Chemistry 3PA3 - Midterm 2014 Solutions

A Casio FX991 calculator, and 1 $8\frac{1}{2} \times 11"$ sheet written on both sides, are the only aids allowed.

$$h = 4.136 \times 10^{-15} \text{ eV s}$$

1. Consider an observable represented by an operator with eigenvalues, 1, 2 and 4. Which of the following statements are **true**, according to the postulates of quantum mechanics? For statements that are false, **change** one (or a few) word(s) or number(s) to make it a true statement. [1 mark each + 1 mark for each corrected false statement]

a. Possible outcomes of measurements of the observable include 1, *3* and 4. *False*

Corrected: "Possible outcomes of measurements of the observable include 1, *2* and 4". Only eigenvalues are observed in a single measurement.

b. The expectation value of this observable must always be between 1 and 4. *True*

The expectation value is a weighted average of the three eigenvalues, 1, 2 and 4. It cannot be lower than the lowest eigenvalue, or higher than the highest eignevalue.

c. If the observable is measured seven times for a given state, and the outcome of the measurement is 4 every time, then the next such measurement will *also* yield the value 4. *False*

Corrected: "If the observable is measured seven times for a given state, and the outcome of the measurement is 4 every time, then the next such measurement will *likely - but not necessarily -* yield the value 4."

The likelihood of 4 is certainly very high. But, no finite number of meaurements can establish certitude.

d. The average of the outcomes of many measurements of this observable (with system initially in the same state) *always comes out to be either* 1, 2 *or* 4. *False*

Corrected: "The average of the outcomes of many measurements of this observable (with system initially in the same state) *is a weighted average of* 1, 2 *and* 4.

e. The expectation value of this observable could have the value, 3.5. *True*

The expectation value can be anything from 1 to 4.

2. Which of the following statements are **true**? For statements that are false, **change** one (or a few) word(s) or number(s) to make it a true statement. [1 mark each + 1 mark for each corrected false statement]

a. For a particle-in-a-box with $\pi^2\hbar^2/(2mL^2) = 1.00$ eV, the two transitions from the ground state with greatest intensity occur at frequencies, 725 THz and 3.63 PHz. *True*

The two greatest intensity transitions from the ground state ($n = 1$) are to $n = 2$ and $n = 4$ (the transition to $n = 3$ is forbidden). For the $n = 1$ to 2 transition,

$$\begin{aligned}\Delta E &= E_2 - E_1 \\ &= \frac{\pi^2\hbar^2 2^2}{2mL^2} - \frac{\pi^2\hbar^2 1^2}{2mL^2} \\ &= \frac{\pi^2\hbar^2}{2mL^2}(4-1) \\ &= 3.00 \text{ eV},\end{aligned}$$

and

$$\nu = \frac{\Delta E}{h} = \frac{3.00 \text{ eV}}{4.136 \times 10^{-15} \text{ eV s}} = 725 \text{ THz}.$$

For the $n = 1$ to 4 transition,

$$\nu = \frac{\Delta E}{h} = \frac{15.00 \text{ eV}}{4.136 \times 10^{-15} \text{ eV s}} = 3627 \text{ THz}.$$

b. Consider a particle in energy state, $\psi_n(x)$, of a box of length, $L = 1$. The probability of finding the particle in the interval, $(0.5, 0.6)$, varies with n, oscillating above and below 0.1. However, it converges to 0.1, as $n \to \infty$. *True*

The probability of finding the particle in the interval, $(0.5, 0.6)$, is given by

$$
\begin{aligned}
P &= \int_{0.5}^{0.6} |\psi_n(x)|^2 \, dx \\
&= \int_{0.5}^{0.6} \left(\sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L} \right) \right)^2 dx \\
&= 2 \int_{0.5}^{0.6} \sin^2(n\pi x) \, dx \qquad L = 1 \\
&= 2 \int_{0.5}^{0.6} \frac{1}{2} (1 - \cos(2n\pi x)) \, dx \\
&= \int_{0.5}^{0.6} (1 - \cos(2n\pi x)) \, dx \\
&= \int_{0.5}^{0.6} dx - \int_{0.5}^{0.6} \cos(2n\pi x) \, dx \\
&= 0.1 - \left[\frac{\sin(2n\pi x)}{2n\pi} \right]_{0.5}^{0.6} \\
&= 0.1 - \frac{1}{2n\pi} (\sin(2n\pi \times 0.6) - \sin(2n\pi \times 0.5))
\end{aligned}
$$

Clearly, as $n \to \infty$, the probability converges to 0.1. For large (but finite) n, this probability oscillates about 0.1 above and below. If you could not remember the integral, or were short on time, you might reason as follows. In line three of the above calculation, the integrand oscillates rapidly between 0 and 1, when n is large. If n is a multiple of 10, then the integral is the average of n the limit as $n \to \infty$, the integral of $|\psi_n(x)|^2$ over any interval equals the product of the average of $2\sin^2(n\pi x)$ over the entire interval (equals 1 because $\psi_n(x)$ is normalized) and the length of the interval, 0.1. For other large n values the difference between the integral and 0.1 is a small portion of the interval where the last oscillation of $2\sin^2(n\pi x)$ is not quite complete. This subinterval is a diminishing portion of the 0.5 to 0.6 interval, as n increases - giving diminishing oscillations about the average value, 0.1.

c. There is only one vibrational transition frequency, from an initial population of diatomic molecules all in the vibrational ground state, because *the spacings between harmonic oscillator energy levels is the same for all levels*. *False*

Corrected: "There is only one vibrational transition frequency, from an initial population of diatomic molecules all in the vibrational ground state, because *of the vibrational selection rule* $\Delta v = +1$ *(*-1 *is not possible from the ground state)*."

d. The harmonic oscillator energy levels increase with quantum number at a slower rate than those of the particle-in-a-box because,

with increasing quantum number, the harmonic oscillator energy eigenfunctions are spread over an increasing range of x values. *True*

e. The vibrational spectrum of an initial population of diatomic molecules, with some in the vibrational ground state and some in the first excited state, consists of two well-separated peaks. *False*

Each portion of the initial population gives the same transition frequency - in the harmonic approximation. Specifically,

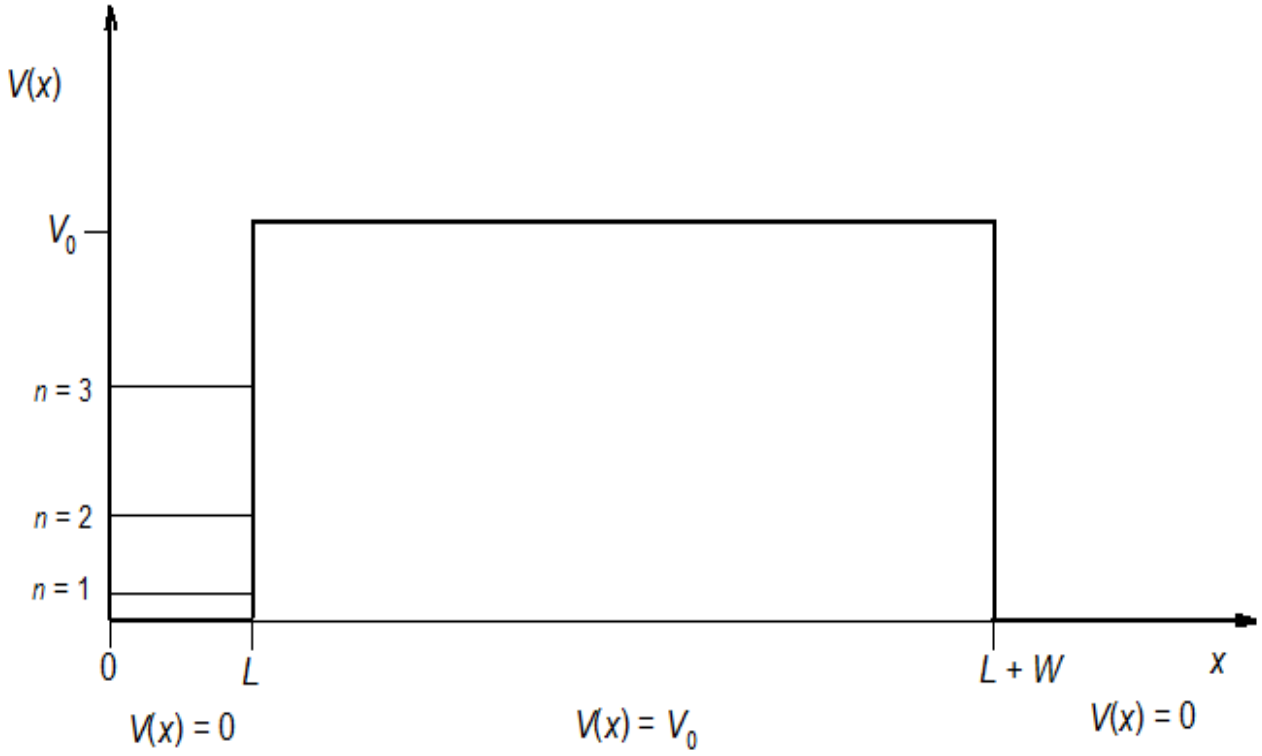
$\Delta_{2\leftarrow 1}E = \Delta_{3\leftarrow 2}E$ harmonic oscillator levels are equally spaced

and

$$\nu_{2\leftarrow 1} = \nu_{3\leftarrow 2}.$$

Anharmonicity (it has the smallest impact for these levels) can split these lines. However, they would not be well separated in frequency.

3. The following diagram shows the potential energy for an electron in one dimension. It consists of a narrow well (width, L) separated from a macroscopically large well by distance $W = 10L$. The bound energy levels of a particle in a box, labeled by associated quantum numbers, are also depicted in the diagram. The energy barrier between the wells, $V_0 = 15E_1$, where E_1 is the ground state energy (the zero point energy).



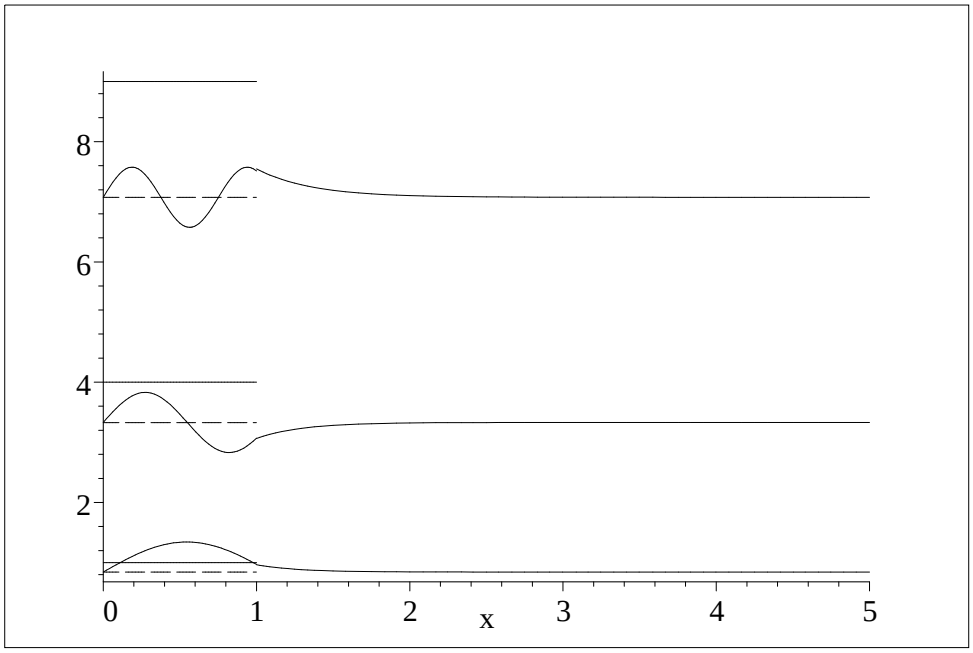
a. Where do the **energy levels** of the particle in this **finite well** appear in the diagram? Do they have **higher** or **lower** energies than the particle-in-a-box levels shown? For which n value is the shift in energy, due to the finite depth of the well, **smallest** or **largest**? [6 marks]

The particle in a well energy levels are lower than corresponding particle in a box energy levels. They are lower by increasing amount as n increases, because the higher energy levels are closer to the top of the well, V_0, and have greater barrier penetration. The increased range of x range lowers the energy by a greater amount.

b. **Sketch** the $n = 1, 2$ and 3 energy eigenfunctions **in the above figure**, using the three particle-in-a-box energy levels as the x axis for each sketch. [6 marks]

Here are the plots of the three bound particle in a well energy eigenfunctions with the associated energy level

used as the x axis.



c. **Order** the n levels according to **increasing** tunneling probability into the wide well on the right. **Explain** your ordering. [4 marks]

The tunneling probability is proportional to the barrier penetration which is greast for the top state here, $n = 3$, and lowest for the ground state, $n = 1$. The order according to increasing tunneling probability is $P_{n=1} < P_{n=2} < P_{n=3}$.

d. Which **one** of the following statements **best** describes what would happen to the tunneling probabilities (of all three levels) if W were decreased to $5L$? [4 marks]

i. The tunneling probabilities would not change.

ii. The tunneling probabilities would increase by a small factor (< 1).

iii. *The tunneling probabilities would increase by a large factor ($>> 1$). However, they would still be very small.*

The tunneling probability varies exponentially with respect to W. Decreasing W by $5L$ significantly enhances the tunneling probability. For example, tunneling probability from the $n = 3$ state increases by a factor,

$$\exp\left(\frac{\sqrt{2m(V_0 - E_3)}}{\hbar} 5L \right) = \exp\left(\sqrt{15 - 2.66^2}\, 5 \right),$$

which is more than 10^6. (Here, I used the actual computed value for E_3. Using $E_3 = 9$ gives similar results - the factor is 2×10^5.) However, the wave function is still about 10^{-6} in size - i.e., very small

iv. The tunneling probabilities would increase by a large factor ($>> 1$). The probability of tunneling would be close to 1 for all three levels.

4. With certain choices of units for distance and energy, the harmonic oscillator Hamiltonian can take the form,

$$\hat{H} = \frac{1}{2}\left(-\frac{d^2}{dy^2} + y^2\right),$$

a. Starting with

$$\hat{a} = \frac{1}{\sqrt{2}}\left(\frac{d}{dy} + y\right)$$

and

$$\hat{a}^\dagger = \frac{1}{\sqrt{2}}\left(-\frac{d}{dy} + y\right),$$

show that

$$\hat{H} = \hat{a}^\dagger\hat{a} + \frac{1}{2}.$$

[5 marks]

For any wavefunction, $\psi(y)$,

$$\begin{aligned}
\hat{a}^\dagger\hat{a}\psi &= .\frac{1}{\sqrt{2}}\left(-\frac{d}{dy} + y\right)\frac{1}{\sqrt{2}}\left(\frac{d}{dy} + y\right)\psi \\
&= .\frac{1}{2}\left(-\frac{d}{dy} + y\right)\left(\frac{d}{dy} + y\right)\psi \\
&= .\frac{1}{2}\left(\left(-\frac{d}{dy}\right)\frac{d}{dy}\psi + \left(-\frac{d}{dy}\right)y\psi + y\frac{d}{dy}\psi + y^2\psi\right) \qquad \text{apply product rule for secon} \\
&= .\frac{1}{2}\left(-\frac{d^2}{dy^2}\psi - \psi - y\frac{d}{dy}\psi + y\frac{d}{dy}\psi + y^2\psi\right) \\
&= \frac{1}{2}\left(-\frac{d^2}{dy^2} + y^2\right)\psi - \frac{1}{2}\psi \\
&= \hat{H}\psi - \frac{1}{2}\psi = \left(\hat{H} - \frac{1}{2}\right)\psi.
\end{aligned}$$

Therefore,

$$\hat{a}^\dagger\hat{a} = \hat{H} - \frac{1}{2}$$

and

$$\hat{H} = \hat{a}^\dagger\hat{a} + \frac{1}{2}.$$

b. Show that

$$\hat{a}^\dagger \psi_\upsilon = \sqrt{\upsilon + 1}\, \psi_{\upsilon+1},$$

where ψ_υ and $\psi_{\upsilon+1}$ are successive energy eigenstates. [10 marks]

Consider the commutator, $\left[\hat{H}, \hat{a}^\dagger\right]$,

$$\begin{aligned}\left[\hat{H}, \hat{a}^\dagger\right] &= \left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right)\hat{a}^\dagger - \hat{a}^\dagger\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right) \\ &= \hat{a}^\dagger\hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a}^\dagger\hat{a} \\ &= \hat{a}^\dagger(\hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a}) \\ &= \hat{a}^\dagger[\hat{a}, \hat{a}^\dagger].\end{aligned}$$

Since

$$\hat{a}\hat{a}^\dagger\psi = .\frac{1}{\sqrt{2}}\left(\frac{d}{dy} + y\right)\frac{1}{\sqrt{2}}\left(-\frac{d}{dy} + y\right)\psi$$

$$= \left(\hat{H} + \frac{1}{2}\right)\psi, \qquad \text{above argument with sign reversal of the non-canceling term f}$$

$$\begin{aligned}[\hat{a}, \hat{a}^\dagger] &= \hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a} \\ &= \hat{H} + \frac{1}{2} - \left(\hat{H} - \frac{1}{2}\right) \\ &= 1,\end{aligned}$$

and

$$\left[\hat{H}, \hat{a}^\dagger\right] = \hat{a}^\dagger[\hat{a}, \hat{a}^\dagger] = \hat{a}^\dagger.$$

Finally, we get

$$\begin{aligned}\hat{H}\hat{a}^\dagger\psi_\upsilon &= \hat{a}^\dagger\hat{H}\psi_\upsilon + \left[\hat{H}, \hat{a}^\dagger\right]\psi_\upsilon \\ &= \hat{a}^\dagger E_\upsilon\psi_\upsilon + \hat{a}^\dagger\psi_\upsilon \\ &= (E_\upsilon + 1)\hat{a}^\dagger\psi_\upsilon, \\ &= \left(\upsilon + \frac{1}{2} + 1\right)\hat{a}^\dagger\psi_\upsilon \\ &= E_{\upsilon+1}\hat{a}^\dagger\psi_\upsilon,\end{aligned}$$

and can conclude that $\hat{a}^\dagger\psi_\upsilon$ is proportional to the eigenstate with $\upsilon + 1$; i.e.,

$\hat{a}^\dagger\psi_\upsilon = c\psi_{\upsilon+1}$. c is real because ψ_υ and $\psi_{\upsilon+1}$ are both real

From

$$\begin{aligned}\langle\hat{a}^\dagger\psi_\upsilon|\hat{a}^\dagger\psi_\upsilon\rangle &= \langle c\psi_{\upsilon+1}|c\psi_{\upsilon+1}\rangle \\ \langle\psi_\upsilon|\hat{a}\hat{a}^\dagger\psi_\upsilon\rangle &= c^2\langle\psi_{\upsilon+1}|\psi_{\upsilon+1}\rangle \qquad \hat{a} \text{ is the Hermitian conjugate of } \hat{a}^\dagger \\ \left\langle\psi_\upsilon\middle|\left(\hat{H} + \frac{1}{2}\right)\psi_\upsilon\right\rangle &= c^2 \\ \left\langle\psi_\upsilon\middle|\left(E_\upsilon + \frac{1}{2}\right)\psi_\upsilon\right\rangle &= \left\langle\psi_\upsilon\middle|\left(\upsilon + \frac{1}{2} + \frac{1}{2}\right)\psi_\upsilon\right\rangle \\ &= (\upsilon + 1)\langle\psi_\upsilon|\psi_\upsilon\rangle = \upsilon + 1\end{aligned}$$

we get

$$c = \sqrt{\upsilon + 1}\,.$$

Label the following matrix elements as **non-zero** or **zero**? [5 marks]

i. $\langle \psi_\upsilon | y \psi_\upsilon \rangle$ *zero*

y can be expressed as sum of $\hat{a}$ and $\hat{a}^\dagger$. υ is raised and lowered by one level - $\psi_{\upsilon+1}$ and $\psi_{\upsilon-1}$ are orthogonal to ψ_υ.

ii. $\langle \psi_\upsilon | y^2 \psi_\upsilon \rangle$ *non-zero*

y^2 maps the υ state to $\upsilon - 2$, υ and $\upsilon + 2$. There is a contribution from ψ_υ which gives a non-zero matrix inner product with ψ_υ.

iii. $\langle \psi_{\upsilon+1} | y \psi_\upsilon \rangle$ *non-zero*

The $\psi_{\upsilon+1}$ component of $y\psi_\upsilon$ gives a non-zero inner product with $\psi_{\upsilon+1}$.

iv. $\langle \psi_{\upsilon+1} | y^2 \psi_\upsilon \rangle$ *zero*

$y^2\psi_\upsilon$ is a combination of $\psi_{\upsilon-2}$, ψ_υ and $\psi_{\upsilon+2}$, all orthogonal to $\psi_{\upsilon+1}$.

v. $\langle \psi_{\upsilon+2} | y \psi_\upsilon \rangle$ *zero*

$y\psi_\upsilon$ is a combination of $\psi_{\upsilon-1}$ and $\psi_{\upsilon+1}$, both orthogonal to $\psi_{\upsilon+2}$.

vi. $\langle \psi_{\upsilon+2} | y^2 \psi_\upsilon \rangle$ *non-zero*

The $\psi_{\upsilon+2}$ component of $y^2\psi_\upsilon$ gives a non-zero inner product with $\psi_{\upsilon+2}$..

5. Consider a particle in a one dimensional box such that $\pi^2\hbar^2/(2mL^2) = 1.00$ eV, and $L = 1$. Suppose the particle is in the state,

$$\psi(x) = \frac{\sqrt{3}}{2}\psi_1(x) + \frac{1}{2}\psi_2(x),$$

where $\psi_1(x)$ and $\psi_2(x)$ are the $n = 1$ and 2 energy eigenstates of the particle.

a. If the **energy** of the particle is measured, what are the possible **outcomes**? [3 marks]

The given state only has ψ_1 and ψ_2 components - all other components are zero. The probability of measuring energy to be E_1 or E_2 is non-zero, while the probability of any other outcome is zero. The possible outcomes are $E_1 = 1.00$ eV and $E_2 = 4.00$ eV.

b. What is the **probability** that 1.00 eV is the outcome of an energy measurement? [4 marks]

The probability of outcome $E_1 = 1.00$ eV is

$$\begin{aligned} |\langle\psi_1|\psi\rangle|^2 &= \left|\left\langle\psi_1\left|\frac{\sqrt{3}}{2}\psi_1 + \frac{1}{2}\psi_2\right\rangle\right|^2 \\ &= \left|\frac{\sqrt{3}}{2}\underbrace{\langle\psi_1|\psi_1\rangle}_{=1} + \frac{1}{2}\underbrace{\langle\psi_1|\psi_2\rangle}_{=0}\right|^2 \\ &= \left|\frac{\sqrt{3}}{2}\right|^2 = \frac{3}{4}. \end{aligned}$$

c. What is the **expectation value** of **energy** for this state? [4 marks]

$$\begin{aligned}
\langle\psi|\hat{H}\psi\rangle &= \left\langle \frac{\sqrt{3}}{2}\psi_1 + \frac{1}{2}\psi_2 \middle| \hat{H}\left(\frac{\sqrt{3}}{2}\psi_1 + \frac{1}{2}\psi_2 \right) \right\rangle \\
&= \left\langle \frac{\sqrt{3}}{2}\psi_1 + \frac{1}{2}\psi_2 \middle| \frac{\sqrt{3}}{2}\hat{H}\psi_1 + \frac{1}{2}\hat{H}\psi_2 \right\rangle \\
&= \left\langle \frac{\sqrt{3}}{2}\psi_1 + \frac{1}{2}\psi_2 \middle| \frac{\sqrt{3}}{2}E_1\psi_1 + \frac{1}{2}E_2\psi_2 \right\rangle \\
&= \frac{\sqrt{3}}{2}\frac{\sqrt{3}}{2}E_1\langle\psi_1|\psi_1\rangle + \frac{\sqrt{3}}{2}\frac{1}{2}E_2\langle\psi_1|\psi_2\rangle \\
&\quad + \frac{\sqrt{3}}{2}\frac{1}{2}E_1\langle\psi_2|\psi_1\rangle + \frac{1}{2}\frac{1}{2}E_2\langle\psi_2|\psi_2\rangle \\
&= \frac{3}{4}E_1 + \frac{1}{4}E_2 = \frac{3}{4}1.00 + \frac{1}{4}4.00 \text{ eV} \\
&= 1.75 \text{ eV}
\end{aligned}$$

d. What is the **expectation value** of **position**, x, for this state? [4 marks]

$$\begin{aligned}
\langle\psi|x\psi\rangle &= \left\langle \frac{\sqrt{3}}{2}\psi_1 + \frac{1}{2}\psi_2 \middle| x\left(\frac{\sqrt{3}}{2}\psi_1 + \frac{1}{2}\psi_2 \right) \right\rangle \\
&= \left\langle \frac{\sqrt{3}}{2}\psi_1 + \frac{1}{2}\psi_2 \middle| \frac{\sqrt{3}}{2}x\psi_1 + \frac{1}{2}x\psi_2 \right\rangle \\
&= \frac{\sqrt{3}}{2}\frac{\sqrt{3}}{2}\underbrace{\langle\psi_1|x\psi_1\rangle}_{=1/2} + \frac{\sqrt{3}}{2}\frac{1}{2}\langle\psi_1|x\psi_2\rangle \\
&\quad + \frac{\sqrt{3}}{2}\frac{1}{2}\underbrace{\langle\psi_2|x\psi_1\rangle}_{=\langle\psi_1|x\psi_2\rangle} + \frac{1}{2}\frac{1}{2}\underbrace{\langle\psi_2|x\psi_2\rangle}_{=1/2} \\
&= \frac{3}{4}\frac{1}{2} + \frac{1}{4}\frac{1}{2} + \frac{\sqrt{3}}{2}\langle\psi_1|x\psi_2\rangle \\
&= \frac{1}{2} + \frac{\sqrt{3}}{2}\int_0^1 x\sin(\pi x)\sin(2\pi x)\,dx
\end{aligned}$$

This would be an acceptable answer, since I did say that trig identities would not be required. Note also that it acceptable to simply use $1/2$ for the expectation values of x in the $n = 1$ and 2 states - no need to do the integrals. For those who did the $\langle\psi_1|x\psi_2\rangle$ integral, the answer is

$$
\begin{aligned}
\langle \psi | x\psi \rangle &= \frac{1}{2} + \frac{\sqrt{3}}{2} \int_0^1 x \sin(\pi x) \sin(2\pi x)\, dx \\
&= \frac{1}{2} + \frac{\sqrt{3}}{2} \int_0^1 x \frac{1}{2} (\cos(\pi x) - \cos(3\pi x))\, dx \\
&= \frac{1}{2} + \frac{\sqrt{3}}{4} \left(\int_0^1 x \cos(\pi x)\, dx - \int_0^1 x \cos(3\pi x)\, dx \right) \\
&= \frac{1}{2} + \frac{\sqrt{3}}{4} \left(\frac{1}{\pi} \int_{x=0}^{x=1} x\, d\sin(\pi x) - \frac{1}{3\pi} \int_{x=0}^{x=1} x\, d\sin(3\pi x) \right) \\
&= \frac{1}{2} + \frac{\sqrt{3}}{4\pi} \left([x \sin(\pi x)]_0^1 - \int_0^1 \sin(\pi x)\, dx - \frac{1}{3} \left([x \sin(3\pi x)]_0^1 - \int_0^1 \sin(3\pi x)\, dx \right) \right) \\
&= \frac{1}{2} + \frac{\sqrt{3}}{4\pi} \left(0 - \frac{1}{\pi} [-\cos(\pi x)]_0^1 - \frac{1}{3} \left(0 - \frac{1}{3\pi} [-\cos(3\pi x)]_0^1 \right) \right) \\
&= \frac{1}{2} + \frac{\sqrt{3}}{4\pi^2} \left([-1 - 1] - \frac{1}{9} [-1 - 1] \right) \\
&= \frac{1}{2} - \frac{\sqrt{3}}{2\pi^2} \left(\frac{8}{9} \right)
\end{aligned}
$$