Chem 440
Fall 2023

Solutions:

1. a. (2+2) Show that $x\hat{p} \neq \hat{p}x$, **by applying** $x\hat{p}$ to the function *f*(*x*), and **then applying** $\hat{p}x$ to the function *f*(*x*), to show that the two results are different.

Solution: $(\hat{x}\hat{p})f = \left(x\frac{\hbar}{i}\frac{\partial}{\partial x}\right)f = x\frac{\hbar}{i}\frac{\partial}{\partial x}f$

$$(\hat{p}\hat{x})f = \left(\frac{\hbar}{i}\frac{\partial}{\partial x}x\right)f = x\frac{\hbar}{i}\frac{\partial}{\partial x}f + f\frac{\hbar}{i}\frac{\partial}{\partial x}x$$

$$= x\frac{\hbar}{i}\frac{\partial}{\partial x}f + f\frac{\hbar}{i}$$

Thus, $\hat{x}\hat{p} \neq \hat{p}\hat{x}$ because the two differ by $\frac{\hbar}{i}f$

b. (3) An eigenfunction of the momentum is a function such that $\hat{p}\psi(x) = \lambda\psi(x)$, where λ is the eigenvalue of the momentum. **Show** that the function $\psi(x) = e^{ip_0x/\hbar}$, where p_0 is a number, is an eigenfunction of the momentum operator.

Solution: $\hat{p}f(x) = \frac{\hbar}{i}\frac{\partial}{\partial x}e^{\frac{ip_0x}{\hbar}} = \frac{\hbar}{i}\left(\frac{ip_0}{\hbar}\right)\left(e^{\frac{ip_0x}{\hbar}}\right) = p_0e^{\frac{ip_0x}{\hbar}} = p_0f(x)$. *f*(*x*) is recovered on the right and side, so *f* is an eigenfunction of momentum.

c. (1) **What is** the momentum eigenvalue λ in part b. equal to?

Solution: The eigenvalue λ in b. is equal to p_0.

d. (1+1) **Is** $g(x) = e^{-ip_0x/\hbar}$ also an eigenfunction of the momentum operator? **How** does the particle move in d. compared to a.?

Solution: Same as in a., but p_0 is replaced by $-p_0$. Yes, *g*(x) is an eigenfunction of the momentum operator. This time the particle moves in the opposite direction because the momentum has the opposite sign as in a.

2. a. (4) **Show** that the wavefunction for the two-electron system is of the form $\psi(x_1)\phi(x_2)$**.** That is, show that $\psi(x_1)\phi(x_2)$ is an eigenfunction of the combined Hamiltonian $H_1 + H_2$.

Solution:

$$\begin{aligned}
&(H_1 + H_2)\psi(x_1)\phi(x_2)\\
&= H_1\psi(x_1)\phi(x_2) + H_2\psi(x_1)\phi(x_2)\\
&= \phi(x_2)H_1\psi(x_1) + \psi(x_1)H_2\phi(x_2)\\
&= \phi(x_2)E_1\psi(x_1) + \psi(x_1)E_2\phi(x_2)\\
&= E_1\psi(x_1)\phi(x_2) + E_2\psi(x_1)\phi(x_2)\\
&= (E_1 + E_2)\psi(x_1)\phi(x_2)
\end{aligned}$$

b. (1) **What is** the total energy of the system?

Solution: $E_{total} = E_1 + E_2$

c. (2) **Write down** the total wavefunction of this system that satisfies the Pauli exclusion principle?

Solution: $\psi(x_1, x_2) = \sigma(x_1)\sigma^*(x_2) - \sigma(x_2)\sigma^*(x_1)$

d. (3) **Show** that this wavefunction satisfies postulate 4: $\psi_{fermion}(1,2) = -\psi_{fermion}(2,1)$.

Solution:

$$\begin{aligned} \psi(x_2, x_1) &= \sigma(x_2)\sigma^*(x_1) - \sigma(x_1)\sigma^*(x_2) \\ &= -\sigma(x_1)\sigma^*(x_2) + \sigma(x_2)\sigma^*(x_1) \\ &= -(\sigma(x_1)\sigma^*(x_2) - \sigma(x_2)\sigma^*(x_1)) \\ &= -\psi(x_1, x_2) \end{aligned}$$

3. a. (1+1) **How many** π electrons does this molecule have in the conjugated system? If retinal has a conjugated length L=15 Å, **what is** the conjugated length of molecule 'X'?

Solution: One per carbon atom, or 10; the length of molecule 'X' is calculated by the ratio L = 15 Å × 10/12 = 12.5 Å

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 'X'?

Solution: Electrons are filled in pairs, so 10 electrons fill the box up to n=5 (HOMO). The LUMO is therefore n=6. The 5→6 transition will be the lowest frequency transition.

c. (3+1) Treat 'X' 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

$$\Delta E = h^2/(8mL^2) \cdot (6^2 - 5^2) = h\nu.$$

Here, $m \approx 9.11 \times 10^{-31}\ kg$ is the electron mass, $L \approx 12.5$ Å $= 1.25\times10^{-9}$ m is the length of 'X', and $h \approx 6.62\times10^{-34}$ J·s is Planck's constant. Thus, solving for ν, $\nu = 6.40\times10^{14}$ Hz. Using $\nu\lambda = c$, we then obtain $\lambda \approx 4.69\times10^{-7}$ m = 469 nm by using the speed of light $c \approx 3\times10^{8}$ m/s.

d. (1+1) **What color** does the lifeform's visual sensitivity peak at? **What is** the color of 'X' itself?

Solution: using the color strip in the "Useful Information," 469 nm is deep blue light being absorbed; the complementary color reflected or transmitted by 'X' is orange.

4. (10 pts.) In class we studied the different effects that heat and light have on hexadiene by examining the conjugated π molecular orbitals. Here, we examine the reaction between two ethene molecules to form cyclobutane. (ethene is C_2H_4 or $H_2C{=}CH_2$ or =)

a. (1+1+1) **How many** π electrons does ethene have? **Draw** the energy level diagram for the π electrons of ethene molecule and **draw** the HOMO and LUMO orbitals next to their energy level. **Fill** the electrons into the lowest energy orbital(s) with correct spin.

Solution: 2 pi electrons, and the diagram is

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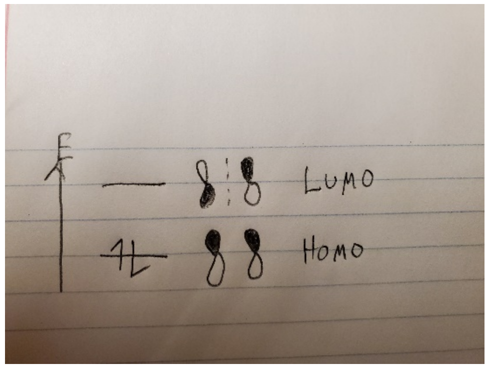
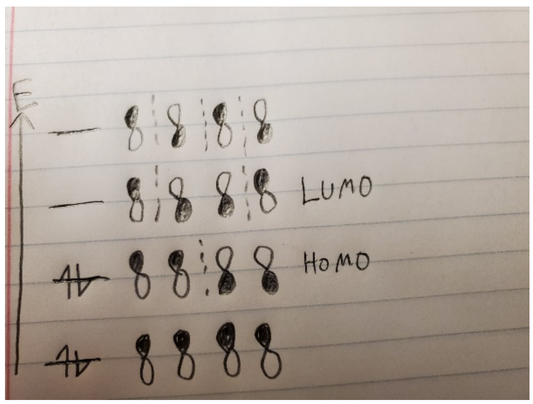


b. (1+1+1) Now imagine the two ethene molecules aligned like == as a π-conjugated system and **draw** the energy levels and molecular orbitals for this 4-electron system, **filling** in the electrons correctly and **labeling** the HOMO and LUMO. Here, the first two orbitals you draw belong to molecule 1, while the second two belong to molecule 2.

Solution:



c. (1+1) Would this reaction proceed naturally through heating, yes or no? Justify your answer in 1 sentence? [Hint: for simplicity, do it for the aligned molecules; it does not affect the most general possible answer.]

Solution: No. In this case, the HOMO indicates that p orbitals of opposite sign would interact, and this is antibonding.

d. (1+1) Would this reaction proceed using light to induce a 1-electron transition, yes or no? Justify your answer in 1 sentence? [Hint: same as in b.]

Solution: Yes. The new HOMO for this process is the LUMO drawn out in part b, where direct bonding results between the innermost two p orbitals when the ethylene molecules com close together.

Note: if you stacked the two ethene molecules side-by-side instead of end-to end like we did above, you still get the same result: only via photoexcitation (light) do you get the orbitals of same phase to overlap, and thus obtain a bond instead of an antibond.