Please write neatly and clearly, and show all working. Allocate time to each question in proportion to the available credit. Keep explanations brief and to the point.

Your name: ____________

SOLUTIONS

SOME POSSIBLY USEFUL INFORMATION:

\( N_A \) or \( L = 6.022 \times 10^{23} \text{ mol}^{-1} \) \( h = 6.626 \times 10^{-34} \text{ J s} \)

\( k_B = 1.38 \times 10^{-23} \text{ J K}^{-1} \) \( c = 2.998 \times 10^8 \text{ m s}^{-1} \)

H atom mass = \( 1.66 \times 10^{-27} \text{ kg} \) electron mass = \( 9.11 \times 10^{-31} \text{ kg} \)

\( R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \)

Planck: \( E = hv \) Schrodinger: \( \hat{H}\psi = E\psi \) de Broglie: \( \lambda = h/p \)

x operator is multiply by x \( p \) operator is \( h/(2\pi) \text{ d/dx} \)

\( E_K \) operator is \( -h^2/(8\pi^2m) \text{ d}^2/\text{dx}^2 \) \( V \) operator is multiply by \( V \)

\( E_v = (v + 1/2)h \) \( v = (k/\mu)^{1/2}/(2\pi) \)

\( g_J = 2J + 1 \) \( B = h/(8\pi^2) \) in Hz \( E_J = Bh(J+1) \)

\( \sin^2x = (1 - \cos 2x)/2 \) \( \cos^2x = (1 + \cos 2x)/2 \)

\[
\int_0^\infty x^n \exp(-ax) = \frac{n!}{a^{n+1}}
\]

Relative population proportional to \( g \exp(-E/(k_B T)) \)

I.P. of one-electron atom proportional to \( Z^2/n^2 \). I.P. of H = 13.6 eV = \( 2.18 \times 10^{-18} \text{ J} \).

\[
|L^2| = l(l + 1) \frac{h^2}{(4\pi^2)}
\]

\( L_z = m_l \frac{h}{2\pi} \)
1) 40 points
Consider the molecule NO (Z for N is 7 and Z is 8 for O).
i) How many valence electrons are there in the molecule?
ii) Draw the molecular orbital energy diagram corresponding to the valence orbitals. Indicate if the MOs are bonding or antibonding, and if they are \( \pi \) or \( \sigma \). If you want to include the core orbitals as well that is fine, but then be sure to label which MOs are valence orbitals.
Assume the diagram is similar to that for \( O_2 \), where the \( \sigma \) orbital arising from an interaction of 2p orbitals lies below the \( \pi \).
iii) Draw in the electronic structure of NO, and use it to determine
(a) the magnetic properties of NO\(^+\), and (b) the bond order in neutral NO. (c) Assuming the bond strength of NO is 250 kJ mol\(^{-1}\), predict the bond strength of NO\(^-\). (d) What is the spin multiplicity of NO\(^-\)?
iv) Briefly state the main reasons why the following orbital interactions have little or no impact on the MO diagram:
(a) 2p\(_x\) on the N atom with 2s on the O atom, and
(b) 2s on the N atom with 1s on the O atom.
v) Name one other diatomic molecule which is isoelectronic with NO\(^-\).

\[ \text{energy} \]

\[ \begin{align*}
\text{energy} & \\
\sigma & \\
\pi & \\
\pi^* & \\
\sigma^* & \\
\end{align*} \]

(iii) a) NO\(^+\) is diamagnetic
\[ \frac{8-3}{2} = 2 \frac{1}{2} \]
b) with strength approx. proportional to B.O., and B.O. of NO\(^+\) = 5,
bond strength \( \propto 250 \text{ kJ mol}^{-1} \times \frac{3}{2} = 300 \text{ kJ mol}^{-1} \)
c) Extra electron in NO\(^-\) yields the following \( \pi^* \) occupation:
\[ \begin{align*}
\text{unsinged electron means} & \ 2S+1 = 3, \text{ a triplet,} \\
\text{orthogonal} & \\
\text{Far apart in energy,} \\
\text{Examples include} & \ O_2 \text{ and NF,} \\
\end{align*} \]
2) 20 points

Starting with expressions for the degeneracy and energy of the Jth rotational level of a linear molecule whose rotational constant is B (in Hz), prove that the most populated rotational level, where \( J = J_{\text{max}} \), satisfies the relation

\[(2J_{\text{max}} + 1)^2 = 2k_B T/(\hbar) \]

where \( T \) is the temperature, \( k_B \) is Boltzmann’s constant and \( \hbar \) is Planck’s constant.

See class discussion.

Relative population
\[
P = (2J+1) e^{-\frac{\hbar B J(J+1)}{kT}}
\]

\[
\frac{dP}{dJ} = (2J+1) e^{-\frac{\hbar B (J+1)}{kT}} 
- \frac{\hbar B}{kT} (2J+1) + e^{-\frac{\hbar (J+1)}{kT}} \cdot 2
\]

\[
= 0 \quad \text{when} \quad J = J_{\text{max}}
\]

\[J_{\text{max}} \text{ satisfies} \quad \frac{(2J+1)^2\hbar}{kT} = 2 \quad \therefore \]

\[
(2J_{\text{max}} + 1)^2 = \frac{2kT}{\hbar}
\]
3) 15 points

i) Consider a bonding MO formed between two different atoms A and B, \( \Phi = 4 \psi_A + 3 \psi_B \), where \( \psi_A \) and \( \psi_B \) are normalized AOs on the atoms A and B, respectively. Normalize \( \Phi \) in terms of the overlap integral, S. What can you say about the electronegativities of atoms A and B?

\[
\int_{\text{all space}} \Phi^* \Phi \, d\tau = \int (4 \psi_A^* + 3 \psi_B^*) (4 \psi_A + 3 \psi_B) \, d\tau
\]

\[
= 16 \int \psi_A^2 \, d\tau + 9 \int \psi_B^2 \, d\tau + 24 \int \psi_A \psi_B \, d\tau
\]

\[
= 16 + 9 + 24 S
\]

\[
\therefore \text{normalized } \Phi = \frac{4 \psi_A + 3 \psi_B}{\sqrt{25 + 24 S}}
\]

Because the coefficient for \( \psi_A \) is larger, that tells us atom A is the more electronegative atom.
The microwave spectrum of the Orion nebula shows an emission line at 231.0 GHz attributed to CO (the relative atomic masses of C and O are 12 and 16, respectively, and the bond length is $1.128 \times 10^{-10}$ m). What is the initial $J$ value for the emitting rotational level?

\[
\mu = \frac{12 + 16}{12 + 16} \text{amu} = 6.857 \text{amu} = \frac{6.857 \text{ amu}}{1000} \text{ kg} = 6.857 \times 10^{-28} \text{ kg},
\]

\[
I = \mu r^2 = 1.189 \times 10^{-26} \times (1.128 \times 10^{-10})^2 \text{ kg m}^2 = 1.499 \times 10^{-46} \text{ kg m}^2
\]

\[
B = \frac{\hbar}{8\pi^2 I} = 5.792 \times 10^{10} \text{ Hz} = 57.92 \text{ GHz},
\]

For emission, rotational energy is lost and $J$ goes down: $\Delta J = -1$.

The energy of the emitted photon is $E = E_J - E_{J-1}$

\[
= \hbar B (J+1) - \hbar B (J-1)J = \hbar B (J^2 + J - J^2 - J) = 2\hbar B J.
\]

The photon's frequency is $\frac{E}{\hbar} = 2BJ = 2310 \text{ GHz}$ here,

\[
2 \times 57.92 \times J = 2310 \quad \therefore \quad J = 1.994 \quad \text{i.e.} \quad J = 2.
\]