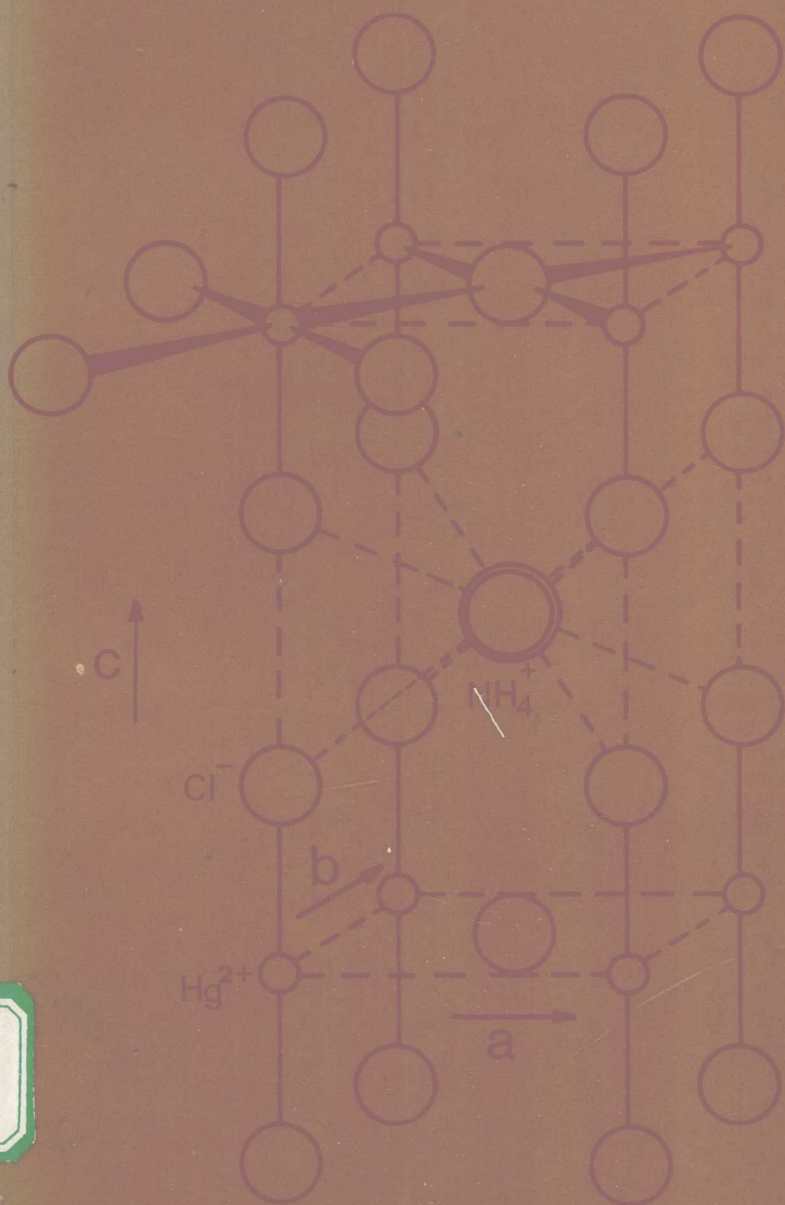


Problems in Inorganic and Structural Chemistry

無機與結構化學習題



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PREFACE

This book originates from a collection of problems and examination questions used in inorganic chemistry courses taught at the Chinese University of Hong Kong since 1968. During most of these years, our inorganic chemistry curriculum consists of a basic sequence of three 3-hour term courses. In the first, a second-year course entitled "Chemical Bonding", the nature of the chemical bond is covered with unusual thoroughness, though mainly in a qualitative and pictorial manner. In the second course, taken by seniors and some graduate students, all the standard topics that may be fruitfully treated using group theory are discussed. This is immediately followed by the third course, in which descriptive inorganic chemistry in a modern setting is taken up. In addition to this basic sequence, students have the option of taking elective courses in inorganic reaction mechanisms, physical methods in inorganic chemistry, and X-ray crystallography. In the light of our experience in teaching these courses, we keenly felt an acute shortage of suitable questions for student assignments and examinations, despite the fact that several problem books in inorganic chemistry are already available. The present compilation is the result of our effort to remedy the situation. Since examination papers and assignments usually include elementary as well as more advanced types of questions, the present collection does betray this unevenness in regard to the degree of difficulty. In an attempt to improve the presentation, we have replaced a significant number of routine examination questions with new ones formulated through consultation of current chemical journals. On the whole, the questions are mainly at the senior level and should be of use to beginning graduate students trained along more traditional lines.

The problems may be broadly divided into two types: theoretical and, for want of a better term, descriptive. In the former, group theory is employed wherever possible and serves as a central theme. In the latter, which constitutes about half of the questions, stability, reactivity, and mechanism of real systems are dealt with. Owing to the limitation of time, our coverage of descriptive inorganic chemistry is far from encyclopedic. Our various preferences and prejudices are manifested in the choice of topics.

The questions are organized into ten chapters. However, the classification is done in a somewhat arbitrary way since, in some cases, one "pigeon-hole" appears to be as appropriate as another. Nevertheless, an attempt has been made to group together questions of a similar nature for the sake of unity and consistency. Some readers may feel that a small number of the problems, especially those on atomic and molecular orbitals, may be more suitable for a book on quantum chemistry. In reality, this reflects how far quantum mechanical applications have found their way into inorganic chemistry. [Of course, the same may be said for organic chemistry.] Still, we have tried to keep the level of mathematical sophistication to a minimum: trigonometry, differential and integral calculus, vector algebra and basic notion of matrices, with which all chemistry undergraduates ought to be familiar. The units used in each question follow those given in the original literature; thus a single set of units is not used throughout the book. In a way, this reflects the current situation in the chemical literature and should not be an undue burden to the reader.

We trust that a conscientious student will try his best in solving a problem before turning to the answer section to check his achievement. It is our firm belief that readers of the book will learn effectively via this route. Because of the breadth of the subject matter covered and space limitation, it is clear that every aspect could not be covered in the given answers, some of which are rather terse while others may seem unduly lengthy. In general, elaboration of basic concepts (often at length for the benefit of the students) are given precedence over detailed factual information and calculations. It must be emphasized that questions of an interpretative nature are often open-ended, and students are strongly urged to seek alternative answers and better understanding by reading through relevant books and monographs in the reference list. Frequently the original literature sources are cited for the individual problems. This provides a convenience to those who wish to delve deeper into the subject. By consulting the source references instructors may exercise an option to modify or expand the questions as formulated here.

In order to keep the cost of the book at a reasonable level, especially for the students in Hong Kong, the book is printed directly from a typescript. The oxidation number of a metal in a coordination compound is denoted by an arabic numeral preceded by the + sign. Enclosing square brackets have been omitted from the formulas of neutral transition metal complexes. The authors take full responsibility for the content and appearance of the typescript and are grateful for the expert typing of Mr. S. K. Hau and illustration of Mr. K. F. Liew.

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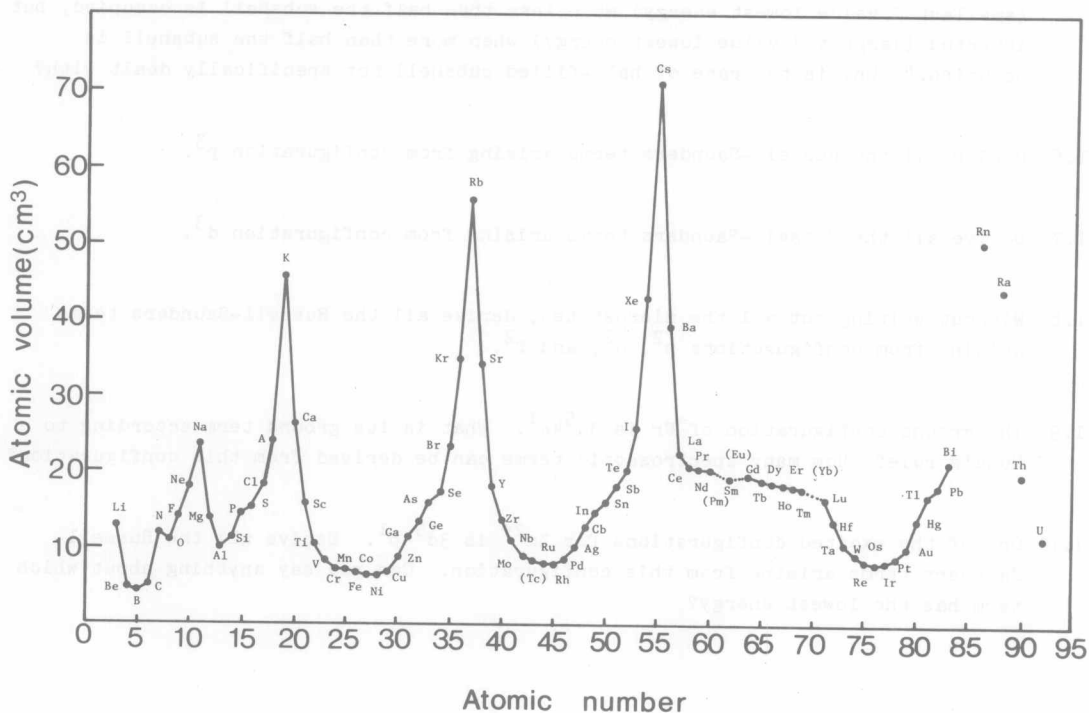
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Chapter 1

Atomic and Molecular Configurations and States

PROBLEMS

- 1.1 (i) How many electrons can be placed in
- a shell with principal quantum number n ?
 - a subshell with quantum numbers n and l ?
 - an orbital?
 - a spin-orbital?
- (ii) How many microstates belong to a term defined by quantum numbers L and S ? Explain clearly your deductions.
- 1.2 Discuss the possible electronic structures of elements 118 and 154. Predict their chemical behavior by extrapolation of known properties of their lower homologs in the periodic table. For simplicity, an abbreviated notation such as $[Rn]6d^{17}s^2$ may be used to describe the electronic configuration of element 89 (actinium). Using the $(n+l)$ rule as a guide, work out the electronic structure of element 103 (lawrencium) and proceed from there. Interested readers may consult the article "Prospects for Further Considerable Extension of the Periodic Table" by G.T. Seaborg in J. Chem. Educ., 40, 626 (1969).
- 1.3 Atomic volume, defined as the volume in cm^3 occupied by one gram atomic weight of an element, was shown by Lothar Meyer in 1869 to be a periodic function of the atomic weight (more correctly the atomic number). With reference to the atomic volume curve shown below, rationalize the following features on the basis of your knowledge of the electronic structure of atoms.



- (i) The alkali metals occupy the maxima.
- (ii) The alkaline earths correspond to a marked decrease in volume.
- (iii) The gaseous and volatile elements lie on the rising portions of the U-shaped curves.
- (iv) Each transition series corresponds to a gradual decrease toward the trough of a U-shaped curve.
- (v) The atomic volumes of corresponding elements of the second (Y to Sb) and third (Lu to Bi) long periods of the periodic table are strikingly similar.

[R.N. Keller, J. Chem. Educ., 28, 312 (1951).]

1.4 The following paragraph is found in a certain supplementary text. Read it carefully and point out any error it may contain.

"The next most stable configuration is ns^1np^1 . (The author here is discussing the spectra of the alkaline earths, which have the ground state configuration ns^2 .) In this case $\ell_1=0$ and $\ell_2=1$, so $L = (0+1), (0+1)-1$; that is, there are two terms arising from this configuration — one of P ($L=1$) and another of S ($L=0$) type. The total spin can be either 1 or 0, depending on whether the two electrons have the same or opposed spins. The value $S=1$ gives rise to triplet terms, and $S=0$ gives rise to singlet terms."

1.5 Part of Hund's rule states: "Multiplets formed from equivalent electrons are regular (smallest J value lowest energy) when less than half the subshell is occupied, but inverted (largest J value lowest energy) when more than half the subshell is occupied." Why is the case of half-filled subshell not specifically dealt with?

1.6 Derive all the Russell-Saunders terms arising from configuration p^3 .

1.7 Derive all the Russell-Saunders terms arising from configuration d^3 .

1.8 Without writing out all the microstates, derive all the Russell-Saunders terms arising from configurations p^2 , d^2 , and f^2 .

1.9 The ground configuration of Cr is $3d^54s^1$. What is its ground term according to Hund's rule? How many spectroscopic terms can be derived from this configuration?

1.10 One of the excited configurations for Zn^{2+} is $3d^94p^1$. Derive all the Russell-Saunders terms arising from this configuration. Can you say anything about which term has the lowest energy?

- 1.11 In 1932, Urey noticed a considerably over-exposed photograph of the visible spectrum of hydrogen showed weak satellite lines on the short wavelength side of the normal Balmer series. He made the (now) obvious conclusion that these satellite lines were due to an isotope of hydrogen, namely deuterium. If the H_{α} line and its satellite were observed at 6564.6 and 6562.8 Å, respectively, calculate M_{H^+}/m and M_{D^+}/M_{H^+} where m , M_{H^+} , M_{D^+} are the masses of the electron, the proton, and the deuterium nuclei, respectively.

Given : $m = 9.109 \times 10^{-28}$ g,

Atomic weight of H = 1.008,

N_0 (Avogadro's number) = 6.022×10^{23} ,

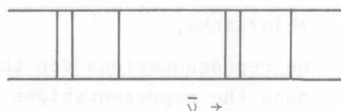
$$\bar{\nu} = R_{\infty} \frac{Z^2}{1+(m/M)} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \text{ for the } n_i \rightarrow n_f \text{ transition in a hydrogen-like system with nuclear mass } M \text{ and charge } +Z,$$

$$R_{\infty} = 109737.31 \text{ cm}^{-1}.$$

- 1.12 Consider the excitation of a 4s electron of the Ca atom to (i) the 4p and (ii) the 3d subshells. Deduce the terms and levels for the two excited-state configurations and interpret the observed emission spectrum of Ca shown below in terms of transitions between these levels with the use of the following selection rules:

$$\Delta L = \pm 1,$$

$$\Delta J = \pm 1, 0 \text{ (except for } J=0 \rightarrow J=0 \text{)}.$$



[G. Herzberg, Atomic Spectra and Atomic Structure, Dover, New York, 1944, pp. 77-78.]

- 1.13 Discuss the electronic structures of the following diatomic molecules using molecular orbital theory. For each species indicate its electronic configuration, number of unpaired electrons, and bond order.
(i) NF^+ , NF , and NF^- ;
(ii) NS^+ and NS .

- 1.14 The electronic configuration of N_2 is $KK(\sigma_s)^2(\sigma_s^*)^2(\pi_{x,y})^4(\sigma_z)^2$, while that of O_2 is $KK(\sigma_s)^2(\sigma_s^*)^2(\sigma_z)^2(\pi_{x,y})^4(\pi_{x,y}^*)^2$. Notice the reverse ordering between the $\pi_{x,y}$ and σ_z orbitals. What kind of interaction causes this reversal? Under what condition would this interaction be significant?

- 1.15 Diatomic species LiF and C_2 have the same number of electrons. How would their molecular orbital energy level diagrams contrast?

- 1.16 Deduce the ground electronic state for all possible configurations (d^n , $n=1, \dots, 9$) in an octahedral complex.

1.17 Gray and co-workers [J. Am. Chem. Soc., 93, 3603 (1971)] have proposed that the ground configuration for ferrocene (symmetry D_{5d}) is $(1a_{1g})^2(1a_{2u})^2(1e_{1g})^4(1e_{1u})^4(1e_{2g})^4(2a_{1g})^2(2e_{1g})^0(e_{2u})^0(2e_{2g})^0 \dots$. Derive the states for the following excited configurations:

- (i) $\dots(2a_{1g})^1(2e_{1g})^1$;
- (ii) $\dots(1e_{2g})^3(2a_{1g})^2(2e_{1g})^1$.

1.18 Derive the states for the following cases:

- (i) A $C_{\infty v}$ molecule with configuration $(\pi)^2$;
- (ii) A C_{3v} molecule with configuration $(e)^2$;
- (iii) An O_h molecule with configuration $(t_{2g})^2$.

1.19 Applying the method outlined by Ford [J. Chem. Educ., 49, 336 (1972)], derive the formulas for calculating the characters of the various states arising from a configuration with five equivalent electrons. In addition, making use of the formulas obtained, derive all the states arising from the $(h_g)^5$ configuration of a molecule with I_h symmetry.

1.20 (i) With the aid of the character table of the double group O' and by means of the formula

$$\chi(\alpha) = \sin(J + \frac{1}{2})\alpha / \sin \frac{1}{2}\alpha,$$

determine the characters of the representations for the states with $J = \frac{1}{2}, 1\frac{1}{2}, 2\frac{1}{2}, \dots$, or $6\frac{1}{2}$. Reduce the representations obtained into the irreducible representations of the O' group.

- (ii) Consider the ground term 4F of configuration d^7 in a crystal field with O_h symmetry. Determine the states arising from this term when both crystal field and spin-orbit interactions are included. In order to check on the results obtained, do this problem by considering both of the following two cases: (a) strong field and small spin-orbit coupling and (b) large spin-orbit coupling and weak O_h field.

[For a discussion on double groups, see F.A. Cotton, Chemical Applications of Group Theory, 2nd edition, Wiley, New York, 1972, pp.289-294.]

- A1.1 (i) (a) $2n^2$; (b) $2(2l+1)$; (c) 2; (d) 1.
 (ii) $(2L+1)(2S+1)$. This value is obtained through summation of the arithmetic series $\{2(L+S)+1\}, \{2(L+S-1)+1\}, \dots, \{2(L-S)+1\}$.
- A1.2 Element 103, Lw : $[\text{Rn}]7s^2 5f^{14} 6d^1$ (usually expressed as $[\text{Rn}]5f^{14} 6d^1 7s^2$).
 Element 118 : $[\text{Rn}]7s^2 5f^{14} 6d^{10} 7p^6$, an inert gas.
 Element 154 : $[\text{Rn}]7s^2 5f^{14} 6d^{10} 7p^6 8s^2 5g^{18} 6f^{14} 7d^2$; this is a metal in group IVB, its principal oxidation state being +4.
- A1.3 (i) The alkali metals correspond to the start of a new external shell and hence an expanded volume.
 (ii) In going from an alkali metal to the next alkaline earth metal, the addition of an electron in the same ns subshell does not compensate entirely for the effect of the increased nuclear charge.
 (iii) These elements correspond to the filling of the np subshells. Their tendency to form covalent and van der Waals solids accounts for the increased atomic volumes.
 (iv) In a transition series successive d electrons are added to an incomplete inner shell. Thus, with an ever-increasing nuclear charge but no compensating increase in the distance of the entering electrons from the nucleus, the atom shrinks.
 (v) Filling of the $4f$ subshells from Ce^{58} to Lu^{71} results in a continuous diminution in atomic size known as the "lanthanide contraction". Consequently the atomic volumes (and more importantly the chemical properties) of corresponding elements in the second and third long periods are remarkably similar, starting with the pair Zr^{40} and Hf^{72} and continuing as far as Ag^{47} and Au^{79} .
- A1.4 Vectors $\ell_1=1$ and $\ell_2=0$ combine to give a resultant $L=1$, giving rise to only 3P and 1P terms, without any S term. Casual application of the formula $L = \ell_1 + \ell_2$, $(\ell_1 + \ell_2) - 1, (\ell_1 + \ell_2) - 2, \dots$ can lead to errors.
- A1.5 Hund's rule is applicable to ground terms only. For a half-filled subshell configuration, the ground term is always an S term, i.e., $L=0$. For such terms, there is only one allowed J value.
- A1.6 The microstates for this configuration may be tabulated in the following manner:

$M_S \backslash M_L$	3/2	1/2	-1/2	-3/2
2		$(1^+ 1^- 0^+)$	$(1^+ 1^- 0^-)$	
1		$(1^+ 1^- 1^+)(1^+ 0^+ 0^-)$	$(1^+ 1^- 1^-)(1^+ 0^+ 0^-)$	
0	$(1^+ 0^+ 1^+)$	$(1^+ 0^+ 1^-)(1^+ 0^- 1^+)(1^+ 0^+ 1^+)$	$(1^- 0^- 1^+)(1^- 0^+ 1^-)(1^+ 0^- 1^-)$	$(1^- 0^- 1^-)$
-1		$(0^+ 0^- 1^+)(1^+ 1^- 1^-)$	$(0^+ 0^- 1^-)(1^- 1^+ 1^-)$	
-2		$(0^+ 1^+ 1^-)$	$(0^- 1^+ 1^-)$	

The terms formed by these twenty microstates are 4S (ground), 2P , and 2D .

A1.7 The microstates for this configuration may be tabulated in the following manner:

$M_L \backslash M_S$	$3/2$	$1/2$	$-1/2$	$-3/2$
5		$(2^+2^-1^+)$	$(2^+2^-1^-)$	
4		$(2^+2^-0^+)(2^+1^+1^-)$	$(2^+2^-0^-)(2^-1^+1^-)$	
3	$(2^+1^+0^+)$	$(2^+1^+0^-)(2^+1^-0^+)$ $(2^-1^+0^+)(2^+2^-1^+)$	$(2^+1^-0^-)(2^-1^+0^-)$ $(2^-1^-0^+)(2^+2^-1^-)$	$(2^-1^-0^-)$
2	$(2^+1^+-1^+)$	$(2^+1^+-1^-)(2^+1^-1^+)$ $(2^-1^+-1^+)(2^+2^-2^+)$ $(1^+1^-0^+)(2^+0^+0^-)$	$(2^+1^-1^-)(2^-1^+-1^-)$ $(2^-1^-1^+)(2^+2^-2^-)$ $(1^+1^-0^-)(2^+0^+0^-)$	$(2^-1^-1^-)$
1	$(2^+0^+-1^+)$ $(2^+1^+-2^+)$	$(2^+0^+-1^-)(2^+0^-1^+)$ $(2^-0^+-1^+)(2^+1^+-2^-)$ $(2^-1^+-2^+)(2^+1^-2^+)$ $(1^+1^-1^+)(1^+0^+0^-)$	$(2^+0^-1^-)(2^-0^+-1^-)$ $(2^-0^-1^+)(2^+1^-2^-)$ $(2^-1^+-2^-)(2^-1^-2^+)$ $(1^+1^-1^-)(1^-0^+0^-)$	$(2^-0^-1^-)$ $(2^-1^-2^-)$
0	$(2^+0^+-2^+)$ $(1^+0^+-1^+)$	$(2^+0^+-2^-)(2^+0^-2^+)$ $(2^-0^+-2^+)(1^+0^+-1^-)$ $(1^+0^-1^+)(1^-0^+-1^+)$ $(1^+1^-2^+)(2^+-1^+-1^-)$	$(2^+0^-2^-)(2^-0^+-2^-)$ $(2^-0^-2^+)(1^+0^-1^-)$ $(1^-0^+-1^-)(1^-0^-1^+)$ $(1^+1^-2^-)(2^-1^+-1^-)$	$(2^-0^-2^-)$ $(1^-0^-1^-)$
-1	$(-2^+0^+1^+)$ $(-2^+-1^+2^+)$	$(-2^+0^+1^-)(-2^+0^-1^+)$ $(-2^-0^+1^+)(-2^+-1^+2^-)$ $(-2^+-1^-2^+)(-2^-1^+2^+)$ $(-1^+-1^-1^+)(-1^+0^+0^-)$	$(-2^+0^-1^-)(-2^-0^+1^-)$ $(-2^-0^-1^+)(-2^+-1^-2^-)$ $(-2^-1^+2^-)(-2^-1^-2^+)$ $(-1^+-1^-1^-)(-1^-0^+0^-)$	$(-2^-0^-1^-)$ $(-2^-1^-2^-)$
-2	$(-2^+-1^+1^+)$	$(-2^+1^+-1^-)(-2^+1^-1^+)$ $(-2^-1^+-1^+)(-2^+-2^-2^+)$ $(-1^+-1^-0^+)(-2^+0^+0^-)$	$(-2^+1^-1^-)(-2^-1^+-1^-)$ $(-2^-1^-1^+)(-2^+-2^-2^-)$ $(-1^+-1^-0^-)(-2^+0^+0^-)$	$(-2^-1^-1^-)$
-3	$(-2^+-1^+0^+)$	$(-2^+-1^+0^-)(-2^+-1^-0^+)$ $(-2^-1^+0^+)(-2^+-2^-1^+)$	$(-2^+-1^-0^-)(-2^-1^+0^-)$ $(-2^-1^-0^+)(-2^+-2^-1^-)$	$(-2^-1^-0^-)$
-4		$(-2^+-2^-0^+)(-2^+-1^+-1^-)$	$(-2^+-2^-0^-)(-2^-1^+-1^-)$	
-5		$(-2^+-2^-1^+)$	$(-2^+-2^-1^-)$	

The terms formed by these microstates are 4F (ground), 4P , 2H , 2G , 2F , $^2D(2)$, and 2P .

A1.8 For p^2 , the L values for the terms are 2, 1, and 0; the spins are either singlet or triplet. Of the six possibilities the ones excluded by the Pauli principle may be crossed out in the following manner:

$$\begin{array}{ccc} 3P & 3P & 3S \\ 1D & 1P & 1S, \end{array}$$

leading to $3P$ (ground), $1D$, and $1S$ from this configuration.

Similarly, for d^2 ,

$$\begin{array}{ccccc} 3G & 3F & 3D & 3P & 3S \\ 1G & 1F & 1D & 1P & 1S, \end{array}$$

with $3F$ as the ground term. For f^2 ,

$$\begin{array}{ccccccc} 3I & 3H & 3G & 3F & 3D & 3P & 3S \\ 1I & 1H & 1G & 1F & 1D & 1P & 1S, \end{array}$$

with $3H$ as the ground term.

A1.9 The ground term for the $3d^5 4s^1$ configuration is $7S$. Since there are 16 terms for the d^5 configuration, there will be 32 terms for $3d^5 4s^1$. [As it is not well known that there are 16 terms for the d^5 configuration, an acceptable answer would be that the $d^5 s$ configuration gives rise to twice as many terms as the d^5 configuration.]

A1.10 The terms arising from configuration $3d^9 4p^1$ are identical to those from $d^1 p^1$: $3F$, $3D$, $3P$, $1F$, $1D$, and $1P$. Since Hund's rule is only applicable to systems with equivalent electrons, nothing definite can be said as to which is the ground term. If Hund's rule held, $3F$ would have the lowest energy. As it turns out, for Zn^{2+} , $3P$ does.

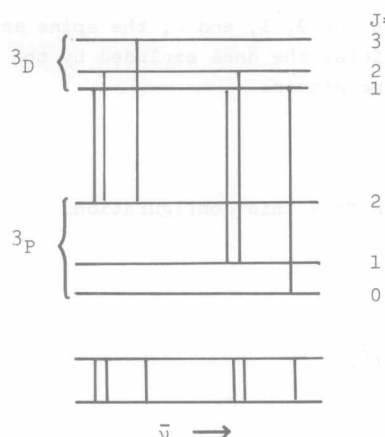
$$A1.11 \quad M_{H^+} \sim M_H = \frac{1.008}{6.022 \times 10^{23}} \text{ g}, \quad M_{H^+}/m = 1838.$$

$$\frac{\lambda_D}{\lambda_H} = \frac{1 + (m/M_{D^+})}{1 + (m/M_{H^+})},$$

$$m/M_{D^+} = 1/3708, \quad M_{D^+}/M_H = 2.017 \sim 2.$$

A1.12 For Ca, the ground state configuration is $4s^2$.

Excited state configuration	Term	Levels
$4s^1 4p^1$	$3P$	$3P_2, 3P_1, 3P_0$
$4s^1 4p^0 3d^1$	$3D$	$3D_3, 3D_2, 3D_1$



A1.13

Molecule	Electronic configuration	Number of unpaired electrons	Bond order
(i) NF^+	$\text{KK}(\sigma_s)^2(\sigma_s^*)^2(\sigma_z)^2(\pi_{x,y})^4$	1	$2\frac{1}{2}$
NF	"	2	2
NF^-	"	1	$1\frac{1}{2}$
(ii) NS^+	$\dots(\sigma_s)^2(\sigma_s^*)^2(\sigma_z)^2(\pi_{x,y})^4$	0	3
NS	"	1	$2\frac{1}{2}$

In (ii) the molecular orbitals arise from the overlap of 2s and 2p orbitals of N with the 3s and 3p orbitals of S.

A1.14 The interaction that causes this reversal is the one between the $2p_\sigma$ and 2s orbitals. This interaction exists in all cases; it becomes significant when the 2s and 2p orbitals are close in energy. The 2s-2p energy separations for B, C, N, O, and F have been estimated as 46, 71, 100, 133, and $223 \times 10^3 \text{ cm}^{-1}$, respectively. Hence the 2s- $2p_\sigma$ interactions in the first three cases may be termed significant.

A1.15 In C_2 , since the interacting atomic orbitals have the same energy (excepting the 2s- $2p_\sigma$ interaction mentioned in the previous problem), the bonding (antibonding) molecular orbitals are significantly lower (higher) in energy than their constituent atomic orbitals. On the other hand, this situation is not found in LiF, whose valence atomic orbital energies have been estimated as (in 10^3 cm^{-1}): -44 for Li 2s; -151 and -374 for F 2p and 2s, respectively. Hence, the bonding orbitals have similar energies as the constituent F atomic orbitals; the antibonding orbitals have similar energies as the constituent Li atomic orbitals. As a result, the bonding orbital electrons reside predominantly on the F atom and a simplified bonding picture may be represented by Li^+F^- .

A1.16

Free ion	High-spin complexes	Low-spin complexes
$d^1, {}^2D$	$t_{2g}^1, {}^2T_{2g}$	_____ *
$d^2, {}^3F$	$t_{2g}^2, {}^3T_{1g}$	_____
$d^3, {}^4F$	$t_{2g}^3, {}^4A_{2g}$	_____
$d^4, {}^5D$	$t_{2g}^3e_g^1, {}^5E_g$	$t_{2g}^4, {}^3T_{1g}$
$d^5, {}^6S$	$t_{2g}^3e_g^2, {}^6A_{1g}$	$t_{2g}^5, {}^2T_{2g}$
$d^6, {}^5D$	$t_{2g}^4e_g^2, {}^5T_{2g}$	$t_{2g}^6, {}^1A_{1g}$
$d^7, {}^4F$	$t_{2g}^5e_g^2, {}^4T_{1g}$	$t_{2g}^6e_g^1, {}^2E_g$
$d^8, {}^3F$	$t_{2g}^6e_g^2, {}^3A_{2g}$	_____
$d^9, {}^2D$	$t_{2g}^6e_g^3, {}^2E_g$	_____

Comments:

- (i) "Obvious" cases: d^1, d^9 , high- and low-spin d^5 , low-spin d^6 , and low-spin d^7 . Many others can be derived by applying the following rule: high-spin complexes with configurations d^{n+5} and d^n have the same orbital ground state.
- (ii) The ground term for d^2 complexes (configuration t_{2g}^2) is ${}^3T_{1g}$ (see A1.18). Also, for d^3 (atomic term 4F) complexes, since a F term splits into A_{2g}, T_{1g} , and T_{2g} in an octahedral field, and with a half-filled configuration t_{2g}^3 , the ground term should be the orbitally non-degenerate ${}^4A_{2g}$. All others may now be obtained readily.
- (iii) Ground terms for tetrahedral complexes may also be readily written down: the ground state of a d^n tetrahedral complex is the same as that of a d^{10-n} octahedral complex. The subscript "g" should however be dropped, since tetrahedral complexes lack an inversion center.

A1.17

- (i) The direct product of a_{1g} and e_{1g} is e_{1g} . Hence the terms arising from the configuration... $(2a_{1g})^1(2e_{1g})^1$ are ${}^1E_{1g}$ and ${}^3E_{1g}$.
- (ii) Similarly, the states arising from the configuration... $(1e_{2g})^3(2a_{1g})^2(2e_{1g})^1$ are ${}^1E_{1g}, {}^1E_{2g}, {}^3E_{1g}$, and ${}^3E_{2g}$.

Recent studies have shown that the familiar D_{5d} sandwich structure of ferrocene has to be revised. In the room temperature monoclinic crystalline form, the molecular center of symmetry required by the space group ($P2_1/a, Z=2$) is only statistical in nature. In both this and the low temperature triclinic form, the ferrocene molecule is neither exactly staggered (D_{5d}) nor eclipsed (D_{5h}), the rings being rotated by about 9° from the eclipsed orientation. In the vapor phase, the equilibrium conformation of ferrocene is eclipsed, and it seems reasonable to assume that the slight deviation from D_{5h} symmetry in the solid is due to packing forces.

[P. Seiler and J.D. Dunitz, Acta Cryst., B35, 1068 (1979); ibid., 2020 (1979); F. Takusagawa and T.F. Koetzle, Acta Cryst., B35, 1074 (1979); A. Haaland, Acc. Chem. Res., 12, 415 (1979).]