

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

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

- 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.
- $O_2$  possesses two low-lying excited electronic states, at  $7900\text{ cm}^{-1}$  and  $13200\text{ cm}^{-1}$  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?
- 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  $2300\text{ cm}^{-1}$ . For  $O_2$  only a small number of bands are observed, and the bands are separated by  $1900\text{ cm}^{-1}$ . 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  $4400\text{ cm}^{-1}$  and  $1600\text{ cm}^{-1}$ , 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)

- 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.
- The vibrational wavenumbers and rotational constants for these states are listed below.

State	$\omega_e / \text{cm}^{-1}$	$B_e / \text{cm}^{-1}$
$^2\Sigma_g^+$	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  $N_2^+$ .

- The electronic emission spectrum of  $N_2^+$  involving the states listed above shows one band with an origin at  $9015.5\text{ cm}^{-1}$  with a band head in the R branch, while another band occurs at  $25556\text{ cm}^{-1}$  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

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

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

- c) 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

- a) The  $k^{\text{th}}$  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  $\phi_m$  is a  $\pi_p$  orbital on atom m. Find its energy within Huckel theory by substitution into the secular equations.

- b) 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.