} \frac{1}{s}$

$\tilde{\nu} = \frac{5.63 \cdot 10^{14} \frac{1}{s}}{2\pi \cdot 2.998 \cdot 10^{8} \frac{m}{s}}$

$\tilde{\nu} = 298880.0299 \frac{1}{cm}$

$\approx 2989 \frac{1}{cm}$ (Atkins table: $2990.95 \frac{1}{cm}$)

c) $\nu = \frac{1}{2\pi}\sqrt{\frac{k_f}{\mu}} \Leftrightarrow \frac{c}{\lambda} = \frac{1}{2\pi}\sqrt{\frac{k_f}{\mu}} \Leftrightarrow c\tilde{\nu} = \frac{1}{2\pi}\sqrt{\frac{k_f}{\mu}}$

$\Leftrightarrow 2\pi c\tilde{\nu} = \sqrt{\frac{k_f}{\mu}} \Leftrightarrow k_f = \mu(2\pi c\tilde{\nu})^2$

d) For $^{12}C^{16}O$ $\quad \mu = \frac{12 \cdot 16}{12+16} \cdot 1.661 \cdot 10^{-27}\, kg$

$$k_f[^{12}C^{16}O_2] = \mu\left(2\pi \cdot 2.998 \cdot 10^8 \frac{m}{s} \cdot 217000 \frac{1}{m}\right)^2$$

$$= 1903.07\ldots \frac{kg}{s^2} \left[\frac{N}{m}\right]$$

For $^{14}C^{16}O$ $\quad \mu = \frac{14 \cdot 16}{14+16} \cdot 1.661 \cdot 10^{-27}\, kg$

$$\tilde{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k_f}{\mu}} = \frac{1}{2\pi c}\sqrt{\frac{1903.07\ldots \frac{N}{m}}{1.24\ldots \cdot 10^{-26}\, kg}}$$

$$\tilde{\nu} = 207954.32\ldots \frac{1}{m} \approx 2080 \frac{1}{cm}$$

P1: The force constant k_f depends on "the stiffness" of the bond. The bond properties depend on electron and proton charges, not as much on the masses of the atoms.

a) $\omega_{AB} = \sqrt{\dfrac{k_{AB}}{\mu_{AB}}}$ $\omega_{A'B} = \sqrt{\dfrac{k_{A'B}}{\mu_{A'B}}}$

Since $k_{AB} = k_{A'B}$

$$(\omega_{AB})^2 \mu_{AB} = (\omega_{A'B})^2 \mu_{A'B}$$

$$\Rightarrow \omega_{A'B} = \omega_{AB} \sqrt{\frac{\mu_{AB}}{\mu_{A'B}}}$$

b) $\omega_{^1H^{35}Cl} = 5.63 \cdot 10^{14} \frac{1}{s}$

i) $$\omega_{^2H^{35}Cl} = 5.63 \cdot 10^{14} \frac{1}{s} \sqrt{\frac{\frac{1 \cdot 35}{1+35} \cdot 1.661 \cdot 10^{-27} kg}{\frac{2 \cdot 35}{2+35} \cdot 1.661 \cdot 10^{-27} kg}}$$

$$= 4.0359\ldots \cdot 10^{14} \frac{1}{s} \approx 4.04 \cdot 10^{14} \frac{1}{s}$$

ii) $$\omega_{^1H^{37}Cl} = 5.63 \cdot 10^{14} \frac{1}{s} \sqrt{\frac{\frac{1 \cdot 35}{1+35} \cdot 1.661 \cdot 10^{-27} kg}{\frac{1 \cdot 37}{1+37} \cdot 1.661 \cdot 10^{-27} kg}}$$

$$= 5.6257\ldots \cdot 10^{14} \frac{1}{s} \approx 5.63 \cdot 10^{14} \frac{1}{s}$$

P2: a) All probability densities for harmonic oscillator states are symmetrical with respect to $x=0$

Hence the probabilities to finding the particle from $x>0$ or $x<0$ are the same which yields $\langle x \rangle = 0$

b) On any given moment it is equally likely to find the harmonic oscillator to move to the positive or the negative direction which yields $\langle p_x \rangle = 0$

c) We note that $E_{k,v} = \frac{p_v^2}{2m}$ is also the expectation value $\langle E_k \rangle_v = \frac{1}{2} E_v$ since there's no other kinetic energy values for given state v.

From $E_{k,v} = \langle E_k \rangle_v$ we get

$$\frac{p_v^2}{2m} = \frac{1}{2} E_v \qquad \Leftrightarrow \quad p_v^2 = m E_v$$

For quantum mechanical harmonic oscillator

$$E_v = \left(v + \tfrac{1}{2}\right) \hbar \omega$$

Note that p_v^2 is also the expectation value

$$\Rightarrow \langle p_x^2 \rangle_v = m \hbar \omega \left(v + \tfrac{1}{2}\right) \Rightarrow m \hbar \sqrt{\frac{k_f}{m}} \left(v + \tfrac{1}{2}\right)$$

$$\Rightarrow \langle p_x^2 \rangle_v = \left(v + \tfrac{1}{2}\right) \hbar \sqrt{m k_f}$$

d) $\langle x \rangle_v = 0$, $\langle p \rangle_v = 0$,

$$\langle x^2 \rangle_v = \left(v+\frac{1}{2}\right)\frac{\hbar}{\sqrt{mk_f}} \qquad \langle p^2 \rangle_v = \left(v+\frac{1}{2}\right)\hbar\sqrt{mk_f}$$

$$\Delta x = \sqrt{\langle x^2\rangle_v - \langle x\rangle_v^2} \qquad \Delta p = \sqrt{\langle p^2\rangle_v - \langle p\rangle_v^2}$$

$$\Delta x = \sqrt{\left(v+\frac{1}{2}\right)\frac{\hbar}{\sqrt{mk_f}}} \qquad \Delta p = \sqrt{\left(v+\frac{1}{2}\right)\hbar\sqrt{mk_f}}$$

e) $$\Delta x \Delta p = \sqrt{\left(v+\frac{1}{2}\right)\frac{\hbar}{\sqrt{mk_f}}}\sqrt{\left(v+\frac{1}{2}\right)\hbar\sqrt{mk_f}}$$

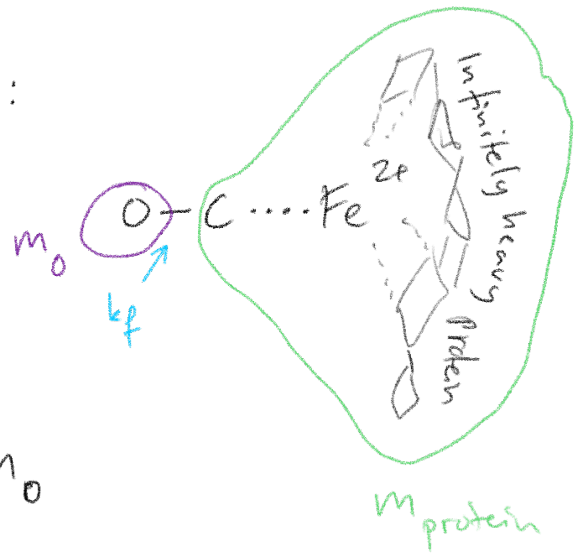
$$\Delta x \Delta p = \sqrt{\left(v+\frac{1}{2}\right)^2\hbar^2\frac{\sqrt{mk_f}}{\sqrt{mk_f}}}$$

$$\Delta x \Delta p = \left(v+\frac{1}{2}\right)\hbar$$

The result satisfies the Heisenberg uncertainty principle because $\left(v+\frac{1}{2}\right)\hbar \geq \frac{\hbar}{2}$ for $v \in [0, \infty]$

f) $\Delta x \Delta p$ in minimum at $v=0$ when $\Delta x \Delta p = \frac{\hbar}{2}$

P3: The system described looks roughly this



Calculate reduced mass:

$$\mu = \frac{m_O m_{protein}}{m_O + m_{protein}}$$

Set $m_{protein} >>>> m_O$

$$\mu \approx \frac{m_O m_{protein}}{m_{protein}} \Rightarrow \mu \approx m_O$$

For $^{12}C^{16}O$ $\tilde{\nu} = 2170 \frac{1}{cm}$

Take formula $\omega_{A'B} = \omega_{AB}\sqrt{\frac{\mu_{AB}}{\mu_{A'B}}}$ from P1

and modify it with $\tilde{\nu} = \frac{\omega}{2\pi c}$ from W3:

$$\tilde{\nu}_{CO\text{-}protein} = \tilde{\nu}_{CO}\sqrt{\frac{\mu_{CO}}{\mu_{CO\text{-}protein}}}$$

$$\tilde{\nu}_{CO\cdot\text{proton}} = \tilde{\nu}_{CO}\sqrt{\frac{\frac{m_O m_C}{m_O + m_C}}{m_O}}$$

$$\tilde{\nu}_{CO\cdot\text{proton}} = 217000\,\frac{1}{m}\sqrt{\frac{\frac{16\cdot 12}{16+12}}{16}}$$

$$\tilde{\nu}_{CO\cdot\text{proton}} = 142059.89\ldots\,\frac{1}{m} \approx 1421\,\frac{1}{cm}$$

P4: The transmission probability can be expressed as $T \approx 16\varepsilon(1-\varepsilon)e^{-2KW}$ (70.20b)

where $K \approx 7 \frac{1}{nm}$

set $W_1 = 2.0\,nm$ and $W_2 = 1.0\,nm$

and compare the transmission probabilities

$$\frac{T_2}{T_1} = \frac{\cancel{16\varepsilon(1-\varepsilon)}e^{-2KW_2}}{\cancel{16\varepsilon(1-\varepsilon)}e^{-2KW_1}}$$

$$\frac{T_2}{T_1} = \frac{e^{-2\cdot 7 \frac{1}{nm} \cdot 1.0\,nm}}{e^{-2\cdot 7 \frac{1}{nm} \cdot 2.0\,nm}} = \frac{e^{-14}}{e^{-28}} = \frac{e^{28}}{e^{14}}$$

$$\frac{T_2}{T_1} = e^{(28-14)} = e^{14} \approx 1.20 \cdot 10^{6}$$