

Work through the notes on the variation principle and Huckel molecular orbital theory.

Question 1 (2000 General Physical Chemistry I, Question 6)

- a) Sketch the molecular orbital diagrams of the hydrogen and oxygen molecules, H_2 and O_2 . Give the term symbols of the ground states of each molecule, explaining the meaning of each label you use.
- b) O_2 possesses two low-lying excited electronic states, at 7900 cm^{-1} and 13200 cm^{-1} above the ground state. Give the term symbols for the two excited electronic states, and rationalise the energy ordering of the ground state and the two excited states. Why are the two low-lying excited electronic states of O_2 expected to have long radiative lifetimes?
- c) The highest electron kinetic energy features in the photoelectron spectra of H_2 and O_2 , associated with the transitions to the lowest electronic states of the ions, both display progressions of bands. For H_2 many bands are observed, and the lower bands in the progression are separated by 2300 cm^{-1} . For O_2 only a small number of bands are observed, and the bands are separated by 1900 cm^{-1} . At higher resolution each of the bands in O_2 is found to be doubled. The vibrational wavenumbers for H_2 and O_2 in their ground electronic states are 4400 cm^{-1} and 1600 cm^{-1} , respectively. For each spectrum give the term symbol(s) for the state(s) of the ion involved. Rationalise the spectral features (both the number of bands and band separations) observed.

Question 2 (1999 General Physical Chemistry II, Question 4)

- a) The lowest three electronic states of the N_2^+ ion have the symmetries $^2\Sigma_g^+$, $^2\Pi_u$, and $^2\Sigma_u^+$, and each can be accessed by removal of one electron from the ground electron configuration of N_2 . Identify the electronic configurations giving rise to each, and discuss the meaning of the term symbols employed.
- b) The vibrational wavenumbers and rotational constants for these states are listed below.

State	$\omega_e / \text{cm}^{-1}$	B_e / cm^{-1}
$^2\Sigma_g^+$	2207.0	1.9317
$^2\Pi_u$	1903.7	1.7444
$^2\Sigma_u^+$	2419.8	2.0746

For the ground state of N_2 , $\omega_e = 2358.6\text{ cm}^{-1}$ and $B_e = 1.998\text{ cm}^{-1}$. Discuss these values in terms of the molecular orbital diagram for N_2 and N_2^+ .

- c) The electronic emission spectrum of N_2^+ involving the states listed above shows one band with an origin at 9015.5 cm^{-1} with a band head in the R branch, while another band occurs at 25556 cm^{-1} with a band head in the P branch. Identify the electronic states involved, giving reasons for your assignment. The wavenumbers of transitions in the R branch are given by

$$\bar{\nu}_J = \bar{\nu}_0 + (B' + B'')(J + 1) + (B' - B'')(J + 1)^2$$

where B' and B'' are the rotational constants for the upper and lower states and $\bar{\nu}_0$ is the band origin.

Question 3

- For a trial wavefunction of the form $\psi = c_A \phi_A + c_B \phi_B$, where ϕ_A and ϕ_B are normalised atomic orbitals on different atoms and c_A and c_B coefficients, derive the secular equations.
- Show that the roots of these equations when the orbitals ϕ_A and ϕ_B are orthogonal ($S_{AB}=0$) are given by

$$E_{\pm} = \frac{H_{AA} + H_{BB}}{2} \pm \frac{1}{2} \left[(H_{AA} - H_{BB})^2 + 4H_{AB}^2 \right]^{\frac{1}{2}}$$

- Find the coefficients c_A and c_B for the molecular orbitals associated with E_+ and E_- for the special cases
 - $H_{AA}=H_{BB}$ (homonuclear diatomics)
 - $H_{AA}=2H_{BB}=\alpha$, $H_{AB}=\alpha/4$.

For i) above, describe and explain the variations in the relative magnitudes of c_A and c_B as the electronegativity of atom A increases relative to atom B.

Question 4

- The k^{th} molecular orbital for a linear chain of N carbon atoms has the form

$$\psi_k \propto \sum_{m=1}^N \phi_m \sin\left(\frac{mk\pi}{N+1}\right)$$

where ϕ_m is a π_p orbital on atom m. Find its energy within Huckel theory by substitution into the secular equations.

- Sketch the lowest three orbitals for a six-membered chain. By considering the relative phases of each molecular orbital on the first and last atoms, show that orbitals with odd values of k are stabilized and those with even values of k are destabilized if the chain is converted to a ring.