Chem 440
Practice Exam

Hour Exam 1

50 minutes - Useful numbers and formulas you may need are given at the end.
You must turn in your answer by 10:55 to get full credit.

1. (10 pts.) The momentum along the x-axis is given by $\hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}$.

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.

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.

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

d. (1+1) **Is** $g(x) = e^{-ip_0x/\hbar}$ also an eigenfunction of the momentum operator? **Why or why not**?

2. (10 pts.) Consider a two-electron molecule, with electron #1 satisfying $H_1\psi(x_1) = E_1\psi(x_1)$ and electron #2 satisfying $H_2\phi(x_2) = E_2\phi(x_2)$.

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 $H_1 + H_2$.

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

Suppose electron #1 is in the σ molecular orbital $\psi \sim \sigma(x_1)$ and electron #2 is in the σ^* molecular orbital $\phi \sim \sigma^*(x_2)$.

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

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

3. (10 pts.) Spectroscopy has detected likely signs of life on *Procyon c*, an exoplanet that revolves around an 11 light year-distant F5 class star that emits bluer light than the sun. The lifeforms with vision may have developed a molecule 'X' with 10 conjugated carbon atoms, vs. the 12 conjugated carbon atoms of retinal.

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'?

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 molecule 'X'?

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

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

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 simply =)

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

b. (1+1+1) Now imagine the two adjacent 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 p orbitals you draw belong to ethene molecule #1, while the second two p orbitals belong to ethene molecule #2.

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; the result is the same for other orientations.]

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 c.]

Useful information:

Average $A = \Sigma\, P_i A_i$ or $A = \int dx P(x) A(x)$; $\ln(x_2)-\ln(x_1)=\ln(x_2/x_1)$; $\ln(x^a) = a \ln(x)$.

$\partial(e^{ikx})/\partial x = ik\, e^{ikx}$; $e^{ikx} = \cos(kx) + i \sin(kx)$ = Real part + Imaginary part.

wavenumber (cm^{-1}) $= \frac{10^7}{\lambda\,(nm)} = \frac{\nu\,(Hz)}{100\,c\,(\frac{m}{s})}$ relates number of cycles per cm to wavelength or frequency

$N! = N(N-1)(N-2) \cdots 3 \cdot 2 \cdot 1$ $\quad c = 2.99792458 \cdot 10^8$ m/s;

1 atomic mass unit ≈ 1.66×10^{-27} kg; mass of electron $m_e \approx 9.109 \times 10^{-31}$ kg

$k_B \approx 1.38 \cdot 10^{-23}$ J/K; Planck's constant $h \approx 6.626 \times 10^{-34}$ J·s; $\hbar = h/2\pi$.

Avogadro's number $N_A = 6.02214076 \cdot 10^{23}$; gas constant $R \approx 8.31$ J/mole/K

Conversions: 1 Å = 0.1 nm = 100 pm; 1 ps = 10^{-12} s; 1 fs = 10^{-15} s

Uncertainty principles: $\Delta x \Delta p = \hbar/2$; $\Delta E \Delta t = \hbar/2$;

Color, wavelength, and complementary color wheel: