Please write neatly and clearly. Allocate time to each question in proportion to the available credit, and keep explanations to the point.

Your name: SOLUTIONS

SOME POSSIBLY USEFUL INFORMATION:

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

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

\[ \hat{x} \text{ operator is multiply by } x \]
\[ \hat{p} \text{ operator is } h/(2\pi) \frac{d}{dx} \]
\[ \hat{E}_k \text{ operator is } -h^2/(8\pi^2 m) \frac{d^2}{dx^2} \]
\[ \hat{V} \text{ operator is multiply by } V \]
\[ L^2 = \ell (\ell + 1) \frac{h^2}{4\pi^2} \]
\[ L_z = m_e h/(2\pi) \]

IP of 1-electron atom proportional to \( Z^2/n^2 \). IP of H = 13.6 eV = 2.18 \times 10^{-18} \text{ J}

\[ \int x^n \exp(-cx) \, dx = \frac{n!}{c^{n+1}} \]
\[ \int \sin^2 x \, dx = \frac{x - 0.5 \sin(2x)}{2} + \text{const} \]
1) 36 points

Draw the molecular orbital energy diagram for the molecule N₂ (Z for N is 7), on the assumption that the σ orbital formed by mixing atomic 2p orbitals lies above the π orbitals formed from 2p orbitals. Label the MOs according to their symmetry, i.e., indicate whether they are σ or π, and show their parity with respect to reflection in a plane and inversion through the center of symmetry. Draw in the electron configuration of N₂. Use your diagram to predict the magnetic properties, spin multiplicity, bond orders and bond strengths of N₂, N₂⁻ and N₂²⁻ and complete the table below.

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MOs

\[ \sigma_\text{u}^+ \] (x)
\[ \pi_\text{g}^- \] (x)
\[ \pi_\text{g}^+ \]
\[ \sigma_\text{u}^- \]
\[ \sigma_\text{u}^- \]
\[ \pi_\text{u}^- \]
\[ \pi_\text{u}^- \]

* = antibonding
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<table>
<thead>
<tr>
<th>Molecule</th>
<th>Magnetic properties</th>
<th>Spin multiplicity</th>
<th>Bond order</th>
<th>Bond strength, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>diamagnetic</td>
<td>1</td>
<td>3</td>
<td>400</td>
</tr>
<tr>
<td>N₂⁻</td>
<td>paramagnetic</td>
<td>2</td>
<td>2(\sqrt{2})</td>
<td>(\frac{2\sqrt{2}}{3} \times 400 = 333)</td>
</tr>
<tr>
<td>N₂²⁻</td>
<td>paramagnetic</td>
<td>3</td>
<td>2</td>
<td>(\frac{2}{3} \times 400 = 267)</td>
</tr>
</tbody>
</table>
2) 10 points
On the axes below, sketch typical potential energy curves for bonding and antibonding MOs.

3) 28 points
i) A bonding molecular orbital \( \Phi \) is defined as \( c_1 \psi_A + c_2 \psi_B \) where \( \psi_A \) and \( \psi_B \) are normalized atomic orbitals on different atoms. Find the normalized wavefunction in terms of the overlap integral \( S \) and \( c_1 \) and \( c_2 \).

ii) If atoms A and B have similar electronegativities, what values of \( c_1 \) and \( c_2 \) do you expect?

iii) If A is much more electronegative than B, what values of \( c_1 \) and \( c_2 \) do you expect?

iv) How are the “best” values of \( c_1 \) and \( c_2 \) defined? Define any principles you rely on.

\[
\int \Phi^2 \, d\tau = \int \left( c_1^2 \psi_A^2 + c_2^2 \psi_B^2 + 2c_1c_2 \psi_A \psi_B \right) \, d\tau = c_1^2 + c_2^2 + 2c_1c_2 S
\]

normalized \( \Phi \) is

\[
\frac{c_1 \psi_A + c_2 \psi_B}{\sqrt{c_1^2 + c_2^2 + 2c_1c_2 S}}
\]

i) Similar values, \( c_1 \approx c_2 \). About 1, before normalization.

ii) \( c_1 \gg c_2 \). \( c_1 \approx 1, c_2 \approx 0 \), before normalization.

iv) The variational principle states that for an approximate \( \psi \), \( \langle E \rangle > \text{exact } E \). Thus the best approximation is the one that yields the most negative \( \langle E \rangle \), where

\[
\frac{\partial \langle E \rangle}{\partial c_1} = \frac{\partial \langle E \rangle}{\partial c_2} = 0.
\]
4) 26 points

Two hybrid orbitals, constructed from normalized atomic s and p orbitals, are
\[ \psi_1 = 3^{-1/2} s - 6^{-1/2} p_x + 2^{-1/2} p_y \quad \text{and} \quad \psi_2 = 3^{-1/2} s - 6^{-1/2} p_x - 2^{-1/2} p_y. \]

i) Prove that \( \psi_2 \) is normalized. Show work.

ii) Prove that \( \psi_1 \) and \( \psi_2 \) are orthogonal. Show work.

i)
\[
\int \psi_1 \psi_2^* \, d\tau = \int \left( \frac{1}{\sqrt{3}} s - \frac{1}{\sqrt{6}} p_x + \frac{1}{\sqrt{2}} p_y \right) \left( \frac{1}{\sqrt{3}} s - \frac{1}{\sqrt{6}} p_x - \frac{1}{\sqrt{2}} p_y \right) \, d\tau
\]
\[
= \int \left( \frac{1}{3} s^2 + \frac{1}{\sqrt{6}} p_x^2 + \frac{1}{2} p_y^2 + \text{cross terms like } \frac{1}{\sqrt{18}} s p_x \right) \, d\tau
\]
\[
= \frac{1}{3} + \frac{1}{6} + \frac{1}{2} = 1
\]

Integrates to zero because different nos on the same atom are orthogonal.

ii)
\[
\int \psi_1 \psi_2^* \, d\tau = \int \left( \frac{1}{\sqrt{3}} s - \frac{1}{\sqrt{6}} p_x + \frac{1}{\sqrt{2}} p_y \right) \left( \frac{1}{\sqrt{3}} s - \frac{1}{\sqrt{6}} p_x - \frac{1}{\sqrt{2}} p_y \right) \, d\tau
\]
\[
= \int \left( \frac{1}{3} s^2 + \frac{1}{\sqrt{6}} p_x^2 - \frac{1}{2} p_y^2 + \text{cross terms} \right) \, d\tau
\]
\[
= \frac{1}{3} + \frac{1}{6} - \frac{1}{2} + 0 = 0.
\]