Chem 442
Spring 2021

Exam 1 Solution

Useful numbers and plots you may need are at the end.

1. (18 pts) **Calculate** the wavelength of light that will be absorbed by the molecule propene (it has a C-C=C backbone) by approximating its electronic structure by an "electron in a box."

This one was similar to problem 2.4 in the book.

a. (2) With *d*(C-C) = 1.54 Å and *d*(C=C) = 1.35 Å, **what is** the length L of the box, assuming the electron can move through the whole carbon skeleton?

Solution: L = 2.89 Å (2 points)

b. (3+3) Of the three π electrons in propene, the first two will fill the n=1 energy level of the box, and the third electron, which will be excited by the light, will be in the n=2 level or "HOMO" (highest occupied molecular orbital). **Write down** the particle-in-a-box energy formula for the third electron in terms of n, h, m_e and L and **calculate** the energy of the n=2 electron in Joules.

Solution: $E_n = \frac{n^2h^2}{8mL^2}$ (3 points)

$$= \frac{(2)^2(6.626 \cdot 10^{-34}\ Js)^2}{8(9.1 \cdot 10^{-31}\ kg)(2.89 \cdot 10^{-10}\ m)^2}$$

$= 2.88 \cdot 10^{-18}$ J (3 points)

c. (3+2) When light is absorbed, the electron goes to the n = 3 level. **Write down** the formula for the energy difference between the n = 3 *and* n = 2 states, and **calculate** the energy difference in Joules.

Solution: $\Delta E = (3^2 - 2^2)\frac{h^2}{8mL^2}$ (3 points)

$$\Delta E = (3^2 - 2^2)\frac{(6.626 \cdot 10^{-34}\ Js)^2}{8(9.1 \cdot 10^{-31}\ kg)(2.89 \cdot 10^{-10}\ m)^2}$$ (2 points)

$= 3.61 \cdot 10^{-18}$ J

d. (3+2) Finally, use Planck's law to convert the energy to a **wavelength in nm**. What part of the **electromagnetic spectrum** at the end of the exam is it?

Solution: $3.61 \cdot 10^{-18} J = \frac{hc}{\lambda} = \frac{(6.626*10^{-34}\ Js)(3.0*10^8\ m/s)}{\lambda}$ (3 points)

$\lambda = 6.2 \cdot 10^{-8}$ m = 55 nm

This is in the extended UV range (2 points)

Note that experiments show that propene absorbs in the mid-UV, at longer wavelengths. The reason is that the Coulomb potential is a 'softer' box than the particle in a box. However, the box approximation gets better the longer the conjugated chain is, as the 'edge effects' are smaller in those cases.

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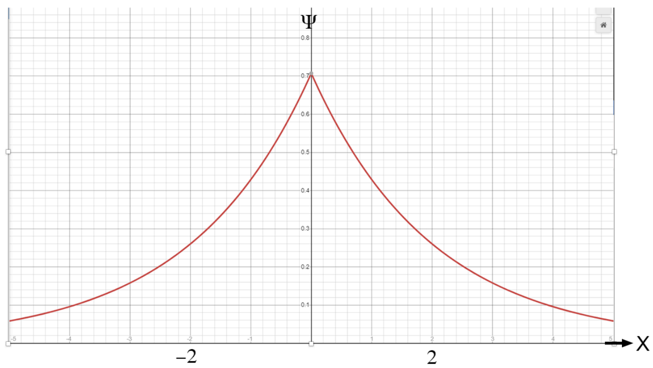
2. (15 pts) The normalized wavefunction $\Psi(x) = \left(\frac{1}{\sqrt{2}}\right)\exp[-|x|/2]$ is also known as a "1s orbital" for an electron whose nucleus sits at x=0. Here x is in Ångstrom units.

a. (4+2+2) **Sketch** the wavefunction roughly between x= -5 to 5 Å, **labeling** the axes "x" and "Ψ" and **indicating** roughly where x=±2 lies on the x-axis.

Solution: This one was similar to problem 1.8 in the book and H12, #2



b. (2+3+2) Calculate the probability of finding the electron at a <u>distance</u> between 3 and 3.1 Å from the nucleus by first **writing down the integral** with correct integration limits, then **evaluating** the integral, and **plug in** the numbers to get the probability.

Solution:

$$P = \int_3^{3.1} |\varphi(x)|^2 dx$$

$$= \int_3^{3.1} \left|\left(\frac{1}{\sqrt{2}}\right)\exp[-|x|/2]\right|^2 dx$$

$$= \frac{1}{2}\int_3^{3.1} e^{-|x|}\, dx \;= \frac{-1}{2} e^{-x}\Big|_3^{3.1}$$

Integrate from 3 to 3.1 ≈ 0.00237

The actual probability is twice that because electrons at -3 to -3.1 Å are also at a <u>distance</u> of between 3 and 3.1 Å from the nucleus. However, we'll give full credit for either answer if you overlooked that!

3. (10 pts) Someone plays the kettle drum.

a. (3+3) If they play on the kettle drum a "low "A" note at 110 Hz for 50 milliseconds (0.05 s), what is the uncertainty in the pitch Δν as a percentage of the frequency ν? **Formula** and **value**.

Solution: This one was similar to H5 #1

$$\Delta\nu\Delta t = \frac{1}{4\pi} \qquad \text{[Note } \nu=\omega/2\pi]$$

Therefore

$$\Delta\nu = \frac{1}{0.2\pi} \approx 1.59 \text{ Hz} \quad \text{(3 points)}$$

$\frac{\Delta v}{v} \times 100\% \approx 1.45\%$ (3 points for the formulas, 3 for the values)

b. (2+2) **Can they distinguish** the "A" from an "A#" at 116.5 Hz? In one sentence, why do you think orchestras use kettle drums, but not snare drums, to play bass melodies in symphonies?

Solution: Yes. (2 points)
Kettle drums sound long enough that one can make out the pitch reasonably well to play a bass melody; snare drums don't. (2 points)

4. (18 pts) If a quantum particle is in state $\Psi(x,t)$, let us show that the average value of the energy from many measurements is given by

$$\langle E \rangle = \bar{E} = \int_{-\infty}^{\infty} dx \Psi^*(x,t) \hat{H} \Psi(x,t),$$

a. (3+3) **Write down** the formula for $P(E = E_n)$ = ? from postulate 4, calling the energy eigenvalues E_n and the eigenfunctions $\varphi_n(x)$. Then recall from the $ bills homework that $\bar{A} = \Sigma a_n P(A = a_n)$ for any observable A. **Combine these two equations** to write an expression for $\langle E \rangle$ in terms of the eigenvalues and eigenfunctions of $\hat{H}$.

b. (3) Now **write down** the same expression for $\langle E \rangle$ again, but multiply out the $|\ |^2$ square modulus explicitly. Something like

$$\int_{-\infty}^{\infty} dx \Psi^*(x,t) \varphi_n(x) \int_{-\infty}^{\infty} dx' \varphi_n^*(x') \Psi(x',t)$$

should appear in your expression (the integral times its complex conjugate). It's always a good idea to give your integration variables different names (here x and x') when you have several integrals in an expression.

c. (3) Your expression for $\langle E \rangle$ has an "E_n" outside the first integral. Since E_n is a constant, you can stick it inside the integral in front of $\varphi_n(x)$, and play the reverse of a trick we have done in class several times: since $\hat{H}\varphi_n(x) = E_n \varphi_n(x)$, you can replace "$E_n$" **by what** in the integral? **Write down** the formula for $\langle E \rangle$ again, this time without E_n in it.

d. (3+3) Remember that any function can be expanded as a linear combination of a complete set of eigenfunctions. For example, $\Psi(x,t) = \Sigma c_m(\mathrm{t})\, \varphi_n(x)$, where $c_m(t) = \int_{-\infty}^{\infty} dx' \varphi_n^*(x') \Psi(x',t)$ is the "overlap integral" between $\varphi_n(x)$ and $\Psi(\mathrm{x},\mathrm{t})$. Look at your expression from part c., and replace one of the integrals by c_m, and **write down** the resulting formula for $\langle E \rangle = \bar{E}$. Finally **do the sum** $\Sigma c_m\, \varphi_n(x)$, which equals $\Psi(x,t)$, and write down your final expression for $\langle E \rangle = \bar{E}$.

Congrats, in 1926 you would have won a Nobel Prize!

Solution: Similar to Practice Exam Fall 2016, Q. 5, if you substitute "H" instead of "A" and "E_n" instead of "a_n"

a. (3 pts)

$$P(E = E_n) = \sum_n E_n \left| \int_{-\infty}^{\infty} dx \varphi_n^*(x) \Psi(x,t) \right|^2$$

(3 pts)

$$\bar{E} = \sum_n E_n \left| \int_{-\infty}^{\infty} dx \varphi_n^*(x) \Psi(x,t) \right|^2$$

b. (3 pts)

$$\bar{E} = \sum_n E_n \int_{-\infty}^{\infty} dx \Psi^*(x,t) \varphi_n(x) \int_{-\infty}^{\infty} dx' \varphi_n^*(x') \Psi(x',t)$$

c. (3 pts)

$$\bar{E} = \sum_n \int_{-\infty}^{\infty} dx \Psi^*(x,t) E_n \varphi_n(x) \int_{-\infty}^{\infty} dx' \varphi_n^*(x') \Psi(x',t)$$

$$= \sum_n \int_{-\infty}^{\infty} dx \Psi^*(x,t) \hat{H} \varphi_n(x) \int_{-\infty}^{\infty} dx' \varphi_n^*(x') \Psi(x',t)$$

d. (3+3 pts)

$$\bar{E} = \sum_n \int_{-\infty}^{\infty} dx \Psi^*(x,t) \hat{H} \varphi_n(x) \int_{-\infty}^{\infty} dx' \varphi_n^*(x') \Psi(x',t)$$

$$= \int_{-\infty}^{\infty} dx \Psi^*(x,t) \hat{H} \sum_n \varphi_n(x) \cdot \int_{-\infty}^{\infty} dx' \varphi_n^*(x') \Psi(x',t)$$

$$= \int_{-\infty}^{\infty} dx \Psi^*(x,t) \hat{H} \sum_n \varphi_n(x) \cdot c_n(t) = \int_{-\infty}^{\infty} dx \Psi^*(x,t) \hat{H} \Psi(x,t)$$

This integral is the overlap coefficient c_n

This last step we discussed in lecture 11: since the time-dependent and time-independent Schrödinger equations are equivalent (via Fourier transform), we can expand any $\Psi(x,t)$ in terms of eigenfunctions of the energy $\varphi_n(x)$; here we included the $e^{-iE_n t/\hbar}$ in the phase factor $c_n(t) = c_n e^{-iE_n t/\hbar}$ to keep the notation shorter, but of course, if you wrote that out in full, that's full credit.

Useful numbers:
1 atomic mass unit = 1.66×10^{-27} kg; mass of electron $m_e = 9.109 \times 10^{-31}$ kg
Planck's constant $h = 6.626 \times 10^{-34}$ J·s; note that $\hbar = 2\pi h$ is about 6.28 times larger.
1 m = 100 cm; 1 Å = 0.1 nm = 100 pm