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:**

\[ N_A \text{ or } L = 6.022 \times 10^{23} \text{ mol}^{-1} \]
\[ h = 6.626 \times 10^{-34} \text{ J s} \]
\[ k_B = 1.38 \times 10^{-23} \text{ J K}^{-1} \]
\[ c = 2.998 \times 10^8 \text{ m s}^{-1} \]
\[ \text{H atom mass} = 1.66 \times 10^{-27} \text{ kg} \]
\[ \text{electron mass} = 9.11 \times 10^{-31} \text{ kg} \]
\[ R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \]

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

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

\[ E_v = (\nu + 1/2) h \nu \]
\[ \nu = (k/\mu)^{1/2}/(2\pi) \]
\[ g_J = 2J + 1 \]
\[ B = h/(8\pi^2I) \text{ in Hz} \]
\[ E_J = Bh(J+1) \]

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

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

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.}

\[ |L^2| = l(l+1) h^2/(4\pi^2) \]
\[ L_z = m_l h/(2\pi) \]
1) 40 points
Consider the molecule B₂ (Z for B is 5).

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 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 that for other early elements, where the σ orbital arising from an interaction of 2p orbitals lies above the π.

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⁺. (d) What is the spin multiplicity of B₂?

iv) Briefly state the main reasons why the following orbital interactions have little or no impact on the MO diagram:

(a) 2pz on one B atom with 2s on the other B atom, and

(b) 2s on one B atom with 1s on the other B atom.

v) Give the formula for one other diatomic molecule, neutral or charged, which is isoelectronic with B₂.

\[\text{B}^2 \] (2s²2p² for both atoms)

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\[\text{Energy}\]

\[\begin{array}{c}
\sigma^+ \\
\pi^+ \\
\sigma \\
\pi \\
\end{array}\]

\[\text{(a) unpaired electrons so paramagnetic}\]

\[\text{(b) Bond order} = 1\]

\[\text{(c) } B_2^+ \text{ loses a bonding electron so new bond order} = \frac{1}{2}.\]

\[\text{Bond strength of } B_2^+, \text{ therefore} \approx \frac{1}{2} \times 300 \text{ kJ mol}^{-1} = 150 \text{ kJ mol}^{-1}.\]

\[\text{(d) } S = \frac{1}{2} + \frac{1}{2} = 1, \quad 2S+1 = 3\]

\[\text{(e) } 2p_z \text{ and } 2s \text{ are orthogonal by symmetry}.\]

\[\text{(f) The } 1s \text{ is tightly held and small, so overlap with the neighboring } 2s \text{ is poor. Also, the } 1s \text{ and } 2s \text{ energies are far apart so the energy change upon interaction is small}.\]

\[\text{v) Candidates include } \text{BeC}, \text{ LiN}, \text{ Be}^+, \text{ Be}^+, \text{ BeB}^-, \text{ LiC}^-\]
Imagine a system defined by a quantum number "q", where the energy of each state is $aq^2$ and the degeneracy is $3q$.

Prove that the most populated level, where $q = q_{\text{max}}$, satisfies the relation $q_{\text{max}}^2 = k_BT/(2a)$ where $T$ is the temperature and $k_B$ is Boltzmann's constant.

Boltzmann probability $\propto e^{-\frac{aq^2}{kT}}$

relative population $P = 3q \cdot e^{-\frac{aq^2}{kT}}$

max $P$ when $\frac{dP}{dq} = 0 = 3q \cdot e^{-\frac{aq^2}{kT}} \cdot -2aq + e^{-\frac{aq^2}{kT}} \cdot 3$

$\therefore \delta = \frac{6}{kT} \cdot q^2 = \frac{3kT}{6a} = \frac{kT}{2a}$. 


3) 10 points

i) Consider the following two linear combinations of atomic orbitals on the same atom. Are they orthogonal? Briefly justify any short cuts you rely on to reach your conclusion.

\[ \psi_1 = s + \frac{1}{\sqrt{2}} p_y + \frac{\sqrt{3}}{\sqrt{2}} p_x \]

\[ \psi_2 = s - \frac{1}{\sqrt{2}} p_y - \frac{\sqrt{3}}{\sqrt{2}} p_x \]

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

\[ = 1 - \frac{3}{2} + 0 = 0 \quad \text{so } \psi_1, \psi_2 \text{, orthogonal.} \]

The integral of cross terms like \( s \cdot p_y \) is zero because any two different atomic orbitals on the same atom are orthogonal.
4) 30 points
i) Sketch the anharmonic potential energy curve for a diatomic molecule, marking in $r_e$, $D_e$ and $D_0$. How does the difference between $D_e$ and $D_0$ depend on the vibrational frequency $v$?

\[ D_e = D_0 + \frac{1}{2} \hbar \nu \]

![Energy diagram](image)

ii) Imagine that new isotopes are substituted so as to increase the reduced mass. Without needing to show work, state whether each of the three quantities $r_e$, $D_e$ and $D_0$ will decrease, increase or stay the same.

iii) Assume the energy of the vibrational level corresponding to quantum number $v$ is equal to

\[ E_v = \hbar \nu \left( (v+1/2) - x_e(v+1/2)^2 \right) \]

where $x_e$ is the anharmonicity constant. Prove that the energy gap between successive levels is

\[ \Delta E_v = \hbar \nu - \hbar \nu x_e(2v+2). \]

What value of $v$ (in terms of $\hbar$, $\nu$ and/or $x_e$) corresponds to the dissociation limit?

\[ E_{v+1} - E_v = \Delta E = \hbar \nu \left[ (v+1/2) - (v+1/2) + x_e(v+1/2)^2 - x_e(v+3/2)^2 \right] \]

\[ = \hbar \nu \left[ 1 + x_e(v^2 + v + 1/4 - v^2 - 3v - 9/4) \right] \]

\[ = \hbar \nu \left[ 1 - x_e(2v + 2) \right]. \]

At the dissociation limit $\Delta E \to 0$

\[ \text{so } x_e = \frac{1}{2v+2} \text{ and } v = \frac{1}{2x_e} - 1. \]