SOME POSSIBLY USEFUL INFORMATION:

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

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

H atom mass = 1.66 \( \times 10^{-27} \text{ kg} \) \hspace{1cm} electron mass = 9.11 \( \times 10^{-31} \text{ kg} \)

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

Planck: \( E = hv \) \hspace{1cm} Schrödinger: \( \hat{H} \psi = E \psi \) \hspace{1cm} de Broglie: \( \lambda = \frac{h}{p} \)

x operator is multiply by x \hspace{1cm} p operator is \( \frac{h}{2\pi} \frac{d}{dx} \)

\( E_K \) operator is \( -\frac{h^2}{(8\pi^2 m)} \frac{d^2}{dx^2} \) \hspace{1cm} V operator is multiply by V

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

\( g_J = 2J + 1 \) \hspace{1cm} \( B = \frac{h}{(8\pi^2 I)} \text{ in Hz} \) \hspace{1cm} \( E_J = BhJ(J+1) \)

\( \sin^2 x = \frac{1 - \cos 2x}{2} \) \hspace{1cm} \( \cos^2 x = \frac{1 + \cos 2x}{2} \)

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

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

\( |L^2| = l(l + 1) \frac{\hbar^2}{4\pi^2} \) \hspace{1cm} \( L_z = m\hbar/(2\pi) \)
1) 50 points
Consider the diatomic species CN (Z for C and N is 6 and 7, respectively).

i) How many valence electrons are there?

ii) Draw the MO energy diagram corresponding to the valence orbitals. If you want to include the core orbitals as well that is fine, but be sure to label which MOs are valence orbitals.

iii) Draw in the electronic structure of CN, and use it to determine the following properties for both neutral CN and the CN⁻ anion:
   (a) the magnetic properties, (b) the bond orders, (c) the spin multiplicities of both molecules, and
   (d) the relative bond strength of CN relative to CN⁻.

iv) Briefly state the main reasons why the following orbital interactions have little or no impact on the energy of CN:
   a) 1s on C with 1s on N, (b) 1s on C with 2s on N, (c) 2s on C with 2pₓ on N.

   i) There are 13 electrons in total, 4 are in 1s orbitals leaving 9 valence electrons.

   iii) CN⁻ has an extra electron in the 2s
   (a) CN paramagnetic, CN⁻ diamagnetic.
   (b) 2s, in 2s and 3 for CN, CN⁻.
   (c) 2s+1 results 2, 1 for CN, CN⁻.
   (d) Bond strength of CN about \( \frac{2\times\frac{1}{2}}{2} \) of CN⁻.

iv) (e) Orbitals tightly bound; little overlap

1s, C  O  O  1s, N

(f) Orbitals far apart in energy:

1s, C  O  O  1s, N

(g) Orbitals not orthogonal.

2s, C  O  O  2p, N.

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2) 50 points
The microwave spectrum of the $^{39}$K$^{35}$Cl molecule has lines spaced by 0.4 cm$^{-1}$. Use this information to deduce the bond length. Starting with the degeneracy and rotational energy, derive J for the most populated rotational level at 400 K. *Be sure to show all work; little credit will be awarded for a formula quoted without derivation.*

\[
\text{rel. pop. } \propto g \exp \left( -\frac{E}{kT} \right) = (2J+1) \exp \left( -\frac{J(J+1)\hbar^2}{kT} \right) = (2J+1) e^{-\frac{J(J+1)\hbar^2}{kT}}.
\]

where \( a = \frac{\hbar}{kT} \).

\[
\text{Max. pop. where } 0 = \frac{dP}{dJ} = (2J+1) e^{-\frac{a}{2}} - a(2J+1) e^{-\frac{a}{2}} - a(2J+1) e^{-\frac{a}{2}} + a(2J+1) = 2.
\]

\[
\Rightarrow a \left( 2J+1 \right)^2 = 2 \Rightarrow 2J+1 = \sqrt{\frac{2}{a}} = \sqrt{\frac{2kT}{\hbar^2}}.
\]

Here, \( 2k = 0.4 \text{ cm}^{-1} \times 2.43 \times 10^{13} \text{ cm}^{-1} \), \( \hbar = 5.996 \times 10^{-34} \text{ J-s} \).

At 400 K, \( 2J+1 = \sqrt{\frac{2 \times 0.4 \times 2.43 \times 10^{13}}{5.996 \times 10^{-34} \times 6.63 \times 10^{-34}}} = 52.7 \)

\[\therefore J = 25.9 \text{ i.e. } 26 \text{ (must be an integer)}.\]
3) 25 points

i) Consider a MO formed between two atoms A and B, \( \Phi = \psi_A + c \psi_B \), where \( c \) is a constant and \( \psi_A \) and \( \psi_B \) are normalized AOs on atoms A and B, respectively. Normalize \( \Phi \) in terms of \( c \) and the overlap integral, \( S \).

\[ \psi_1 = s + (3/2)^{0.5} p_x - (1/2)^{0.5} p_y \]
\[ \psi_2 = s - (3/2)^{0.5} p_x + (1/2)^{0.5} p_y \]

ii) Are the following two linear combinations of AOs on a single atom orthogonal? Be sure to explain your reasoning.

\[ \int_{\text{all } \text{space}} \Phi^* \Phi \, d\tau = \int (\psi_A + c \psi_B)^* (\psi_A + c \psi_B) \, d\tau = \int (\psi_A^2 + 2c \psi_A \psi_B + c^2 \psi_B^2) \, d\tau \\
= 1 + 2cS + c^2 \]

So normalized \( \Phi \) is 
\[ \frac{\psi_A + c \psi_B}{\sqrt{1 + 2cS + c^2}} \]

\[ \int \psi_1^* \psi_2 \, d\tau = \int (s + \sqrt{3/2} p_x - \frac{1}{\sqrt{2}} p_y)(s - \sqrt{3/2} p_x + \frac{1}{\sqrt{2}} p_y) \, d\tau \\
= \int (s^2 - \frac{3}{2} p_x^2 - \frac{1}{2} p_y^2 + \text{cross terms}) \, d\tau \],

Upon integration all "cross terms" like \( s \cdot p_x \to 0 \) become \( s \) and \( p_x \) on the same atom are orthogonal. The integral becomes

\[ 1 - \frac{3}{2} \frac{1}{2} = -1 \to \text{ not orthogonal} \]