HW #4

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1. A Chemical Bond

(a) With no interference, probability = sum of the individual probabilities:

$$P = |\psi_1|^2 + |\psi_2|^2 = (0.35)^2 + (0.22)^2 = 0.1225 + 0.0484 = \boxed{0.1709}$$

(b) With constructive interference, add the amplitudes before squaring:

$$P = |\psi_1 + \psi_2|^2 = (0.35 + 0.22)^2 = (0.57)^2 = \boxed{0.3249}$$

(c) The wave probability (0.32) is almost double the probability if there was no interference (0.17). This increased electron density between the two positive nuclei creates a covalent bond that holds them together. Because of the constructive interference, there is a higher probability of finding the electron between the two nuclei, which lowers the overall energy of the system and forms a stable bond.

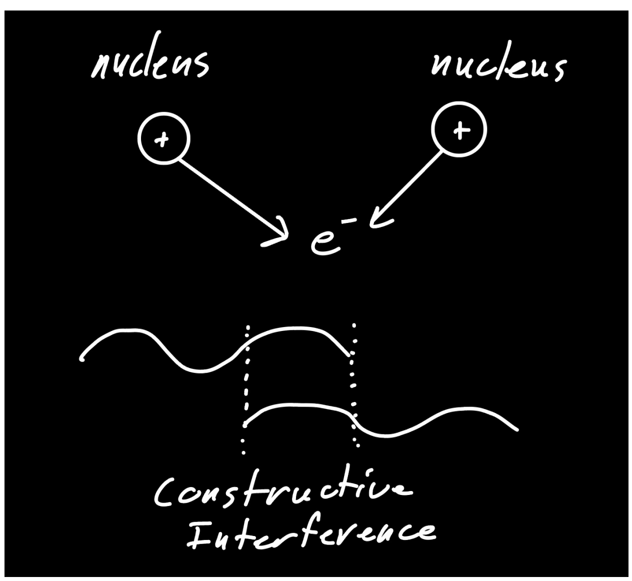

Figure 1: Constructive interference increases electron density between two nuclei.

2. Hydrogen Atom

(a) The longest wavelength has least energy, which is the $E_3 \to E_2$ transition.

$$E_3 = -1.5 \text{ eV}$$

$$E_2 = -3.4 \text{ eV}$$

$$\Delta E = E_3 - E_2 = -1.5 - (-3.4) = 1.9 \text{ eV}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{1241 \text{ eV} \cdot \text{nm}}{1.9 \text{ eV}} \approx \boxed{653 \text{ nm (a red wavelength)}}$$

(b)

$$E_1 = -13.6 \text{ eV}$$

$$E_5 = -0.54 \text{ eV}$$

$$\Delta E = E_5 - E_1 = -0.54 - (-13.6) = \boxed{13.06 \text{ eV}}$$

(c)

$$\frac{P(E_5)}{P(E_1)} = e^{-\Delta E/k_B T} = \frac{1}{1000}$$

$$-\frac{13.056}{k_B T} = \ln(\frac{1}{1000}) = -6.908$$

$$k_B T = \frac{13.056}{6.908} = 1.890 \text{ eV}$$

$$T = \frac{1.890 \text{ eV}}{8.617 \times 10^{-5} \text{ eV/K}} = \boxed{21{,}900 \text{ K}}$$

3. Chemical Reactions

(a) The diagram shows potential energy versus position with wave functions for each state (A, B, and transition).

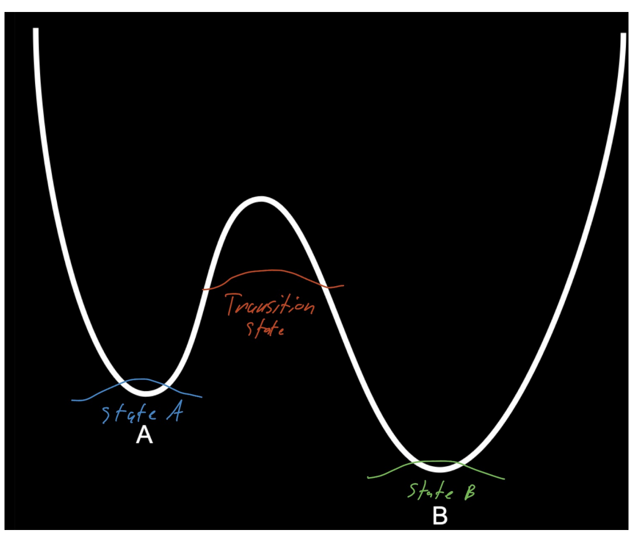

Figure 2: Double-well potential with localized states A and B and a higher-energy transition state near the barrier.

Each well has quantized standing-wave states. The $n = 1$ mode is the ground state (lowest energy) and has no internal node; higher-n states have more nodes and higher energy. This is analogous to a particle in a box,

$$E_n = \frac{n^2 h^2}{8mL^2}.$$

So state A and state B are shown as localized low-energy standing waves in their respective wells. To convert A $\to$ B, the system must pass through the high-energy configuration near the barrier top (the transition state).

(b)

$$\text{rate} = \frac{k_B T}{h} e^{-E_b/(k_B T)}, \qquad \text{time} = \frac{1}{\text{rate}}.$$

At $T = 310\,\text{K}$,

$$k_B T = (8.617 \times 10^{-5}\,\text{eV/K})(310\,\text{K}) = 0.02671\,\text{eV}, \qquad \frac{k_B T}{h} = 6.46 \times 10^{12}\,\text{s}^{-1}.$$

$$E_b = 0.1\,\text{eV}: \quad \text{rate} = (6.46 \times 10^{12}) e^{-0.1/0.02671} = 1.53 \times 10^{11}\,\text{s}^{-1}, \quad \text{time} = \frac{1}{\text{rate}} \approx 6.5 \times 10^{-12}\,\text{s}.$$

$$E_b = 1\,\text{eV}: \quad \text{rate} = (6.46 \times 10^{12}) e^{-1/0.02671} = 3.42 \times 10^{-4}\,\text{s}^{-1}, \quad \text{time} = \frac{1}{\text{rate}} \approx 2.9 \times 10^{3}\,\text{s} \approx 48\,\text{min}.$$

$$E_b = 10\,\text{eV}: \quad \text{rate} = (6.46 \times 10^{12}) e^{-10/0.02671} \approx 3 \times 10^{-150}\,\text{s}^{-1}, \quad \text{time} \approx 3 \times 10^{149}\,\text{s}.$$