Name:

Instructions:
Check the exam to make sure that it contains exactly 6 different pages, including this one and a periodic table at the end.

Some useful constants and equations:

\[ R_H = 109,737 \text{ cm}^{-1} \quad N_A = 6.022 \times 10^{23} \text{ mol}^{-1} \]

\[ m_e = 9.109 \times 10^{-31} \text{ kg} \quad h = 6.626 \times 10^{-34} \text{ J s} \quad \hbar = h/2\pi \]

\[ c = 2.998 \times 10^8 \text{ m s}^{-1} \quad k_B = 1.381 \times 10^{-23} \text{ J K}^{-1} \quad \text{1 amu} = 1.661 \times 10^{-27} \text{ kg} \]

\[ \lambda = h/p \quad \Delta E = h c R_H(1/n_i^2 - 1/n_f^2) \]

\[ \lambda \nu = c \quad \tilde{\nu} = 1/\lambda \quad E = h \nu \quad \Delta x \Delta p \geq \hbar/2 \]

\[ E_{\text{vib}} = (n + \frac{1}{2})h\nu, \quad n = 0, 1, 2, \ldots \quad \nu = (k/\mu)^{1/2}/2\pi \quad \text{(vibrational frequency)} \]

\[ \mu = m_A m_B/(m_A + m_B) \quad \text{(reduced mass)} \]

\[ E_{\text{rot}} = J(J+1)h^2/8\pi^2 I, \quad J = 0, 1, 2, \ldots \quad (2J+1)-\text{degenerate} \quad I = \mu r_0^2 \]

\[ v = \frac{\gamma B_0}{2\pi} \quad (\gamma = 26.75 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1} \text{ for } ^1\text{H}) \]

\[ A = - \log(T) = \varepsilon b c \]

\[ k_{\text{ret}} = \frac{1}{\tau_D} \left( \frac{R_0}{r} \right)^6 \]

\[ q = \sum_n g_n e^{-\beta e_n}, \quad p_n = \frac{g_n e^{-\beta e_n}}{q} \]

\[ \ln(N!) \approx N\ln N - N \quad \text{Bond Order} = (1/2)[n(\text{bonding}) - n(\text{antibonding})] \]
Part 1. Write the letter of the answer which best satisfies each statement or question in the blank at the left. Please check your answers. Credit will only be given for the letter written in the blank (3 points each).

C 1. What is the degeneracy of the 2p orbitals of the helium atom?
   (A) 1  (B) 2  (C) 3  (D) 4

D 2. An electron of the hydrogen atom has angular momentum quantum number \( l = 3 \). Which of the following is not a possible value of the magnetic quantum number, \( m_l \)?
   (A) -2  (B) 0  (C) 2  (D) 4

C 3. Which of the following diatomic molecules is paramagnetic?
   (A) \( \text{H}_2 \)  (B) \( \text{Li}_2 \)  (C) \( \text{B}_2 \)  (D) \( \text{N}_2 \)

D 4. Which of the following wave functions does not satisfy the Pauli Principle?
   (A) \([1s(1)2s(2) + 2s(1)1s(2)][\alpha(1)\beta(2)-\beta(1)\alpha(2)]\)
   (B) \([1s(1)2s(2) + 2s(1)1s(2)][\beta(1)\alpha(2)-\alpha(1)\beta(2)]\)
   (C) \([1s(1)2s(2) - 2s(1)1s(2)][\alpha(1)\beta(2)+\beta(1)\alpha(2)]\)
   (D) \([1s(1)2s(2) + 2s(1)1s(2)][\alpha(1)\beta(2)-\beta(1)\alpha(2)+ \alpha(1)\alpha(2)]\)

A 5. Which of the following depicts the shape of the 2\( \sigma \) molecular orbital of \( \text{Li}_2 \)? The molecule is oriented as \( \text{Li}^-\text{Li} \).

(A)  

B 6. If, for a particular Hamiltonian, the trial wave function used in the variational method happens to be the exact ground state wave function, the energy obtained using this trial wave function is always \( \) the exact ground state energy.
   (A) equal to  (B) greater than  (C) less than

B 7. In the partition function, \( q = \sum_n g_n e^{-\beta \epsilon_n} \), possible units for \( \beta \) are
   (A) Joules  (B) Joules\(^{-1}\)  (C) Kelvin  (D) Kelvin\(^{-1}\)

B 8. Compared to the fluorescence spectrum, the absorption spectrum appears at \( \)
   (A) lower frequency  (B) higher frequency  (C) the same frequency

C 9. Consider a FRET pair where \( R_0 = 4.72 \text{ nm} \). At what distance is the rate of energy transfer twice the excited state decay rate in the absence of acceptor?
   (A) 4.72 nm  (B) 2.36 nm  (C) 4.21 nm  (D) 9.44 nm

A 10. What property of \( N \) is preferred when using Stirling’s approximation for \( \ln(N!) \)?
   (A) \( N \) should be large  (B) \( N \) should be small  (C) \( N \) should be even  (D) \( N \) should be odd
Part II. Short answer: Answer the following in the space provided. (12 points each)

1. Suppose that the intensity of light at 422 nm leaving a 3.00-cm cell is 88% of the intensity of the incoming light at the same wavelength. The cell contains a solution of 1.32 x 10^{-1} g L^{-1} of the compound and the molecular weight of the compound is 110.0 g mol^{-1}. What is the molar extinction coefficient of the compound?

\[
c = \frac{(1.32 \times 10^{-1} \text{ g L}^{-1})}{(110.0 \text{ g mol}^{-1})} = 1.20 \times 10^{-3} \text{ M}
\]

\[
-\log_{10}(0.88) = \varepsilon bc = \varepsilon (3.00 \text{ cm})(0.0012 \text{ mol L}^{-1})
\]

\[
\varepsilon = 15.4 \text{ L mol}^{-1} \text{ cm}^{-1}
\]

2. Calculate the frequency of the radiofrequency field in resonance with \(^1\)H when the magnetic field strength is \(B_0 = 5.50\) T.

The condition for resonance is \(\nu = \frac{\gamma B_0}{2\pi}\).

For \(^1\)H, \(\gamma = 26.75 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}\). Then

\[
\nu = \frac{26.75 \times 10^7 \text{ rad} \cdot \text{T}^{-1} \cdot \text{s}^{-1}}{2\pi} (5.50 \text{ T}) = 2.34 \times 10^8 \text{ s}^{-1}.
\]

3. The vibrational frequency of \(\text{Br}_2\) is 325 cm\(^{-1}\). At what temperature will the population of the first excited state be 10% that of the ground state?

\[
\frac{n_1}{n_0} = \frac{1}{10} = \exp \left[ \frac{-(E_1 - E_0)}{k_B T} \right] = \exp \left[ \frac{-(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(325 \text{ cm}^{-1})(3.00 \times 10^{10} \text{ cm} \cdot \text{s}^{-1})}{(1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1})T} \right]
\]

Solving for \(T\) we find \(T = 203\) K.
Part III. Write your answer to the problems below in the space provided. Please show all work. Partial credit will be given based on work shown. (17 points each)

1. You have a system with 3 states with energies $\varepsilon_1$, $\varepsilon_2$ and $\varepsilon_3$. Take the ground state energy, $\varepsilon_1$, to be 0.

   (a) Write the partition function, $q$, for this 3 state system at temperature, $T$. (5 points)

   $$q = 1 + \exp(-\varepsilon_2/k_BT) + \exp(-\varepsilon_3/k_BT).$$

   (b) You observe at $T = 300$ K that the probability for the system to be in the ground is $p_1 = 0.9$. Calculate $q$. (5 points)

   $$p_1 = e^0/q = 1/q = 0.9,$$

   so $q = 10/9$

   (c) You furthermore observe that the probability for the system to be in states 2 and 3 are, respectively, $p_2 = 0.09$ and $p_3 = 0.01$ at $T = 300$ K. What are the energies $\varepsilon_2$ and $\varepsilon_3$ of states 2 and 3 relative to the ground state ($\varepsilon_1 = 0$)? (7 points)

   $$p_2 = \exp(-\varepsilon_2/k_BT) / q = 0.9 \exp(-\varepsilon_2/k_BT) = 0.09,$$

   so $\exp(-\varepsilon_2/k_BT) = 1/10$

   $$\varepsilon_2 = k_BT \ln 10 = (1.381 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K}) \ln 10 = 9.53 \times 10^{-21} \text{ J}.$$

   $$p_3 = \exp(-\varepsilon_3/k_BT) / q = 0.9 \exp(-\varepsilon_3/k_BT) = 0.01,$$

   so $\exp(-\varepsilon_3/k_BT) = 1/90$

   $$\varepsilon_3 = k_BT \ln 90 = (1.381 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K}) \ln 90 = 1.86 \times 10^{-20} \text{ J}.$$. 
2. Write the electron configuration for \( \text{C}_2 \), \( \text{C}_2^+ \) and \( \text{C}_2^- \). The energies of the molecular orbitals for these diatomics are in the order \( 1\sigma < 1\sigma^* < 2\sigma < 2\sigma^* < 1\pi < 3\sigma < 1\pi^* < 3\sigma^* \). Write the bond order for \( \text{C}_2 \), \( \text{C}_2^+ \) and \( \text{C}_2^- \). Order \( \text{C}_2 \), \( \text{C}_2^+ \) and \( \text{C}_2^- \) from shortest to longest bond length and lowest to highest bond energy. Also order \( \text{C}_2 \), \( \text{C}_2^+ \) and \( \text{C}_2^- \) from lowest to highest vibrational frequency.

The electron configuration of \( \text{C}_2 \) is \((1\sigma)^2(1\sigma^*)^2(2\sigma)^2(2\sigma^*)^2(1\pi)^4\). The bond order is 2.

The electron configuration of \( \text{C}_2^+ \) is \((1\sigma)^2(1\sigma^*)^2(2\sigma)^2(2\sigma^*)^2(1\pi)^3\). The bond order is 1.5.

The electron configuration of \( \text{C}_2^- \) is \((1\sigma)^2(1\sigma^*)^2(2\sigma)^2(2\sigma^*)^2(1\pi)^4(3\sigma)^1\). The bond order is 2.5.

Bond Length: \( \text{C}_2^- < \text{C}_2 < \text{C}_2^+ \).

Bond Energy: \( \text{C}_2^+ < \text{C}_2 < \text{C}_2^- \).

Vibrational Frequency: \( \text{C}_2^+ < \text{C}_2 < \text{C}_2^- \).

I_____________  II_____________  III_____________  Total_____________