

University of Canterbury

## End-of-year Examinations 2009

Prescription Number(s): CHEM 373

Paper Title: Chemical Physics

Time Allowed: Two hours

Number of pages: Six

This paper is divided into **TWO** sections.

SECTION A: Answer **BOTH** questions.  
(Worth two-thirds of total marks.)

SECTION B: Answer **ONE** question out of  
**THREE**.  
(Worth one-third of total marks.)

*TURN OVER*



**SECTION A**

(Answer **BOTH** questions in this section.)

1. (a) Explain briefly the following terms:
    - (i) Bohr correspondence principle
    - (ii) second-order energy, and
    - (iii) raising operator.
  - (b) Explain why Hermitian operators are important in quantum mechanics.
  - (c) Under what conditions can the variation method be applied to calculate an approximate wavefunction for an excited state.
  - (d) Outline the approximations made in Hückel molecular orbital theory.
  - (e) Show that  $[L^2, L_z] = 0$ . What is the significance of the result?
- 
2. Complete **FIVE** of the following tasks (a) – (g):
    - (a) Outline, with examples, the advantages of Fourier-transform spectroscopy using a broad-band radiation source, over conventional spectroscopy with one or more slits and a dispersive element such as a grating.
    - (b) Describe a method of doing spectroscopy with a narrow-band radiation source that is not limited by the large Doppler width of the absorption line of a gaseous sample.
    - (c) Explain why cold-cathode lamps are used as light sources during analysis by atomic absorption spectroscopy.
    - (d) Explain why it is often an advantage to do spectroscopy with a sample that is being carried into vacuum by a supersonic jet of helium gas.
    - (e) Explain the fundamental difference between Fourier-transform nmr and Fourier-transform infrared spectroscopy.
    - (f) Explain why femtosecond laser spectroscopy does not have very good wavelength resolution.
    - (g) Outline the advantages, in low light-intensity spectroscopy such as Raman spectroscopy, of using a CCD detector rather than a slit followed by a photomultiplier.

*TURN OVER*

## SECTION B

(Answer ONE question from this section.)

3.  $\text{OWF}_4$  is a tetragonal-pyramidal molecule with  $C_{4v}$  symmetry, the character table for which is given below. The tungsten atom is bound to four fluorine atoms in a square planar arrangement, with the oxygen atom in the apical position above the tungsten.

$C_{4v}$	$E$	$2C_4$	$C_2$	$2\sigma_v$	$2\sigma_d$		
$A_1$	1	1	1	1	1	$z$	$x^2 + y^2, z^2$
$A_2$	1	1	1	-1	-1	$R_z$	
$B_1$	1	-1	1	1	-1		$x^2 - y^2$
$B_2$	1	-1	1	-1	1		$xy$
$E$	2	0	-2	0	0	$(x, y), (R_x, R_y)$	$(yz, xz)$

- (a) How many independent vibrational modes does  $\text{OWF}_4$  have?
- (b) Determine the characters for the following representations under each of the symmetry classes of the  $C_{4v}$  point group:
- $\Gamma_{3N}$
  - $\Gamma_{\text{trans}}$
  - $\Gamma_{\text{rot}}$
- (c) From the results in (b), determine the characters for the representation  $\Gamma_{\text{vib}}$ . Use these to determine the reduced form of  $\Gamma_{\text{vib}}$  – that is as a sum of irreps.
- (d) Define a set of internal basis coordinates that describes the *stretching* vibrations of  $\text{OWF}_4$ . By consideration of the number of unshifted stretching coordinates, show that the reduced form of the representation for the *stretching* vibrations is
- $$\Gamma_{\text{str}} = 2A_1 \oplus B_1 \oplus E$$
- (e) From your results in (c) and (d), determine reduced form of the representation for the *bending* vibrations;  $\Gamma_{\text{bend}}$ .
- (f) Derive symmetrised linear combinations for the *stretching* modes of  $\text{OWF}_4$ . **Sketch diagrams for each.**

*Question 3 continued on following page*

**Question 3 continued**

- (g) The vibrational data below were obtained for the *stretching* modes of  $\text{OWF}_4$ . Use these data to assign frequencies to each of the vibrational modes in (f). **Explain your reasoning.**

$\nu$ ( $\text{cm}^{-1}$ )	Raman activity	
	zz polarisation	IR activity
1055	yes	yes
733	yes	yes
698	no	yes
631	no	no

**Useful equations:**

$$a_q = \frac{1}{h} \sum_R n_R \chi(R) \chi_q(R)$$

$$S_r^q = \mathfrak{N} \sum_g \chi_q(g) g(r)$$

4. (a) Explain briefly the following terms:

- (i) Hamilton's equations of motion;
- (ii) free electron molecular orbital theory;
- (iii) degenerate perturbation theory; and
- (iv) Walsh diagram.

- (b) In deriving the expressions for the first-order corrections to the energy and the wave-function in non-degenerate perturbation theory, we write:  $\psi_n^{(1)} = \sum c_i \psi_i^{(0)}$ , where  $\psi_i^{(0)}$  is an eigenfunction of  $H^{(0)}$ . **Define** the term  $H^{(0)}$ . **Why** is this expression exact?

- (c) The total angular momentum operator  $J = L + S$ , where  $L$  is the orbital angular momentum operator and  $S$  is the spin angular momentum operator.

Evaluate:  $J^2 P_0$

- (d) The  $\pi$  molecular orbitals for the cyclopropyl anion are:

$$\Phi_1 = 1/\sqrt{3} (\phi_1 + \phi_2 + \phi_3)$$

$$\Phi_2 = 1/\sqrt{2} (\phi_1 - \phi_2)$$

$$\Phi_3 = 1/\sqrt{6} (-\phi_1 - \phi_2 + 2\phi_3)$$

Determine the energies of each orbital in the Hückel molecular-orbital approximation.

**TURN OVER**

5. **Either**

- (a) Give an account of the Herzberg-Teller effect as it relates to the 'forbidden' 260 nm absorption band of benzene.

**Or**

- (b) Give an account of Hund's coupling cases as they relate to the classification of electronic states of diatomic molecules.

**END OF PAPER**