

University of Canterbury

End of Year Examinations 2007

Prescription Number(s):	CHEM 273
Paper Title:	Physical Chemistry

Time Allowed: TWO HOURS

Number of pages: SIX

Answer **THREE** questions out of
FOUR.

All questions are of equal value

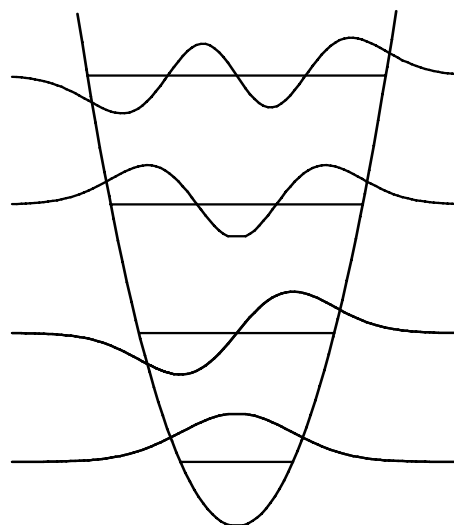
TURN OVER

1. The diagram below illustrates wave functions for the four lowest-energy states of a quantum-mechanical harmonic oscillator.

(a) Sketch a similar diagram that illustrates the *probability density functions* for these states.

(b) With respect to your diagram in (a), define the terms

- (i) quantised energy level;
- (ii) node; and
- (iii) normalisation.



(c) Comment on the following features of a quantum-mechanical harmonic oscillator, comparing them with the classical case:

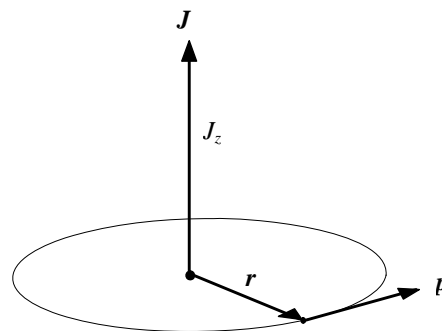
- (i) the minimum energy of the system;
- (ii) the probability of finding the particle outside the parabolic well; and
- (iii) the most probable positions of the particle in very high energy levels.

(d) A particle with a mass of 10^{-26} kg oscillates in a frictionless parabolic well with a frequency of $1.59 \times 10^{13} \text{ s}^{-1}$. The energy of the particle is 3.69×10^{-20} J.

- (i) What is the vibrational quantum number (ν) for the particle?
- (ii) What is the minimum amount of energy that is associated with a change of the state of the particle?
- (iii) What is the force constant (k) of the parabolic potential?

(e) The quantum harmonic-oscillator model is often used to describe the vibrations of diatomic molecules, but in this regard the Morse-oscillator model is superior. Qualitatively describe the latter (using diagrams, but no equations), contrasting it with the harmonic-oscillator model and indicating the reasons for its superiority.

2. A quantum mechanical particle of mass m is constrained to a circular orbit of radius r in a plane about the z axis. The orbital angular momentum vector, $\mathbf{J} = \mathbf{r} \times \mathbf{p}$, has magnitude J_z . The de Broglie wavelength of such a particle is given by



$$\lambda = \frac{2\pi r}{M_J} \quad (1)$$

$$\text{where } M_J = 0, \pm 1, \pm 2, \pm 3 \dots \quad (2)$$

- (a) Why is the de Broglie wavelength restricted according to equation 1?
- (b) In terms of the motion of the particle, what is the difference between the positive and negative values of M_J ?
- (c) Starting with the de Broglie equation, show that the momentum and rotational kinetic energy of such a system are given, respectively, by equations 2 and 3.

$$p = \frac{M_J \hbar}{r} \quad (2)$$

$$E_J = \frac{M_J^2 \hbar^2}{2mr^2} \quad (3)$$

- (d) The six-electron aromatic π system of benzene can be approximated as a quantum mechanical system of the type described above.
- (i) Draw and label an energy-level diagram, up to $M_J = \pm 2$, for such a system.
- (ii) On your diagram, assign the six electrons to the orbitals that they would occupy in the lowest-energy state of the system.
- (iii) Indicate on your diagram the lowest-energy electronic transition for the π electrons of benzene.
- (e) Benzene exhibits a very strong ultraviolet transition at ~ 180 nm.
- (i) Calculate the energy (in joules) of a photon with this wavelength.
- (ii) Determine an approximate radius for the benzene ring.

[For an electron, $\hbar^2/2m = 6.10 \times 10^{-31} \text{ J m}^2$. Other useful constants are $h = 6.626 \times 10^{-34} \text{ J s}$ and $c = 2.998 \times 10^8 \text{ m s}^{-1}$]

3. When the Born-Oppenheimer approximation applies, the total energy of a gas-phase diatomic molecule can be written as

$$T = T_e + G(v) + F(J)$$

where T_e is the electronic energy, the vibrational energy $G(v)$ is given by

$$G(v) = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + \dots,$$

the rotational energy $F(J)$ is given by

$$F(J) = B_v J(J + 1) - D_v J^2(J + 1)^2 + \dots,$$

and

$$B_v = B_e - \alpha(v + 1/2) + \dots,$$

is the rotational constant of the molecule in vibrational level v . Here ω_e is the vibrational frequency at the equilibrium internuclear distance and the dots ... indicate that it is possible to add further small terms on the right-hand side of each equation.

- (a) [30% of marks]

Explain the physical origins of the quantities $\omega_e x_e$, D_v and α .

- (b) [20% of marks]

Outline the Franck-Condon principle which governs the relative intensities of different vibrational bands in a molecule undergoing an electronic transition.

- (c) [30% of marks]

Ignoring the correction terms involving the quantities $\omega_e x_e$, D_v and α , and taking the selection rule to be $\Delta J = \pm 1$ for the R and P branches, respectively, derive expressions for the line positions in the P and R branches of the fundamental infrared absorption band of a diatomic molecule.

- (d) [20% of marks]

Sketch the infrared band of part (c), showing the relative intensities of the absorption lines, and briefly explain the variation of intensity with the J value in the lower state.

4. Atomic carbon and atomic lead both have an electron configuration of the type

$$(filled\ shells)p^2$$

where the filled shells contribute nothing to the atom's spin or orbital angular momentum.

- (a) [50% of marks]

Show that this configuration gives rise to terms 3P , 1D and 1S in Russell-Saunders coupling, when due account is taken of the Pauli exclusion principle.

- (b) [25% of marks]

The energies (units: cm^{-1}) of the lowest electronic states of carbon and lead are given in the following table:

State	C	Pb
3P_0	0	0
3P_1	16	7,819
3P_2	43	10,650
1D_2	10,194	21,458
1S_0	21,648	29,467

Discuss the relative magnitudes of the energy differences between the three 3P states, and between the 3P , 1D and 1S terms, in relation to the transition from Russell-Saunders to $j-j$ coupling.

- (c) [25% of marks]

All of the above states are of even (g) symmetry with respect to inversion. There is also a fairly low-lying 3P term of odd (u) symmetry. Draw one or more energy level diagrams, showing which transitions are likely to occur with significant intensity in the electronic spectra of atomic carbon and atomic lead, and state the selection rules involved.

END OF PAPER