

University of Canterbury

End of Year Examinations 2007

Prescription Number(s):	CHEM 466
Paper Title:	Theoretical Chemistry

Time Allowed: THREE HOURS

Number of pages: EIGHT

Answer **FOUR** questions out of **SIX**.

All questions are of equal value

TURN OVER

1. (a) In the Russell-Saunders coupling scheme, the angular momenta of a many-electron atom are quantised by the quantum numbers L , S , J and M_J .
- Briefly explain what is meant by Russell-Saunders coupling.
 - Show vectorially that if L , S , J and M_J are *good* quantum numbers, then M_L and M_S must be *poor* quantum numbers.
- (b) The free iron atom has a $^5D(d^6)$ ground state term, which is split by first-order spin-orbit coupling according to eq 1.

$$E_{SO} = \frac{A_{LS}}{2} \{J(J+1) - L(L+1) - S(S+1)\} \quad (1)$$

The energies of the levels in this multiplet (in cm^{-1}) are

0
415
704
888
978

- Is the 5D multiplet regular or inverted? Explain.
- Determine the quantum numbers L and S for the 5D term, and assign a J quantum number to each level.
- Show that the energy difference between two adjacent spin-orbit levels is,

$$E_J - E_{J-1} = A_{LS} J \quad (2)$$

Hence determine an average value for the ground-state spin-orbit coupling constant of Fe.

- (c) Briefly describe the $j-j$ coupling scheme and explain the conditions under which it should be used in preference to Russell-Saunders coupling.

TURN OVER

2. (a) Using high-symmetry (Wigner) coupling coefficients, the Wigner-Eckart theorem can be written as

$$\langle \psi_{\alpha}^a | \hat{O}_{\phi}^f | \phi_{\beta}^b \rangle = \begin{pmatrix} a \\ \alpha \end{pmatrix} \begin{pmatrix} a^* & f & b \\ \alpha^* & \phi & \beta \end{pmatrix} \langle \psi^a || \hat{O}^f || \phi^b \rangle$$

- (i) Describe all of the coefficients and symbols in this equation.
- (ii) Explain how the Wigner-Eckart theorem simplifies quantum-mechanical manipulations.
- (iii) What are the advantages of high-symmetry coupling coefficients over Clebsch-Gordan coefficients?
- (b) The complex ion $[\text{Co}(\text{NH}_3)_6]^{3+}$ has O_h symmetry and a ${}^1A_{1g}$ ground state. The only electric-dipole allowed transitions from the ground state are ${}^1T_{1u} \leftarrow {}^1A_{1g}$.

- (i) Using the Wigner-Eckart theorem and the tables on the next page, show that the magnetic-dipole operator $\hat{\mu}_z$ (or $\hat{\mu}_0$) is diagonal in the complex O_h basis for T_{1u} .
- (ii) In an applied magnetic field of strength B along the z direction, the energy of state $|{}^1T_{1u} \alpha\rangle$ is

$$E_{\alpha} = E({}^1T_{1u}) + \alpha g \mu_B B$$

where $\alpha = 0, \pm 1$ and $\mu_B = -\gamma_e \hbar$ is the Bohr magneton. Show that g is given by

$$g = \frac{-1}{\sqrt{6}\hbar} \langle {}^1T_{1u} || \hat{L}^t_{1g} || {}^1T_{1u} \rangle$$

- (iii) Describe an experiment that would allow you to determine both the magnitude and the sign of the g value for a ${}^1T_{1u}$ excited state of $[\text{Co}(\text{NH}_3)_6]^{3+}$.

Question 2 continued on following page

Question 2 continued

Operator transformation coefficients in the complex O basis		
\hat{O}	$\langle f \hat{O} \phi\rangle$	$f \quad \phi$
V_{-1}, R_{-1}	-1	$T_1 \quad -1$
V_0, R_0	1	$T_1 \quad 0$
V_{+1}, R_{+1}	-1	$T_1 \quad 1$

$2jm$ and $ a^*\alpha^*\rangle$ in the complex O basis		
$ \alpha\alpha\rangle$	$2jm$	$ a^*\alpha^*\rangle$
$A_1 a_1$	1	$A_1 a_1$
$T_1 -1$	1	$T_1 1$
$T_1 0$	-1	$T_1 0$
$T_1 1$	1	$T_1 -1$

3jm in the complex O basis							
T_1	T_1	A_1	$3jm$	T_1	T_1	T_1	$3jm^\dagger$
-1	1	a_1	$1/\sqrt{3}$	-1	0	1	$-1/\sqrt{6}$
0	0	a_1	$-1/\sqrt{3}$				

TURN OVER

3. (a) All possible states of a system can be represented as vectors in an abstract Hilbert space. Explain the following quantum mechanical terms in relation to this concept.
 - (i) Ket vector;
 - (ii) completeness theorem;
 - (iii) overlap integral;
 - (iv) change of state;
 - (v) orthonormality.
- (b) Explain briefly what you understand by the following terms:
 - (i) Hohenberg-Kohn theorems;
 - (ii) coupled-cluster approximation; and
 - (iii) multiconfigurational self consistent field (MCSCF) method
4. Outline the development of the theory of unimolecular reactions, from the simplest Lindemann theory up to a Master equation treatment.

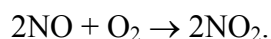
5. (a) What are the assumptions made in the molecular mechanics method? Describe some refinements and extensions that have been made to the simple valence-force field model, explaining why they are necessary for some molecular systems.
- (b) Explain briefly the following terms:
- (i) zero differential overlap (ZDO) approximation;
 - (ii) 6-31G* basis set;
 - (iii) Mulliken population analysis;
 - (iv) exchange operator; and
 - (v) Roothaan equations.
- (c) In describing an *ab-initio* calculation, the term “level of theory” is used. This can apply to both the theoretical method used and the basis set applied. What do you understand by this term? Your answer should indicate what attributes give a higher level of theory.

6. (a) Derive the transition-state theory expression

$$k_{\text{rate}} = \frac{k_{\text{B}}T}{h} \frac{Q^{\ddagger}}{Q_{\text{A}}Q_{\text{B}}} \exp(-\Delta H^{\ddagger} / RT)$$

for the rate constant of a reaction between species A and B, stating all the assumptions made.

- (b) Show that this expression gives the same result as simple collision theory for a reaction in which the reactants A and B are monatomic.
- (c) Show that transition-state theory predicts that pre-exponential factor in the above expression should be much smaller than the value given by simple collision theory if the reactants A and B are diatomic or polyatomic molecules, i.e. that the 'probability factor' of simple collision theory should be much less than 1 for such a reaction.
- (d) Show that transition-state theory predicts that the rate constant should decrease with increasing temperature for a termolecular reaction with little or no activation enthalpy, for example:



END OF PAPER