SOME POSSIBLY USEFUL INFORMATION:

N_A or L = 6.022 x 10^{23} \text{ mol}^{-1} \quad h = 6.626 \times 10^{-34} \text{ Js}

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

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

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

Planck: E = hv \quad \text{Schrodinger: } \hat{H}\psi = E\psi \quad \text{de Broglie: } \lambda = \hbar/p

x operator is multiply by x \quad p operator is \quad h/(2\pi i) d/dx

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

\sin^2 x = (1 - \cos 2x)/2 \quad \cos^2 x = (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) \hbar^2/(4\pi^2) \quad \text{L}_z = m_l \hbar/(2\pi)
1) 40 points
Consider the molecule B₂ (Z for B is 5).

i) How many valence electrons are there in the molecule? 6

ii) Draw the molecular orbital energy diagram corresponding to the valence orbitals. Indicate if the MOs are bonding or antibonding, and if they are π or σ. 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 others for early elements in the periodic table, where the σ orbital arising from an interaction of 2p orbitals lies above the π. Explain briefly why this happens.

iii) Draw in the electronic structure of B₂, and use it to determine
(a) the magnetic properties of B₂, and (b) the bond order in B₂. (c) Assuming the bond strength of B₂ is 300 kJ mol⁻¹, predict the bond strength of B₂⁺.

iv) Briefly state the main reasons why the following orbital interactions have little or no impact on the MO diagram:
(a) 2pₓ on one B atom with 2s on the other B, and
(b) 2s on one B with 1s on the other B.

v) Name one other diatomic molecule which is isoelectronic with B₂.

\[ \text{i)} \ 6 \ ii) 2p\sigma \text{ mixes with } 2s\sigma \text{ pushing up } 2p\sigma \text{ (and lowering so that } 2p\sigma \text{ is above } 2s\sigma^* \text{)} \\
\text{iii)} \ a) 2\text{ unpaired electrons therefore paramagnetic} \\
\text{b)} B.O. \text{ is } 1 \ (2e^- \div 2). \\
\text{c)} B.O. \text{ of } B_2^+ \text{ is } 12 \ \\
\text{bond strength } M \cdot M = 300 \text{ kJ mol}^{-1} = 150 \text{ kJ mol}^{-1} \]

\[ \sigma \text{ overlap here cannot that from here} \]

\[ \text{upon mixing energy change is small} \]
2) 30 points

i) An approximate wavefunction that describes an atomic orbital contains an adjustable parameter \( a \). With this approximate \( \psi \), the expectation value of the total energy \( E \) is found to be of the form \( \langle E \rangle = a - C a^{1/3} \) where \( C \) is a positive combination of physical constants. Use the variational principle to find the best value of \( a \) in terms of \( C \).

\[
\frac{d \langle E \rangle}{da} = 1 - \frac{1}{3} C a^{-2/3} = 0 \text{ at minimum,}
\]

so \( 3 = C a^{-2/3} \) and \( a^{2/3} = C/3 \).

\[
a = (C/3)^{3/2}.
\]

ii) When an alkali metal (Group 1) atom has its single outer electron in an \( s \) orbital the atom has a single energy, but if the electron is promoted to a \( p \) orbital, two energies are possible for the atom. Why?

i) The variational principle says that the best approximation minimizes \( \langle E \rangle \), because \( \langle E \rangle \) is above the exact energy.

\[
\frac{d \langle E \rangle}{da} = 1 - \frac{1}{3} C a^{-2/3} = 0 \text{ at minimum,}
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\]

ii) See notes. When the \( e^- \) is in a \( p \) orbital with \( l = 1 \), there is an opportunity for spin-orbit interaction and two states are possible, with the \( e^- \)'s spin aligned either with or against the orbital angular momentum, so that total angular momentum is \( j = l \pm \frac{1}{2} \) is given by \( j = \frac{1}{2} \) or \( j = \frac{3}{2} \). When the \( e^- \) is in an \( s \) orbital, \( l = 0 \) and there is no spin-orbit coupling.
3) 30 points
i) Consider a bonding MO formed between two different atoms A and B, \( \Phi = 3 \psi_A + 5 \psi_B \), where \( \psi_A \) and \( \psi_B \) are normalized AOs on atoms A and B, respectively. Normalize \( \Phi \) in terms of the overlap integral, S. What can you deduce about the electronegativities of atoms A and B?

ii) Are the following two linear combinations of AOs on a single atom orthogonal? You may assume the individual atomic orbitals are normalized. Be sure to explain your reasoning carefully and any results you rely on.

\[ \psi_1 = (s - p_x + p_y + p_z) \]
\[ \psi_2 = (s + p_x - p_y + p_z) \]

\[ \int \psi_1^* \psi_2 \, d\tau = \int (s^2 + p_x^2 + 25p_y^2 + 20s^2) \, d\tau \]

\[ = 9 + 25 + 20S = 34 + 20S \]

Normalized \( \psi \) is \( \frac{3\psi_A + 5\psi_B}{\sqrt{34 + 20S}} \)

Because the coefficient of \( \psi_B \) is larger, B is more electronegative.

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

\[ = 1 - 1 - 1 + 1 + 0 = 0 \]

Yes, orthogonal.

Cross terms like \( s \cdot p_x \) integrate to zero because any two different orbitals on the same atom are orthogonal.