Chem 440
Spring 2024

Hour Exam 1

Useful numbers and formulas you may need are given at the end.
You must turn in your answer by 11:55 to get full credit.

1. Consider the RNA sequence AGUCCAG_CCGUCGUA, with a base missing.

a. (2) **What is** the probability, P(U), that uracil occurs in the known part of the sequence?

Solution: U occurs 3 times in the sequence of 15 bases, so the probability is 3/15

b. (2) **What is** the probability, P(G), that guanine occurs in the known part of the sequence?

Solution: G occurs 4 times in the sequence of 15 bases, so the probability is 4/15

c. (2) **What is** the probability that whenever there is a U, there is a G before it? That is what is *P*(G|U) in the known part of the sequence?

Solution: Of the 3 times U occurs, a G is before it all 3 times, so the probability P(G|U) is 1

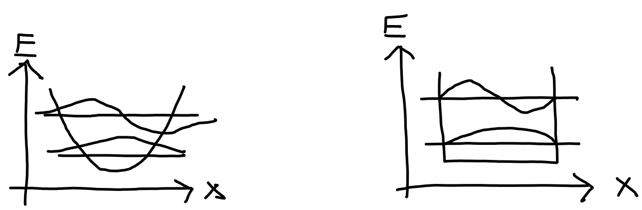
d. (2+1+1) Use Bayes' formula to **find** P(U|G), the probability that the next base is U given that the previous base was G. **What odds** do you give of U being the missing base? **Is this** a reasonable guess for the missing base?

Solution: P(U|G) = P(G|U)P(U)/P(G) = (1)(3/15)/(4/15) = 0.75. Yes, this is a reasonable guess for the missing base: likely tpo be there, but not 100% because there was a G where we don't know if it had a U after it or not.

2. (10 pts) Let's calculate some probabilities of being in a classically forbidden region.

a. (2) **Sketch** the potential energy of a spring ($\frac{1}{2} kx^2$) and of a box; don't forget the 'x' and 'E' axes on each plot.

Solution:



b. (2+2) **Draw the two** lowest energy levels and **sketch the two** lowest energy wavefunction into each plot, paying attention to the 'forbidden regions'.

Solution: see above

c. (1) For the box with infinitely high walls, **what is** the probability of being in the forbidden region? [Hint: no calculation needed if your sketch is correctly drawn)

Solution: 0 (no classically forbidden region because the energy outside the box is ∞)

d. (3) The *n*=1 state of a spring with wavefunction $\Psi(x) \approx 2.422xe^{-3x^2/2}$ has one of its classically forbidden regions between *x*=1 and infinity. **Calculate** the probability of being in the "forbidden region" at *x* >1. [Hint: remember probability density $P(x) = |\Psi(x)|^2$, and $|e^a|^2 = e^{2a}$.]

Solution:

$$\Psi(x) \approx 2.422xe^{-\frac{3x^2}{2}}$$

$$P_{forbidden} = \int_{x_{max}=1}^{\infty} dx\, |\Psi(x)|^2 = (2.422)^2 \int_{1}^{\infty} dx\, x^2 e^{-3x^2} = 5.85\ (0.0094)$$

$$\boldsymbol{P_{forbidden} \approx 0.055}$$

⇨ ≈5.5% chance to find the particle in the forbidden region at x>1.

3. (10 pts) H_2^+ is the simplest molecule, with two protons and one electron.

a. (4) **Write down** the Schrödinger equation for the electron with the nuclei at a fixed distance R from one another. [Hint: Consider the kinetic energy terms of the electron and the Coulomb energy terms for each pair of particles.]

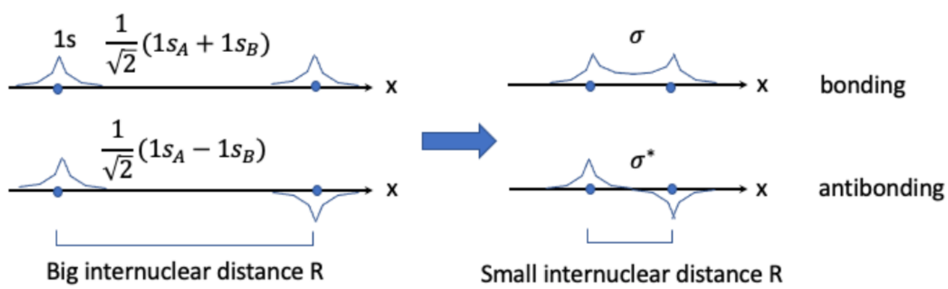
Solution:

$$\left\{-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2} - \frac{Z_A e^2}{4\pi\epsilon_0}\frac{1}{r_{eA}} - \frac{Z_B e^2}{4\pi\epsilon_0}\frac{1}{r_{eB}} + \frac{Z_A Z_B e^2}{4\pi\epsilon_0}\frac{1}{R}\right\}\Psi = E\Psi$$

b. (2) Both + or - 1s wavefunctions solve the Schrödinger equation on hydrogen atoms ":A" and "B": squaring these wavefunction gives the same probability. Draw the bonding wavefunction on both the nuclei of H_2^+ when the nuclei are **far apart** and when they are **close together**.

c. (2) **Repeat** (b) for the antibonding wavefunction: protons close together and far apart.

Solutions:



d. (1+1) If a H_2^+ molecule is excited from the ground state bonding orbital to excited state anti-bonding orbital, **what** happens to the molecule and **why**?

Solution:

When an H_2^+ molecule is excited , this leads to the decomposition of H_2^+ molecule into H atom and H^+ ion. The reason is that the electron is excited to the anti-bonding orbital, which has very little probability for the electron being between the nuclei, and nuclear repulsion raises the energy of the antibonding (excited) state.

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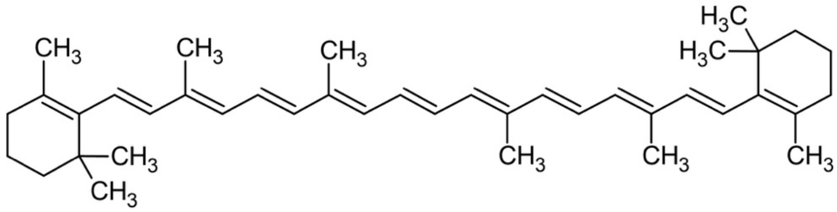
4. (10 pts) β-Carotene is a conjugated molecules with 22 conjugated carbon atoms. The conjugated length of β-Carotene is 20 Å.



a. (2) **How many** π electrons does this molecule have in the conjugated system?

Solution: 22 π electrons

b. (2) For the "electrons in a box" model, **what are** the quantum numbers n and n+1 of the two energy levels that give the lowest-frequency transition of β-carotene?

Solution: Electrons are filled in pairs, so 22 electrons fill the box up to n=11 (HOMO). The LUMO is therefore n=12. The 11 to 12 transition will be the lowest frequency transition.

c. (3+1) Treat β-carotene like a box, and **calculate** the frequency of light absorbed by the transition in b., and **also calculate** the wavelength absorbed.

Solution: Use the particle in a box energy formula and Planck's law to get

$$\Delta E = h^2 * \frac{(12^2 - 11^2)}{8mL^2} = h\nu$$

Here, $m \approx 9.11 * 10^{-31} kg$ is the electron mass, L≈ 20 Å = 2 ×10^{-9} m is the length of β-Carotene, and h ≈ 6.62×10^{-34} J*s is Planck's constant. Thus, solving for ν, $\nu = 5.22 * 10^{14}$ Hz. Using νλ=c, we then obtain $\lambda \approx 5.74 * 10^{-7} m = 574\ nm$ by using the speed of light c ≈ 3×10^8 m/s.

d. (1+1) **What** color does β-Carotene absorb best? **What** "complementary" color is β-Carotene itself?

Solution: using the color strip in the "Useful Information," 574 nm is yellow light being absorbed; the complementary color reflected or transmitted is purple. Note that this is not quite right for the color of carotene, which experimentally absorbs around 500 nm; the box model would have to be replaced by a full quantum calculation of the HOMO and LUMO energies. There are however purple carotenoids!

Useful information:

1 atomic mass unit = 1.66 x 10^{-27} kg; mass of electron m_e = 9.109 x 10^{-31} kg

Planck's constant $h = 6.626 \times 10^{-34}$ J·s; note that $\hbar = h/2\pi$ is about 6.28 times smaller.

1 Å = 0.1 nm = 100 pm; $c \approx 3 \cdot 10^8$ m/s

$\partial/\partial x\ e^{ax} = a e^{ax}$

$\int e^{-x/a}\, dx = -a\, e^{-x/a}$

$(1/a) \cdot \int x \cdot e^{-x/a}\, dx = -(a+x) e^{-x/a}$

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$\int_1^\infty x^{2\cdot} e^{-3x^2}\, dx = 0.0094$

$\lim_{x\to\infty} xe^{-x/a} = 0$ and $\lim_{x\to\infty} xe^{-bx^2} = 0$ for a or b.

Bayes' Rule: $P(A|B) = \frac{P(B|A)P(A)}{P(B)}$

Color and wavelength, and complementary color wheel