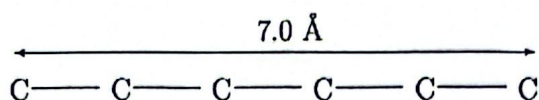


1 Don't box me in (65 pts)

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



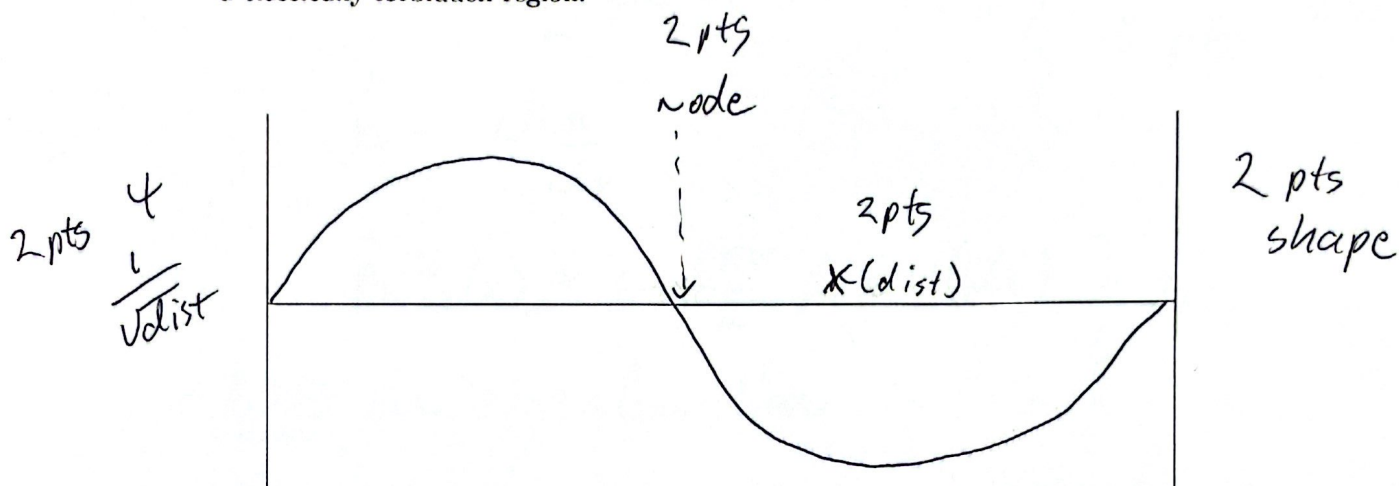
- 1.1 (8 pts) Write down (don't solve!) the Schrödinger equation for one electron in this particle-in-a-box system. Include as much detail, including boundary conditions, as possible.

$$-\frac{\hbar^2}{2m_e} \frac{d^2}{dx^2} \psi(x) = E \psi(x) \quad 4 \text{ pts}$$

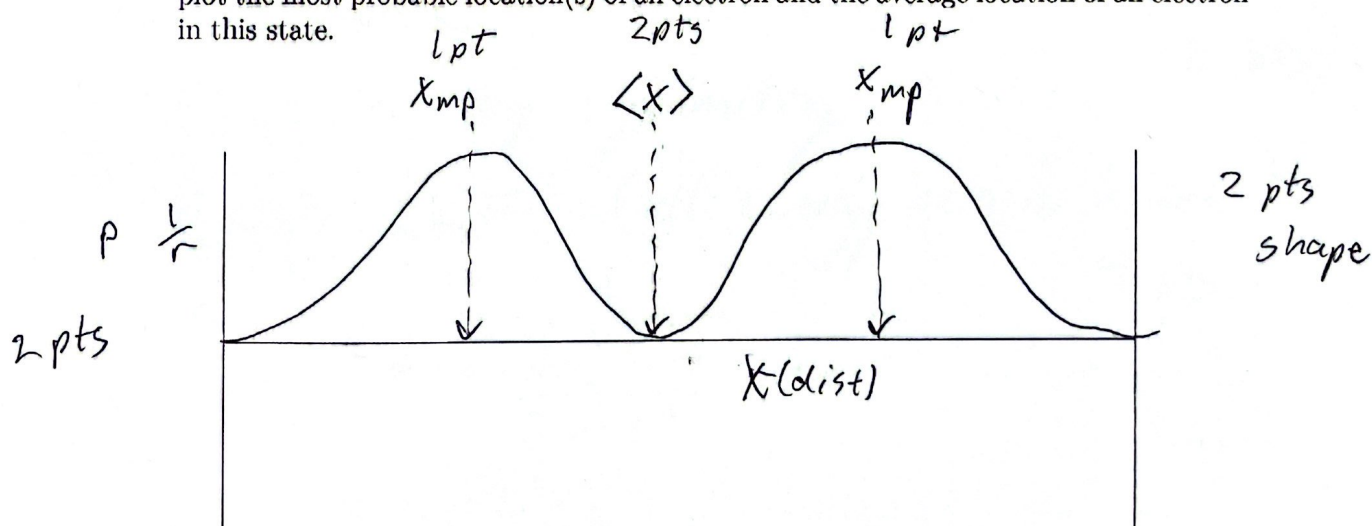
$$\psi(0) = \psi(L) = 0 \quad 4 \text{ pts}$$

$$L = 7.0 \text{ \AA}$$

- 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 $n = 2$ 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 $n = 2$ 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.



$$\langle x \rangle = L/2 \text{ by symmetry}$$

$$x_{mp} = L/4, 3L/4 \text{ by symmetry}$$

- 1.4 (6 pts) Is the $n = 2$ 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 $n = 2$ state?

$$\psi_2(x) = \sqrt{\frac{2}{L}} \sin \frac{2\pi x}{L}$$

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

} 2 pts

$$\hat{p}_x \psi_2(x) \propto \cos \frac{2\pi x}{L} \neq i \cdot \psi_2(x)$$

} 2 pts

Not an eigenfunction

Do not know particle momentum } 2 pts

- 1.5 (8 pts) The uncertainty in the momentum, Δp_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 $n = 2$ particle-in-a-box state. *Hint:* No integrals necessary. Use physical reasoning plus what you know about the relationship between p^2 and kinetic energy. You can leave your answer in units of \hbar/L , where $L = 7 \text{ \AA}$ is the size of the box.

2 pts

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

$$\langle p_x^2 \rangle = 2mE \text{ (all energy here is kinetic)}$$

4 pts

$$= 2m \cdot \frac{(2)^2 \pi^2 \hbar^2}{2mL^2}$$

$$= 4\pi^2 \hbar^2 / L^2$$

$$\Delta p_x = \sqrt{\langle p_x^2 \rangle} = 2\pi \hbar / L$$

2 pts

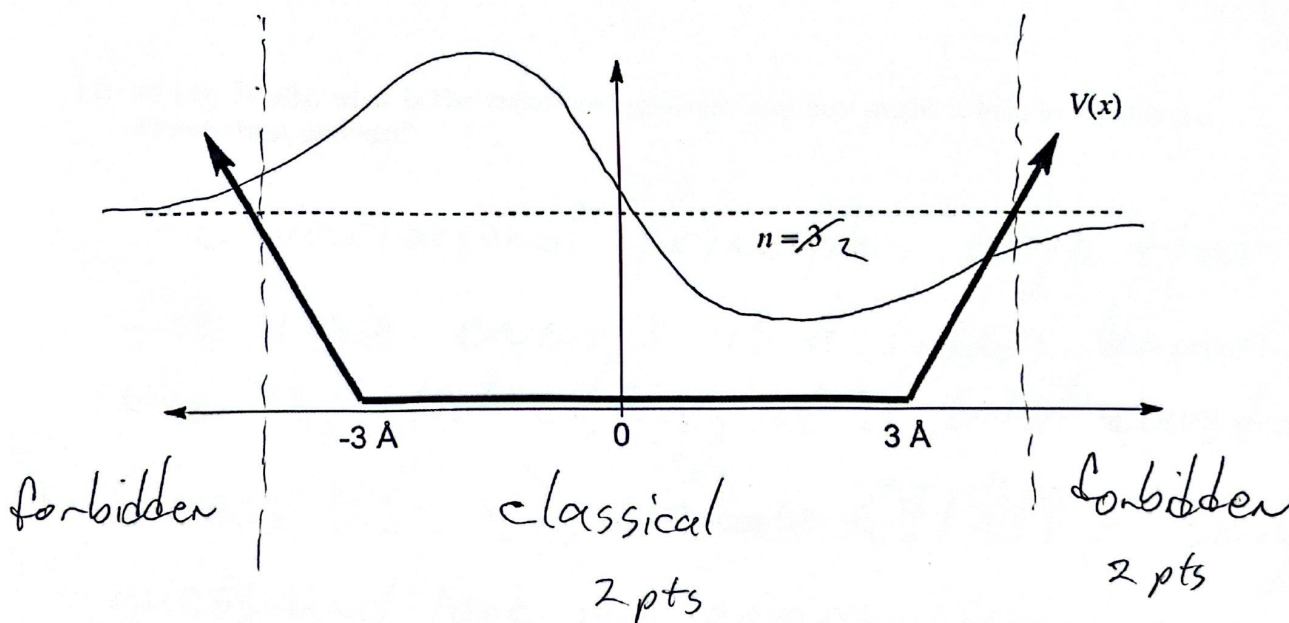
- 1.6 (5 pts) Calculate the minimum uncertainty in the position Δx of an $n = 2$ electron, in units of L , the size of the box.

$$\Delta x \geq \frac{\hbar}{2\Delta p_x} = \frac{\hbar}{2\left(\frac{2\pi\hbar}{L}\right)} = \frac{L}{4\pi} \approx 5.6 \text{ \AA}$$

3 pts 2 pts

- 1.7 (8 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 $n = 2$ state in this model has the energy shown by the dashed line. Sketch with as much qualitative detail as possible the corresponding $n = 2$ wavefunction along the dashed line. Indicate on your graph (a) the classical region and (b) the forbidden region.

4 pts shape



- 1.8 (8 pts) Another shortcoming of the particle-in-a-box model is that it neglects the electrostatic interactions between the electrons themselves. Write down the Schrödinger equation for *two* electrons in a one-dimensional box. Include as much detail, including boundary conditions, as possible.

4 pts
$$\left\{ -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 + \frac{e^2}{4\pi\epsilon_0} \frac{1}{|x_1 - x_2|} \right\} \psi(x_1, x_2) = E \psi(x_1, x_2)$$

4 pts
$$\begin{aligned} \psi(0, x_2) &= \psi(L, x_2) = 0 \\ \psi(x_1, 0) &= \psi(x_1, L) = 0 \end{aligned}$$

- 1.9 (6 pts) Briefly, what is the variational principle, and how might it help in solving the two-electron problem?

6 pts the variational principle says that the true energy is a lower bound on the expected energy of a trial wavefunction. Guess $\Psi(x_1, x_2)$, evaluate $\langle \Psi | \hat{H} | \Psi \rangle$, vary guess and look for energy minimum.

→ be generous, as long as answer is in correct spirit

2 Last hurrah (18 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.

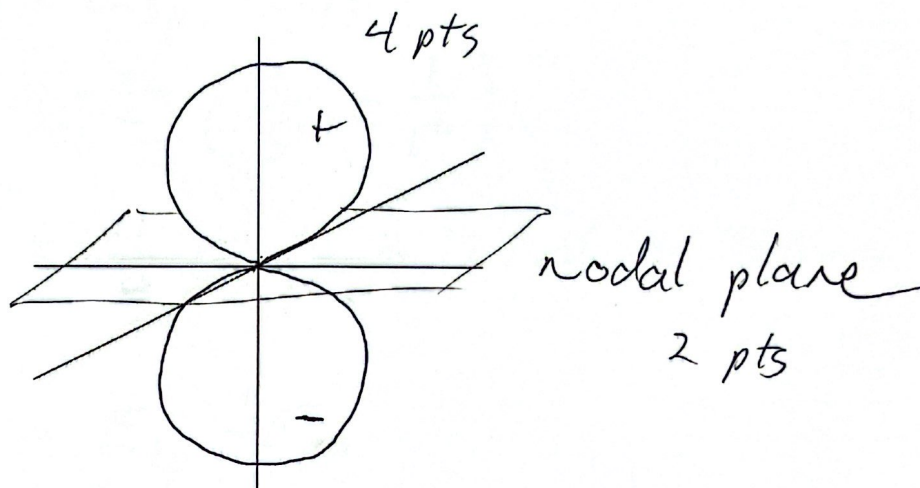
2.1 (4 pts) Provide one possible set of quantum numbers for this electronic state.

1 pt 1 pt 1 pt 1 pt

$$n = 3 \quad l = 1 \quad m_l = 0 \quad m_s = 1/2$$

(other answers possible)

2.2 (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.



- 2.3 (8 pts) The 3p hydrogen is observed to spontaneously emit light. Provide a complete set of quantum numbers and corresponding energy of the emitted photon (in units of E_H) for each of the possible final states.

selection rule says $\Delta l = \pm 1$

3p must do $\Delta l = -1$ to
either 2s or 1s.

$$(\Delta E_{\text{atom}} = -E_{\text{photon}})$$

$$3 \rightarrow 1 \quad -\Delta E = E_{3p} - E_{1s}$$

$$2 \text{ pts} \quad = -\frac{E_H}{2} \left(\frac{1}{3^2} - \frac{1}{1^2} \right)$$

$$2 \text{ pts} \quad = \frac{4}{9} E_H \quad \sim 12.1 \text{ eV} \quad \sim 102 \text{ nm}$$

$$3 \rightarrow 2 \quad -\Delta E = E_{3p} - E_{2s}$$

$$2 \text{ pts} \quad = -\frac{E_H}{2} \left(\frac{1}{3^2} - \frac{1}{2^2} \right)$$

$$2 \text{ pts} \quad = \frac{5}{72} E_H \quad \sim 1.89 \text{ eV} \quad \sim 656 \text{ nm}$$

3 Quantum atoms (17 pts)

Quantum mechanics helps us explain periodic trends in the properties of atoms. Consider the halogens, Group 7: F, Cl, Br, I.

3.1 (4 pts) What do you expect for the *spin multiplicity* of each atom?

all are p^5 $S = \frac{1}{2}$ $2S+1 = 2 = \text{doublet}$
4 pts

3.2 (5 pts) Rank the atoms in terms of their first ionization energy (i.e., minimum energy to remove a valence electron), from least to greatest first ionization energy.

$I < Br < Cl < F$ 2 pts order
3 pts rank

removing e^- from higher n (principal QM)
state/orbital/wavefunction

3.3 (5 pts) Rank the atoms in terms of the light energy ($h\nu$) necessary to eject a 1s electron from them, from least to greatest energy.

$F < Cl < Br < I$ 2 pts order
3 pts rank

Larger Z , lower energy 1s

3.4 (3 pts) Briefly, what does it mean to determine the wavefunctions of many-electron atoms "self-consistently"?

Often we write $v_{ee}[\psi]$, i.e. e^-e^- interaction potential is a function of (unknown ψ).
Guess ψ , construct $v_{ee}[\psi]$, solve for new ψ , repeat until $\psi_{in} = \psi_{out}$.
3 pts