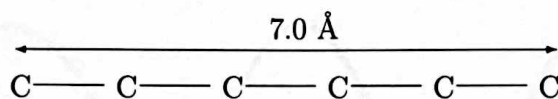


**1 Don't box me in (57 pts)**

The one-dimensional particle-in-a-box is a simple but useful model for the energy levels available to the  $\pi$  electrons of a conjugate alkene. Consider the six-carbon conjugated chain (hexatriene,  $C_6H_8$ ). The individual C–C distances are  $1.4 \text{ \AA}$ , so the  $\pi$  system can be modeled as a one-dimensional, infinitely deep box  $7.0 \text{ \AA}$  wide.

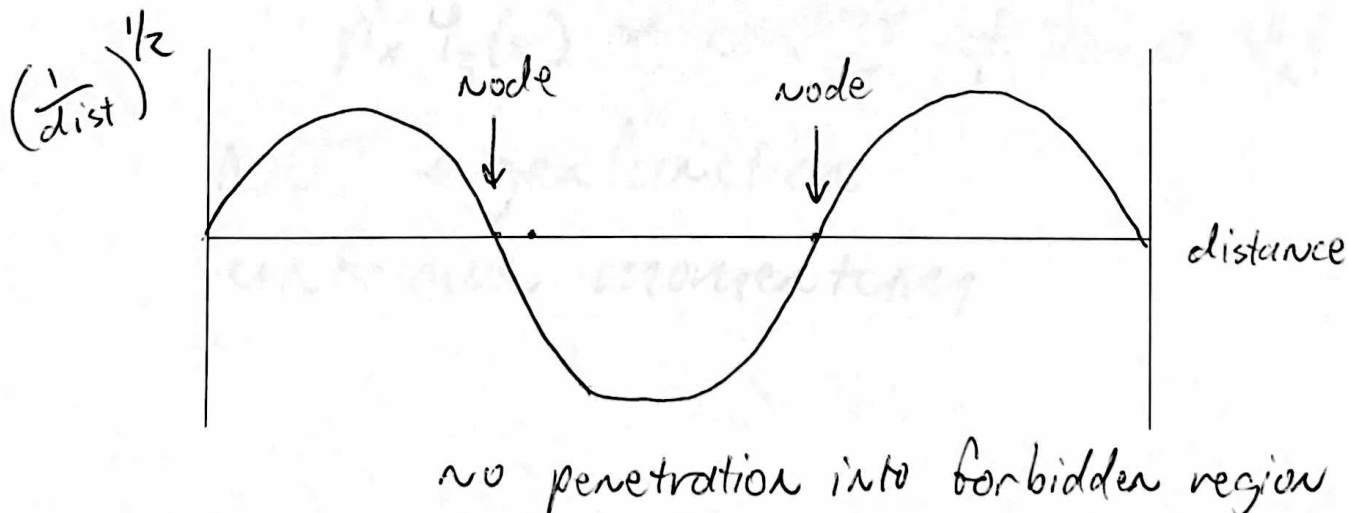


- 1.1 (8 pts) Write down (don't solve!) the Schrödinger equation for one electron in this particle-in-a-box system. Include as much detail, including boundary conditions, as possible.

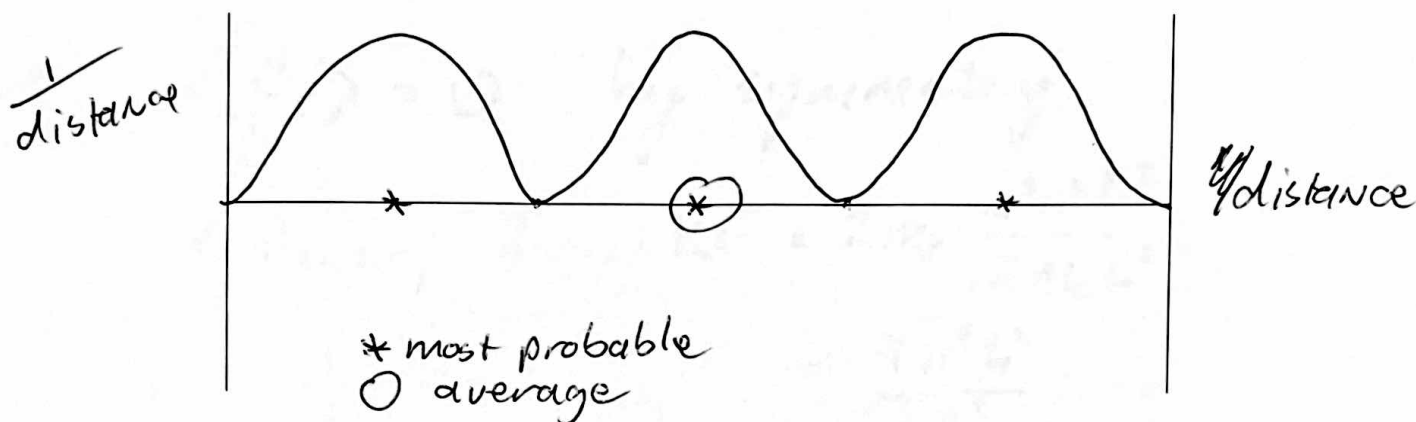
$$-\frac{\hbar^2}{2m_e} \frac{d^2}{dx^2} \psi(x) = E \psi(x) \quad 0 < x < 7$$

$$\psi(0) = \psi(7) = 0$$

- 1.2 (8 pts) In its ground state, hexatriene has two electrons in each of the three lowest-energy quantum levels,  $n = 1, 2, 3$ . In the graph below, sketch out the *wavefunction* for the  $n = 3$  particle-in-a-box state. Specify dimensionally correct units on all axes. Mark the locations of any nodes and any regions where the wavefunction has finite value in a classically forbidden region.



- 1.3 (8 pts) In the graph below, sketch out the *probability distribution function* for the  $n = 3$  particle-in-a-box state. Specify dimensionally correct units on all axes. Mark on the plot the most probable location(s) of an electron and the average location of an electron in this state.



- 1.4 (8 pts) Is the  $n = 3$  wavefunction an eigenfunction of the momentum operator,  $\hat{p}_x$ ? What does your answer tell you about what you know about the momentum of an electron in the  $n = 3$  state?

$$\hat{p}_x = -i\hbar \frac{d}{dx}$$

$$\psi_3(x) \propto \sin \frac{3\pi x}{L}$$

$$\hat{p}_x \psi_3(x) \propto \cos \frac{3\pi x}{L} \neq \text{const.} \cdot \psi_3(x)$$

NOT eigenfunction  
unknown momentum

1.5 (10 pts) The *uncertainty* in the momentum,  $\Delta p_x$ , is defined as:

$$\Delta p_x = (\langle p_x^2 \rangle - \langle p_x \rangle^2)^{1/2}$$

Calculate the uncertainty in the momentum of an electron in the  $n = 3$  particle-in-a-box state. *Hint:* No integrals necessary. Use reasoning plus what you know about the relationship between  $p^2$  and kinetic energy.

$$\langle p_x \rangle = 0 \quad \text{by symmetry}$$

$$\begin{aligned} \langle p_x^2 \rangle &= 2m_e \cdot KE = 2m_e \cdot \frac{n^2 \pi^2 \hbar^2}{2m_e L^2} \\ &= \frac{9\pi^2 \hbar^2}{L^2} \end{aligned}$$

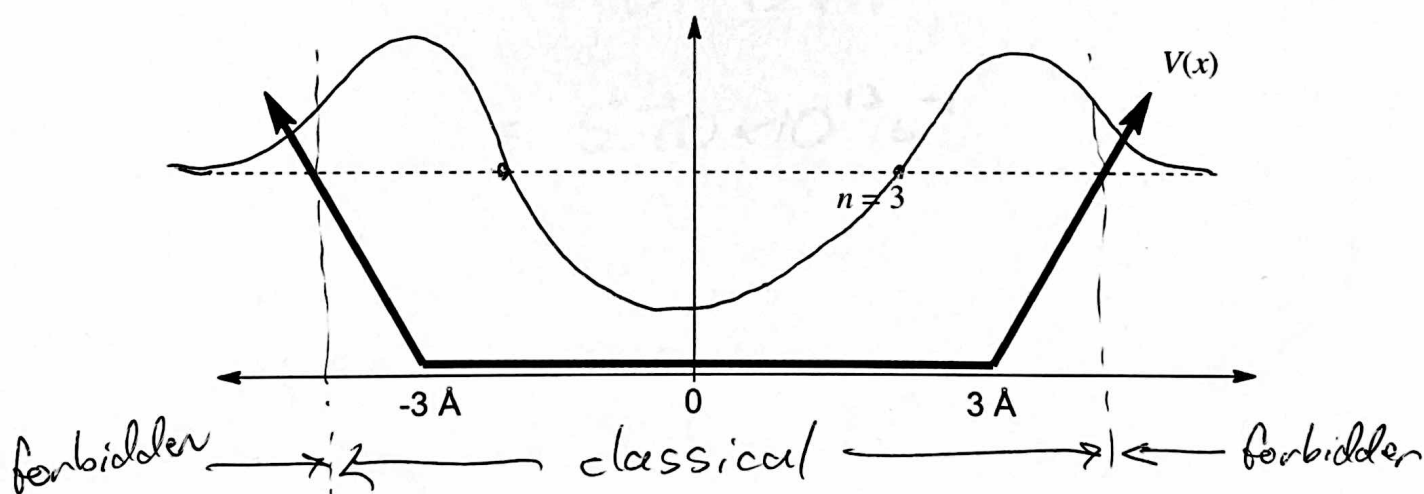
$$\Delta p_x = \langle p_x^2 \rangle^{1/2} = \frac{3\pi \hbar}{L}$$

1.6 (5 pts) Calculate the minimum uncertainty in the position  $\Delta x$  of an  $n = 3$  electron.

$$\Delta x \Delta p_x \geq \hbar/2$$

$$\Delta x \geq \frac{\hbar}{2\Delta p_x} = \frac{\hbar}{2} \cdot \frac{7}{3\pi\hbar}$$

1.7 (10 pts) One shortcoming of the particle-in-a-box model is that the ends of the hexatriene molecule do not behave like infinitely high potential walls. In a more realistic "particle-in-a-sloping-box" model, the potential energy rises linearly towards infinity at either end of the molecule, as shown by the bold lines below. The  $n = 3$  state in this model has the energy shown by the dashed line. Sketch with as much qualitative detail as possible the corresponding  $n = 3$  wavefunction along the dashed line. Indicate on your graph (a) the classical region and (b) the forbidden region.



**2 Spring Break (16 pts)**

A vibrating hydrogen bromide (HBr) molecule behaves to a good approximation like a harmonic oscillator. Hydrogen comes in two isotopes, H and D (deuterium), and the reduced masses of each isotopomer are as follows:

	Reduced mass (kg)
HBr	$1.67 \times 10^{-27}$
DBr	$3.24 \times 10^{-27}$

- 2.1 (8 pts) The vibrational frequency of HBr is observed to be  $7.94 \times 10^{13} \text{ s}^{-1}$ . Assuming the force constant is the same in the two molecules, what is the vibrational frequency of DBr?

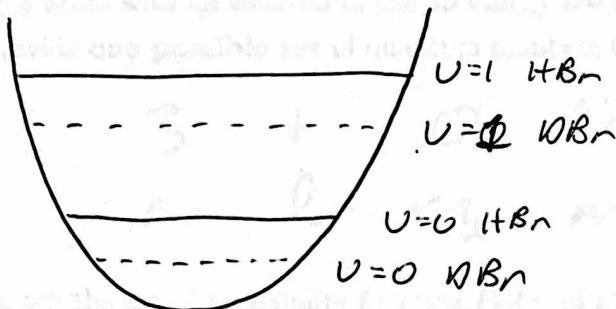
$$\nu \propto m^{-1/2}$$

$$\nu_{\text{DBr}} = \nu_{\text{HBr}} \left( \frac{\mu_{\text{HBr}}}{\mu_{\text{DBr}}} \right)^{1/2}$$

$$= \nu_{\text{HBr}} \cdot 0.718$$

$$= 5.70 \times 10^{13} \text{ s}^{-1}$$

2.2 (8 pts) At thermal equilibrium at 300 K, will you find a larger fraction of HBr or DBr molecules in the first excited ( $v = 1$ ) vibrational state? How much larger?



more DBr

$$\begin{aligned}
 \frac{p_{\text{DBr}}}{p_{\text{HBr}}} &= \frac{e^{-(v+1/2)h\nu_{\text{DBr}}/kT}}{e^{-(v+1/2)h\nu_{\text{HBr}}/kT}} \\
 &= e^{-3/2 h/kT (\nu_{\text{DBr}} - \nu_{\text{HBr}})} \\
 &= e^{5.37} \\
 &= 216
 \end{aligned}$$

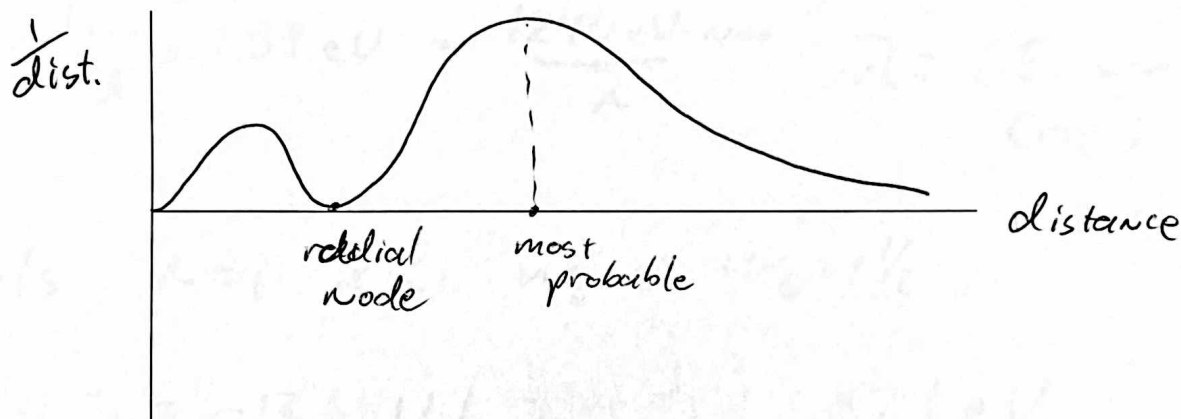
**3 Last hurrah (27 pts)**

The hydrogen atom is our last exactly solvable quantum mechanical problem. Consider an excited hydrogen atom with an electron in the 3p energy level.

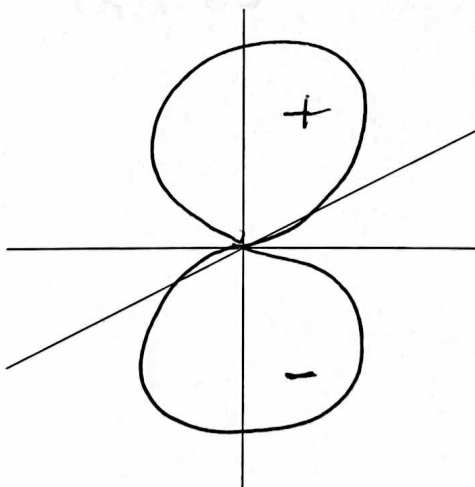
3.1 (4 pts) Provide **one possible set** of quantum numbers for this electronic state.

$$\begin{array}{cccc} 3 & 1 & 0 & +\frac{1}{2} \\ n & l & m_l & m_s \end{array}$$

3.2 (8 pts) Sketch the radial probability function  $P_{31}(r)$  of this p electron. Provide dimensionally correct units on both axes. Indicate the most probable distance of the electron from the nucleus on your graph and the location of any nodes.



3.3 (6 pts) Sketch a possible 3p electron angular wavefunction  $Y(\theta, \phi)$ . Be sure to indicate any nodes and to indicate the sign of the wavefunction as appropriate.



- 3.4 (9 pts) The 3p hydrogen is observed to spontaneously emit light. Provide a complete set of quantum numbers and corresponding wavelengths (in nm) for each of the possible final states.

$$\Delta l = \pm 1 \Rightarrow 3p \rightarrow 2s \quad 3p \rightarrow 1s$$

$$3p \rightarrow 2s \quad n=2 \quad l=0 \quad m_l=0 \quad m_s=+\frac{1}{2}$$

$$\Delta E = -13.6 \text{ eV} \cdot \left( \frac{1}{3^2} - \frac{1}{2^2} \right) = +1.89 \text{ eV}$$

$$\frac{hc}{\lambda} = 1.89 \text{ eV} = \frac{1240 \text{ eV} \cdot \text{nm}}{\lambda} \quad \lambda = 656 \text{ nm} \quad (\text{red})$$

$$3p \rightarrow 1s \quad n=1 \quad l=0 \quad m_l=0 \quad m_s=+\frac{1}{2}$$

$$\Delta E = -13.6 \text{ eV} \left( \frac{1}{3^2} - \frac{1}{1^2} \right) = 12.1 \text{ eV}$$

$$\lambda = \frac{1240 \text{ eV} \cdot \text{nm}}{12.1 \text{ eV}} = 103 \text{ nm} \quad (\text{hard x-ray})$$