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:

\[ R_H = 109,737 \text{ cm}^{-1} \quad N_A = 6.02 \times 10^{23} \text{ mol}^{-1} \]

\[ m_e = 9.11 \times 10^{-31} \text{ kg} \quad h = 6.63 \times 10^{-34} \text{ J s} \quad \hbar = h/2\pi \]

\[ c = 3.00 \times 10^8 \text{ m s}^{-1} \quad k_B = 1.38 \times 10^{-23} \text{ J K}^{-1} \quad 1 \text{ amu} = 1.661 \times 10^{-27} \text{ kg} \]

\[ \lambda = h/p \quad \Delta E = h c \frac{R_H}{n_i^2 - n_f^2} \]

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

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

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

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

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

\[ A = - \log(T) = \epsilon b c \quad k_{\text{ret}} = \frac{1}{T_D} \left( \frac{R_0}{r} \right)^6 \]

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

\[ \ln(N!) \approx N \ln N - N \quad \text{Bond Order} = (1/2)[n(\text{bonding}) - n(\text{antibonding})] \]
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).

1. Which of the following diatomic molecules is paramagnetic?
   (A) Li₂  (B) N₂  (C) O₂  (D) F₂

2. An electron of the hydrogen atom has angular momentum quantum number \( l = 2 \). Which of the following is a possible value of the principle quantum number, \( n \)?
   (A) 0  (B) 1  (C) 2  (D) 3

3. The electronic configuration of the carbon atom in its ground state is \( 1s^22s^22p^2 \). Following Hund’s rule, we can conclude that
   (A) there are no d electrons  (B) both 2p electrons have the same spin
   (C) the 2s electrons have the same spin  (D) the 2p electrons have opposite spin

4. Which of the following wave functions satisfies the Pauli Principle?
   (A) \([1s(1)2s(2) + 2s(1)1s(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)]\)
   (B) \([1s(1)2s(2) + 2s(1)1s(2)]\alpha(1)\alpha(2)\)
   (C) \([1s(1)2s(2) + 2s(1)1s(2)][\alpha(1)\beta(2) + \beta(1)\alpha(2)]\)
   (D) \([1s(1)2s(2) + 2s(1)1s(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2) + \alpha(1)\alpha(2)]\)

5. Which of the following depicts the shape of the \( 1\pi \) molecular orbital of \( C_2 \)? The molecule is oriented as \( C = C \).
   (A)  (B)  (C)  (D) 

6. The variational theorem states that, for a particular Hamiltonian, the energy obtained using a trial wave function is always _____ the exact ground state energy.
   (A) equal to  (B) less than or equal to  (C) greater than or equal to

7. In the partition function, \( q = \sum_{n} g_{n} e^{-\beta \varepsilon_n} \), \( \beta \) stands for
   (A) \( k_B T \)  (B) \( 1/k_B T \)  (C) \( T \)  (D) \( 1/T \)

8. For which of the following is the chemical shift of the \(^1H\) NMR spectrum greatest?
   (A) CH₃I  (B) CH₃Br  (C) CH₃Cl  (D) CH₃F

9. Consider a FRET pair. At what distance, \( r \), is the rate of energy transfer equal to the excited state decay rate for the isolated donor?
   (A) \( R_0 \)  (B) \( 2R_0 \)  (C) \( 1/R_0 \)  (D) \( R_0^6 \)

10. Which of the following is a close approximation to \( \ln(N!) \) when \( N = 120 \)?
    (A) 4.79  (B) 9.57  (C) 454.5  (D) 574.5
Part II. Short answer: Answer the following in the space provided. (12 points each)

1. The vibrational frequency of I$_2$ is 208 cm$^{-1}$. At what temperature will the population of the first excited state be half that of the ground state?

\[ \frac{n_1}{n_0} = \frac{1}{2} = \exp \left[ \frac{-(E_1 - E_0)}{k_B T} \right] = \exp \left[ \frac{-(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(208 \text{ cm}^{-1})(3.00 \times 10^{10} \text{ cm} \cdot \text{s}^{-1})}{(1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1})T} \right] \]

Solving for $T$ we find $T = 432 \text{ K}$.

2. The molar extinction coefficient of a certain compound of molecular weight 142.0 g mol$^{-1}$ is $1.20 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 322 nm. Calculate the percent of incoming light intensity that is transmitted when light at 322 nm passes through a 2.00-cm cell containing a $1.30 \times 10^{-2} \text{ g L}^{-1}$ solution of this compound.

\[ A = \varepsilon bc \]

\[ A = (1.20 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1})(2.00 \text{ cm})(1.30 \times 10^{-2} \text{ g L}^{-1}/142.0 \text{ g mol}^{-1}) = 0.220 \]

\[ T = 10^{-A} = 10^{-0.220} \]

\[ T \times 100\% = 60.3 \% \]

3. Calculate the value of $B_0$ for $^1\text{H}$ to be in resonance if the radiofrequency field has a frequency of 350. MHz.

The condition for resonance is

\[ B_0 = \frac{2\pi\nu}{\gamma} \]

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

\[ B_0 = \frac{2\pi\nu}{\gamma} = \frac{2\pi\nu}{\gamma} = \frac{2\pi(350 \times 10^6 \text{s}^{-1})}{26.75 \times 10^7 \text{ rad T}^{-1} \text{s}^{-1}} = 8.22 \text{ T} \]
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. (a) Consider a two-state system in which the low energy level is \(1.24 \times 10^{-21}\) J, the high energy level is \(2.62 \times 10^{-21}\) J, and the temperature of the system is 300 K. Determine the partition function, \(q\), and the probability that each of the two states is occupied. (10 points)

\[
q = 1 + \exp\left[-\frac{(\varepsilon_2 - \varepsilon_1)}{k_B T}\right] = 1 + \exp\left[-\frac{1.38 \times 10^{-21}}{(1.38 \times 10^{-23}) (300 K)}\right] = 1.717.
\]

\[
p_1 = \frac{1}{q} = 0.583
\]

\[
p_2 = \frac{\exp\left[-\frac{1.38 \times 10^{-21}}{(1.38 \times 10^{-23}) (300 K)}\right]}{q} = 0.417
\]

(b) You have a system with 2 states. You observe the probabilities \(p_1 = 0.9\) and \(p_2 = 0.1\) at \(T = 300\) K. What is the energy \(\varepsilon_2\) of state 2 relative to the ground state (\(\varepsilon_1 = 0\))? (7 points)

\[
q = 1 + \exp\left(-\frac{\varepsilon_2}{k_B T}\right).
\]

\[
p_1 = \frac{1}{q} = 0.9, \text{ so } q = 10/9
\]

\[
p_2 = \frac{\exp\left(-\frac{\varepsilon_2}{k_B T}\right)}{q} = 0.9 \exp\left(-\frac{\varepsilon_2}{k_B T}\right) = 0.1, \text{ so } \exp\left(-\frac{\varepsilon_2}{k_B T}\right) = 1/9
\]

\[
\varepsilon_2 = k_B T \ln 9 = (1.381 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})\ln 9 = 9.10 \times 10^{-21} \text{ J}.
\]
2. Write the electron configuration for $F_2^+$, $F_2$ and $F_2^-$. The energies of the molecular orbitals for these diatomics are in the order $1\sigma < 1\sigma^* < 2\sigma < 2\sigma^* < 3\sigma < 1\pi < 1\pi^* < 3\sigma^*$. Write the bond order for $F_2^+$, $F_2$ and $F_2^-$. Order $F_2^+$, $F_2$ and $F_2^-$ from shortest to longest bond length and lowest to highest bond energy. Also order $F_2^+$, $F_2$ and $F_2^-$ from lowest to highest vibrational frequency.

The electron configuration of $F_2^+$ is $(1\sigma)^2(1\sigma^*)^2(2\sigma)^2(2\sigma^*)^2(3\sigma)^2(1\pi)^2(1\pi^*)^3$. The bond order is 1.5.

The electron configuration of $F_2$ is $(1\sigma)^2(1\sigma^*)^2(2\sigma)^2(2\sigma^*)^2(3\sigma)^2(1\pi)^4(1\pi^*)^4$. The bond order is 1.

The electron configuration of $F_2^-$ is $(1\sigma)^2(1\sigma^*)^2(2\sigma)^2(2\sigma^*)^2(3\sigma)^2(1\pi)^4(1\pi^*)^4(3\sigma^*)^1$. The bond order is 0.5.

Bond Length: $F_2^+ < F_2 < F_2^-$. 

Bond Energy: $F_2^- < F_2 < F_2^+$. 

Vibrational Frequency: $F_2^- < F_2 < F_2^+$.