

University of Canterbury

End of Year Examination 2006

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

Time Allowed: THREE HOURS

Number of pages: EIGHT

Answer **FOUR** questions, including at least ONE question from each Section A and B.

All questions are of equal value.

TURN OVER

SECTION A
(Answer at least ONE question from this section)

1. (a) Explain briefly what you understand by the following terms:

- (i) exchange operator;
- (ii) zero differential overlap approximation;
- (iii) Hohenberg-Kohn theorems.

(b) The ground-state Hartree-Fock wavefunction Ψ for the Be atom is

$$|1s \bar{1s} 2s \bar{2s}|$$

Write down expressions for:

- (i) the one-particle density matrix $P(1)$;
- (ii) the orbital energy ϵ_{2s} ;
- (iii) the matrix element $\langle \Psi | H | \Psi \rangle$;
- (iv) the Hamiltonian matrix element between the ground-state wavefunction and the singlet state obtained by the excitation of an electron from the 2s orbital to 3s orbital:

$$\frac{1}{\sqrt{2}} (|1s \bar{1s} 2s \bar{3s}| - |1s \bar{1s} \bar{2s} 3s|)$$

(c) What is the Born-Oppenheimer approximation? Why is it important?

2. (a) Explain briefly what you understand by the following terms:
- (i) Hylleraas-Pekeris wavefunction for He;
 - (ii) two-particle density matrix;
 - (iii) coupled-cluster approximation.
- (b) Compare the molecular-orbital and valence-bond approximations for H_2 in a minimal basis set approximation.
- (c) In the valence-bond description of H_3 , the following two determinants appear:

$$\phi_1 = |h_a \bar{h}_b h_c| \quad \text{and}$$

$$\phi_2 = |h_a h_b \bar{h}_c|$$

Write down an expression for:

(i) $\langle \phi_1 | \phi_2 \rangle$

(ii) $\left\langle \phi_1 \left| -1/2 \sum_i \nabla_i^2 \right| \phi_2 \right\rangle$

Note: h_a , h_b , and h_c are non-orthogonal. All functions are normalised.

3. (a) Explain briefly the following terms:
- (i) refinements and extensions to a simple force field in molecular mechanics;
 - (ii) Clebsch-Gordan coupling coefficients;
 - (iii) flux (in quantum-mechanical scattering theory);
 - (iv) the first Born approximation.
- (b) From your reading of calculations on H₂O, **briefly** describe **TWO** methods of calculating the electronic structure of a molecule that include correlation energy.
4. (a) For an spd^2 configuration of an atom:
- (i) Determine the terms that arise in the LS coupling scheme;
 - (ii) Which of the terms in (i) would you expect to have the lowest energy? Why?
- (b) For an sp^2d configuration of an atom:
- (i) Write down the wavefunction for the 5G_6 state with $m_J = 6$.
 - (ii) Use lowering operators to determine the **normalised** wavefunction for the 5G_6 state with $m_J = 5$.
- (c) Evaluate the following matrix elements:
- (i) $\langle \bar{p}_0 | H_{s.o.} | p_{-1} \rangle$
 - (ii) $\langle d_0 | H_{s.o.} | \bar{d}_1 \rangle$
- (d) Given the rotational kinetic energy for an oblate symmetric top is:
- $$T = \frac{1}{2} (P_a^2 + P_b^2) / I_a + \frac{1}{2} P_c^2 / I_c,$$
- where a, b and c are body-fixed axes, use appropriate angular momentum relationships to obtain an expression for the rotational energy levels of an oblate symmetric top.

SECTION B

TURN OVER

(Answer at least **ONE** question from this section)

5. For a many-electron atom in a magnetic field of inductance B , the Hamiltonian operation can be written

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_{\text{rep}} + \hat{\mathcal{H}}_{\text{SO}} + \hat{\mathcal{H}}_B$$

- (a) Describe the types of energy and interactions that are represented by each of the operators on the right of this equation.
- (b) In one sense, $\hat{\mathcal{H}}_{\text{rep}}$ involves greater complexity than the other operators on the right. What is this sense?
- (c) The fact that $\hat{\mathcal{H}}_{\text{rep}}$ does not commute with the one-electron operator $(\hat{l}_z)_k$ for electron k can be seen from the commutator:

$$[\hat{\mathcal{H}}_{\text{rep}}, (\hat{l}_z)_k] = \frac{i\hbar e^2}{4\pi\epsilon_0} \sum_{i \neq k} (\mathbf{r}_k \times \mathbf{r}_i)_z / r_{ik}^3$$

But, despite this result, $\hat{\mathcal{H}}_{\text{rep}}$ *does* commute with the operator $\hat{L}_z = \sum_k (\hat{l}_z)_k$. Explain.

- (d) For light atoms in a weak magnetic field, the states are designated $|L S J M_J\rangle$, and the corresponding Zeeman energies are given by:

$$E_{\text{Zeeman}} = g \mu_B B M_J$$

Using a vector model, show that

$$g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$$

- (e) Qualitatively describe the Paschen-Back effect and explain briefly (no equations) how you could deal with cases of intermediate magnetic-field strength.
6. (a) The great orthogonality theorem can be written

$$\langle \psi_{\alpha}^a | \phi_{\beta}^b \rangle = \delta_{a,b} \delta_{\alpha,\beta} |a|^{-1/2} \langle \psi^a | \phi^b \rangle$$

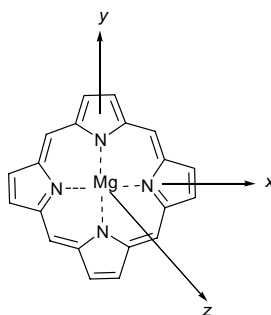
Explain in words what this means.

- (b) The Wigner-Eckart theorem can be written

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

Describe all of the coefficients and symbols in this equation. Explain how the Wigner-Eckart theorem simplifies quantum-mechanical manipulations.

- (c) Magnesium porphin (MgPor; below) has D_{4h} symmetry and a ${}^1A_{1g}$ ground state. The only electric-dipole allowed transitions from the ground state are ${}^1E_u \leftarrow {}^1A_{1g}$



- (i) Using Wigner-Eckart theorem and the tables on page 8, show that the magnetic dipole operator $\hat{\mu}_z$ (or $\hat{\mu}_0$) is diagonal in the complex D_{4h} basis for 1E_u .
- (ii) If the MgPor molecules are oriented so that their principal symmetry axes are parallel to an applied magnetic field (B/z), then the energy of state $|{}^1E_u \alpha\rangle$ is

$$E_{\alpha} = E({}^1E_u) + \alpha g \mu_B B / 2$$

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

$$g = \frac{\sqrt{2}}{\hbar} \langle {}^1E_u | \hat{L}^{\Lambda_{2g}} | {}^1E_u \rangle$$

Operator transformation coefficients in the complex- D_{4h} basis

\hat{O}	$\langle f \hat{O} \phi\rangle$	$f \quad \phi$
$\hat{m}_{\pm 1}$	-1	$E_u \quad \pm 1$
\hat{m}_0	1	$A_{2u} \quad a_2$
$\hat{\mu}_{\pm 1}$	-1	$E_g \quad \pm 1$
$\hat{\mu}_0$	1	$A_{2g} \quad a_2$

$2jm$ and $ a^* \alpha^*\rangle$ in the complex- D_4 basis		
$ a \alpha\rangle$	$2jm$	$ a^* \alpha^*\rangle$
$A_1 \quad a_1$	1	$A_1 \quad a_1$
$A_2 \quad a_2$	-1	$A_2 \quad a_2$
$B_1 \quad b_1$	1	$B_1 \quad b_1$
$B_2 \quad b_2$	-1	$B_2 \quad b_2$
$E \quad \pm 1$	1	$E \quad \mp 1$

$3jm$ in the complex- D_4 basis							
A_1	A_1	A_1	$3jm$	A_2	A_2	A_1	$3jm$
a_1	a_1	a_1	1	a_2	a_2	a_1	-1
B_1	B_1	A_1	$3jm$	B_2	B_2	A_1	$3jm$
b_1	b_1	a_1	1	b_2	b_2	a_1	-1
E	E	A_1	$3jm$	E	E	A_2	$3jm^\dagger$
-1	1	a_1	$1/\sqrt{2}$	-1	1	a_2	$-1/\sqrt{2}$

Tables headed $3jm^\dagger$ are multiplied by -1 for odd permutations of their columns

END OF PAPER