A. F. Williams

A Theoretical Approach to Inorganic Chemistry

Springer-Verlag Berlin Heidelberg New York

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With 144 Figures

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ISBN 3-540-09073-8 Springer-Verlag Berlin Heidelberg NewYork
ISBN 0-387-09073-8 Springer-Verlag NewYork Heidelberg Berlin

Library of Congress Cataloging in Publication Data.
Williams, Alan Francis, 1950-. A theoretical approach to inorganic chemistry.
Includes bibliographies and index. 1. Chemistry, Inorganic. 2. Molecular orbitals.
3. Quantum chemistry. I. Title. OD152.3.W54 546 78-26415

Printed in Germany.

Offsetprinting and Binding: Konrad Triltsch, Würzburg
2152/3020-543210

Foreword

Dr. Alan Williams has acquired a considerable experience in work with transition metal complexes at the Universities of Cambridge and Geneva. In this book he has tried to avoid the variety of ephemeral and often contradictory rationalisations encountered in this field, and has made a careful comparison of modern opinions about chemical bonding. In my opinion this effort is fruitful for all students and active scientists in the field of inorganic chemistry. The distant relations to group theory, atomic spectroscopy and epistemology are brought into daylight when Dr. Williams critically and pedagogically compares quantum chemical models such as molecular orbital theory, the more specific L.C.A.O. description and related "ligand field" theory, the valence bond treatment (which has conserved great utility in antiferromagnetic systems with long internuclear distances), and discusses interesting, but not too well-defined concepts such as electronegativity (also derived from electron transfer spectra), hybridisation, and oxidation numbers.

The interdisciplinary approach of the book shows up in the careful consideration given to many experimental techniques such as vibrational (infra-red and Raman), electronic (visible and ultraviolet), Mössbauer, magnetic resonance, and photoelectron spectra, with data for gaseous and solid samples as well as selected facts about solution chemistry. The book could not have been written a few years ago, and is likely to remain a highly informative survey of modern inorganic chemistry and chemical physics.

Geneva, January 1979

C.K. Jørgensen

Introduction

> *”It is in the nature of an hypothesis, when once a man has conceived it, that it assimilates everything to itself, as proper nourishment, and from the first moment of your begetting it, it generally grows the stronger by everything you see, hear, read or understand. This is of great use.“*
>
> *Laurence Sterne*
> *’The life and opinions of Tristram Shandy‘*

It has become almost traditional to begin inorganic chemistry books with a remark on the growth of the subject in the past 25 years. For the student of chemistry, this has resulted in a great increase in the amount of material he has to learn, much of which is separated into apparently unrelated topics such as ligand field theory, electron deficient compounds, the ionic model, etc. This book is intended to show that an approach that takes as its starting point the elementary molecular orbital model of the chemical bond may be developed painlessly to cover the whole subject, and to throw into relief the particularities, differences and similarities of the various sub-divisions of inorganic chemistry. I hope that this will not only aid the understanding and the memorisation of inorganic chemistry, but will also help the reader develop a certain chemical intuition. The book is intended to illustrate the use of theoretical models in studying chemistry, and *not* the use of chemistry in supplying facts for the delectation of theories.

The theoretical approach I advocate is essentially qualitative, and is intended to provide a basis for the subject as a whole, rather than an accurate method of calculation or prediction in a narrow field. The theories of chemical bonding themselves are not particularly complicated, but their application requires a critical understanding, and a good deal of common sense. I have attempted to follow a logical course in presenting the various subjects, but it should be borne in mind that the division into chapters is artificial: the reactivity of a molecule is directly related to its electronic structure, even if the subjects are discussed in different chapters. Certain sections treating more advanced or more mathematical topics are marked with an asterisk, and may be skipped at a first reading.

The quantum mechanics and group theory used in the book are introduced in the first chapter. I have used a certain amount of mathematics wherever it simplifies the discussion, but have also included non-mathematical summaries at the end of each section as it is important that the reader has a sound understanding of the physical principles to follow the remainder of the book. It is interesting to note that the 'complicated' mathematical part of the subject dates mostly from the 1920's, whilst the more qualitative application of quantum mechanics is much more recent.

Chapter 2 introduces L.C.A.O. molecular orbital theory for simple molecules, and endeavours to emphasise the physical principles of the method; in Chap. 3 this approach is used to describe the electronic structures of a wide variety of inorganic compounds. Chapter 4 treats the electronic spectra and magnetic properties of inorganic compounds, and is concerned mainly with d and f block elements. Chapter 5 discusses some other theories of chemical bonding, the use of thermodynamic data in inorganic chemistry, and some of the general concepts often used in descriptive chemistry. The relationship between electronic structure and reactivity is discussed in Chap. 6. Chapter 7 is an illustrative chapter showing the application of the approach introducted in previous chapters to the hard facts of descriptive chemistry. The final chapter gives a résumé of the spectroscopic methods referred to in the text, and discusses their chemical usefulness.

The book presents an approach to the subject, and not a complete treatment of inorganic chemistry, an impossible task in a book of this length. I have given references to more detailed treatments of the topics discussed in the bibliographies at the end of each chapter. At the end of each chapter there are also a few problems which further illustrate points discussed in the text, and indicate other applications. Most problems require only a few moments of reflection, and I hope that the reader will look at them as they are intended to encourage the use of his own critical faculties and common sense. Those nervous about quantum mechanics may find the first two chapters the most difficult, but, if they can understand the physical principles introduced therein, the rest of the book may be followed with little difficulty; the word 'theoretical' is not included in the title as a euphemism for complicated. I hope that the book will give a wide view of the subject, and will serve as a useful complement to more detailed descriptive studies of inorganic chemistry.

I should like to thank the Master and Fellows of Emmanuel College, Cambridge whose award of a Research Fellowship enabled me to take the opportunity of writing this book, and Professor *W. Haerdi*, Director of the Département de Chimie Minérale, Analytique et Appliquée of the University of Geneva where the book was finished. I am particularly grateful to Professor *C.K. Jørgensen* of Geneva, who kindly wrote the Foreword, and Dr. *A.G. Maddock* of Cambridge, both of whom not only read the whole manuscript and made many helpful comments and corrections, but also, by their enthusiasm for the subject and their willingness to discuss it, have made a substantial contribution to such knowledge of inorganic chemistry as the author may possess. I also thank Drs. *L. Balsenc, U. Burger*, Professor *M. Marcantonatos*, and Dr. *V. Parthasarathy* for having read and commented on parts of the book, and Dr. *N. Thalmann-Magnenat* for the figures reproduced from her thesis. Such errors and blemishes as remain are due to the author's intransigence or ignorance.

Two of the less agreeable aspects of writing a book are the effects in the author's temper and the volume of typing produced: both difficulties were faced with great tolerance by my wife, and this book is accordingly dedicated to her with apologies.

Geneva, January 1979

A.F. Williams

Contents

Sections marked with an asterisk may be omitted at the first reading.

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1. Quantum Mechanics and Atomic Theory

Inorganic chemistry is concerned with the chemistry of over an hundred elements, forming compounds whose stability ranges from that of mountains and minerals to species with lifetimes of less than a millisecond. Clearly, if the subject is to be more than a vast catalogue of apparently unrelated facts, we must seek a theoretical foundation which will enable us to rationalise and relate as many observations as possible. From this point of view, the development of ideas of chemical periodicity (by Mendeleyev and others) during the latter half of the nineteenth century stands as the starting point of theoretical inorganic chemistry. The first periodic table was drawn up on the basis experimental observations; soon after the introduction of quantum theories of the atom, it was shown by Rutherford and Bohr that the same table could be derived from the electronic structure of the individual elements. Following this demonstration, all theories of chemistry have been based more or less rigorously on the quantum theory of matter.

Exact calculations in quantum chemistry rapidly become very complicated, but the remarkable success of quantum mechanics in explaining spectra, and the reasonable success of approximate calculations give a sound justification for the use of quantum mechanics as a starting point. The quality of quantum chemical calculations is improving steadily, and for compounds of the first row of the Periodic Table, the accuracy and predictive power of some methods are now chemically useful. Nonetheless, for most inorganic compounds, calculations are only of value when a large number of effects can either be ignored, satisfactorily approximated, or replaced by experimentally determined values.

The approach in this book will be mainly qualitative, and we shall be more interested in physical principles than in mathematical details; we will try to justify the assumptions and approximations made by recourse to experimental evidence, most frequently that obtained from spectroscopic measurements. This chapter is concerned with establishing the elements of quantum mechanics that we shall need, the use of symmetry to simplify our calculations, and the approximate quantum treatment of atomic structure. Those who find quantum mechanics frightening should note that there is a simplified summary at the end of each section and that sections marked with an asterisk are rather more mathematical and may be omitted at a first reading. This is not a quantum chemistry book, and the treatment given is very brief; those completely unfamiliar with quantum mechanics may wish to consult one of the many introductions to quantum chemistry (see Bibliography, page 37).

s-block		d-block										p-block					
1 **H** $1s^1$						2 **He** $1s^2$											
3 **Li** $2s^1$	4 **Be** $2s^2$											5 **B** $2s^2 2p^1$	6 **C** $2s^2 2p^2$	7 **N** $2s^2 2p^3$	8 **O** $2s^2 2p^4$	9 **F** $2s^2 2p^5$	10 **Ne** $2s^2 2p^6$
11 **Na** $3s^1$	12 **Mg** $3s^2$											13 **Al** $3s^2 3p^1$	14 **Si** $3s^2 3p^2$	15 **P** $3s^2 3p^3$	16 **S** $3s^2 3p^4$	17 **Cl** $3s^2 3p^5$	18 **Ar** $3s^2 3p^6$
19 **K** $4s^1$	20 **Ca** $4s^2$	21 **Sc** $3d^1 4s^2$	22 **Ti** $3d^2 4s^2$	23 **V** $3d^3 4s^2$	24 **Cr** $3d^5 4s^1$	25 **Mn** $3d^5 4s^2$	26 **Fe** $3d^6 4s^2$	27 **Co** $3d^7 4s^2$	28 **Ni** $3d^8 4s^2$	29 **Cu** $3d^{10} 4s^1$	30 **Zn** $3d^{10} 4s^2$	31 **Ga** $4s^2 4p^1$	32 **Ge** $4s^2 4p^2$	33 **As** $4s^2 4p^3$	34 **Se** $4s^2 4p^4$	35 **Br** $4s^2 4p^5$	36 **Kr** $4s^2 4p^6$
37 **Rb** $5s^1$	38 **Sr** $5s^2$	39 **Y** $4d^1 5s^2$	40 **Zr** $4d^2 5s^2$	41 **Nb** $4d^4 5s^1$	42 **Mo** $4d^5 5s^1$	43 **Tc** $4d^5 5s^2$	44 **Ru** $4d^7 5s^2$	45 **Rh** $4d^8 5s^1$	46 **Pd** $4d^{10}$	47 **Ag** $4d^{10} 5s^1$	48 **Cd** $4d^{10} 5s^2$	49 **In** $5s^2 5p^1$	50 **Sn** $5s^2 5p^2$	51 **Sb** $5s^2 5p^3$	52 **Te** $5s^2 5p^4$	53 **I** $5s^2 5p^5$	54 **Xe** $5s^2 5p^6$
55 **Cs** $6s^1$	56 **Ba** $6s^2$	57 **La** $5d^1 6s^2$	72 **Hf** $5d^2 6s^2$	73 **Ta** $5d^3 6s^2$	74 **W** $5d^4 6s^2$	75 **Re** $5d^5 6s^2$	76 **Os** $5d^6 6s^2$	77 **Ir** $5d^7 6s^2$	78 **Pt** $5d^9 6s^1$	79 **Au** $5d^{10} 6s^1$	80 **Hg** $5d^{10} 6s^2$	81 **Tl** $6s^2 6p^1$	82 **Pb** $6s^2 6p^2$	83 **Bi** $6s^2 6p^3$	84 **Po** $6s^2 6p^4$	85 **At** $6s^2 6p^5$	86 **Rn** $6s^2 6p^6$
87 **Fr** $7s^1$	88 **Ra** $7s^2$	89 **Ac** $6d^1 7s^2$															

lanthanides

58 **Ce** $4f^1 5d^1 6s^2$	59 **Pr** $4f^3 6s^2$	60 **Nd** $4f^4 6s^2$	61 **Pm** $4f^5 6s^2$	62 **Sm** $4f^6 6s^2$	63 **Eu** $4f^7 6s^2$	64 **Gd** $4f^7 5d^1 6s^2$	65 **Tb** $4f^9 6s^2$	66 **Dy** $4f^{10} 6s^2$	67 **Ho** $4f^{11} 6s^2$	68 **Er** $4f^{12} 6s^2$	69 **Tm** $4f^{13} 6s^2$	70 **Yb** $4f^{14} 6s^2$	71 **Lu** $4f^{14} 5d^1 6s^2$
90 **Th** $6d^2 7s^2$	91 **Pa** $5f^2 6d^1 7s^2$	92 **U** $5f^3 6d^1 7s^2$	93 **Np** $5f^4 6d^1 7s^2$	94 **Pu** $5f^6 7s^2$	95 **Am** $5f^7 7s^2$	96 **Cm** $5f^7 6d^1 7s^2$	97 **Bk** $5f^9 7s^2$	98 **Cf** $5f^{10} 7s^2$	99 **Es** $5f^{11} 7s^2$	100 **Fm** $5f^{12} 7s^2$	101 **Md** $5f^{13} 7s^2$	102 **No** $5f^{14} 7s^2$	103 **Lw** $5f^{14} 6d^1 7s^2$

actinides

Table 1.1. The periodic Table. The atomic numbers and valence shell electron configurations of the elements

A. Elements of Quantum Mechanics

Quantum mechanics postulates that any system may be completely described by a wave function ψ which is a function of all the variables of the system. For an isolated hydrogen atom, if the nucleus is taken as the origin of the coordinate system, the wave function will be a function only of the coordinates of the electron. We require for all wave functions discussed in this book that they be solutions of the time independent Schrödinger equation:

$$\mathcal{H}\,\psi = E\,\psi \tag{1.1}$$

where ψ is the wave function of the system we are discussing, E is the energy of the system described by ψ, and $\mathcal{H}$ is a well-defined mathematical operator called the Hamiltonian. An *operator* is a mathematical entity which, acting on a function, changes it (for example, in the expression $\frac{d}{dx}\,(f\,(x))$, $\frac{d}{dx}$ is an operator, since the result is a new function; similarly, $1/x$ may be regarded as an operator, since the product $\frac{1}{x} \cdot f\,(x)$ gives a new function). Operators are generally denoted by script letters. The Hamiltonian operator, which is related to the energy of the system, is constructed according to a set of quantum mechanical rules and consists of a sum of terms representing every contribution to the energy of the system. Thus, for the hydrogen atom, the operator will have components from the kinetic energy of the electron, and the potential energy of the electron nucleus interaction. A hydride ion (H^-) with two electrons will have kinetic energy terms (one for each electron), and potential energy terms due to electron-nuclear and electron-electron interactions.

The Schrödinger equation is a specific example of a general mathematical equation known as an *eigenvalue* equation, which has the form:

$$\text{(operator)} \cdot \text{(function)} = \text{(number)} \cdot \text{(the same function)} \tag{1.2}$$

In general, only a certain set of functions will obey Eq. (1.2), and when the product of an operator and a function gives the same function multiplied by a simple number, the function is said to be an *eigenfunction* of the operator, and the simple number is known as the *eigenvalue.* Thus:

$$\text{(operator)} \cdot \text{(eigenfunction)} = \text{(eigenvalue)} \cdot \text{(eigenfunction)} \tag{1.3}$$

The Schrödinger equation is thus nothing more than the eigenvalue equation of the energy operator, the Hamiltonian; furthermore, since the equation will hold only for specific values of E and ψ, we see that we have arrived at a quantisation of energy levels. The Eq. (1.3) is frequently found in quantum mechanics, and each experimentally observable quantity is the eigenvalue of a corresponding operator. If a given wave function is not an eigenfunction of a particular operator, then the experimental observable associated with the operator is not well defined; thus, if a wave function is *not* an eigenfunction of the Hamiltonian, then the energy of the system is not well defined, and is *indeterminate,* i.e. an exact value cannot be measured. Our requirement that the Schrödinger equation be obeyed is thus a requirement that our system has a well defined energy which does not change with time.

A wave function which is a solution to the Schrödinger equation (and henceforth, we shall use the term wave function only for such solutions) may also be an eigenfunction for other operators. In the case of the hydrogen atom, the wave functions are also eigenfunctions of the orbital angular momentum operators $\mathscr{L}^2$ and $\mathscr{L}_z$ (the square of the orbital angular momentum, and its component along one, arbitrarily chosen axis), and consequently the wave functions have well defined and measurable values of these quantities. The condition for a function to be an eigenfunction of two operators O_1, O_2 is that O_1 followed by O_2 has the same result as O_2 followed by O_1, or that O_1 and O_2 *commute.* The commutativity of operators, and consequent measurability of their observables is closely related to Heisenberg's uncertainty principle.

If every physically observable quantity is the eigenvalue of its corresponding operator, what is the physical interpretation of the wave function itself? Born suggested that the value of the square of the wave function ψ^2 (for complex wave functions, the square of the modulus $\psi^*\psi$ or $|\psi|^2$) of a particle at a point **r** is the probality that the particle is at that point. Turning again to the hydrogen atom, the value of $|\psi|^2$ at a given point is the probability of finding the electron there. However, Heisenberg's uncertainty principle warns us against regarding the electron as localised at a particular point; we should do better to regard the electron as having a certain probality density within a certain volume element which is equal to the integral of $|\psi|^2$ within that volume. The concept of electron density is extremely useful in discussing electronic wave functions, and we adopt Born's interpretation without further question.

If the electron exists at all, the sum of its probability density over all space must equal 1. This may be expressed by the integral

$$\int_{\text{all space}} \psi^* \cdot \psi \, d\tau = 1 \tag{1.4}$$

The function ψ is said to be *normalised.* Since $\mathscr{H}\psi = E\,\psi$, multiplying both sides of Eq. (1.1) by ψ^* gives:

$$\psi^* \cdot \mathscr{H}\,\psi = \psi^* E\,\psi$$

We may now integrate both sides of this equation over all space, noting that E is a number and may therefore be taken outside the integral to give:

$$\int_{\text{all space}} \psi^* \mathscr{H} \psi \, d\tau = E \int_{\text{all space}} \psi^* \psi \, d\tau = E \tag{1.5}$$

We have thus obtained an explicit expression for the energy of the system.

The wave function ψ must satisfy certain conditions: it must be single valued, since at any point there can only be one value of the probability; it must be continuous, as must its first derivative (i.e. $\frac{d\psi}{dx}$); it must obey the boundary conditions of the system. Thus, for the hydrogen atom, the wave function must fall to zero at infinite distance from the nucleus for the electron clearly has an infinitely small probability density at this distance. The imposition of boundary conditions in Eq. (1.1) severely restricts the number of solutions, and is of vital importance in establishing quantisation of energy.

a) The Hydrogen Atom

This is the only system of chemical significance for which the Schrödinger equation can be solved exactly, apart from the trivial extensions to He^+, Li^{2+}, Be^{3+} etc., all having only a nucleus and one electron. The exact calculation is found in many texts[1], so let us look only at the qualitative features. First, we must construct the Hamiltonian operator – this contains a term for the kinetic energy of the electronic motion, and also for the electron nucleus attraction. This second term ($-e^2/4\pi\epsilon_0 \mathbf{r}$) falls off as $1/\mathbf{r}$, the distance of the electron from the nucleus; since this function ($1/\mathbf{r}$) has spherical symmetry about the nucleus, it will clearly be a good idea to adopt a coordinate system which reflects this. We therefore place the nucleus at the origin, and solve the equation using spherical polar coordinates, r, θ, ϕ for the electron's position. The equation is thus:

$$(\mathscr{H}_{\text{kin}} + \mathscr{H}_{\text{electron-nucleus}})\,\psi(\mathrm{r}, \theta, \phi) = E\,\psi(\mathrm{r}, \theta, \phi) \tag{1.6}$$

The solutions are given by:

$$\psi(\mathrm{r}, \theta, \phi) = R(n, l, \mathrm{r})\; Y(l, m, \theta, \phi) \tag{1.7}$$

where for Eq. (1.6) to hold, n, l, and m have integral values, and specify the forms of the two functions R and Y; it is more usual to specify these functions by writing n, l, and m as subscripts:

$$\psi_{nlm}(\mathrm{r}, \theta, \phi) = R_{nl}(\mathrm{r}) \cdot Y_{lm}(\theta, \phi) \tag{1.8}$$

n, l, and m are quantum numbers which specify the wave function. It is found that the energy E_{nlm} corresponding to the wave function ψ_{nlm} is

$$E_{nlm} = \mathrm{K}/n^2 \tag{1.9}$$

where K is a product of various fundamental quantities. Since E does not depend on l and m, the functions ψ_{nlm} correspond to the same energy of the system for all l and m if n is fixed. However, Eq. (1.8) is only valid if l and m have integral values obeying the following rules:

$$0 \leqslant l < n \quad ; -l \leqslant \mathrm{m} \leqslant +l$$

thus for fixed values of n and l there are $(2l + 1)$ solutions of the Schrödinger equation. For fixed n there are $\sum_{0}^{n-1}(2l + 1) = n^2$ separate solutions all with the same energy. Separate solutions of the Schrödinger equation with the same energy are said to be degenerate. Thus we may say that solutions of the Schrödinger equation for the isolated hydrogen atom are of the form $\psi_{nlm}(\mathrm{r}, \theta, \phi) = \mathrm{R}_{nl}(\mathrm{r})\, \mathrm{Y}_{lm}(\theta, \phi)$, are degenerate for all l, m, given fixed n, and that $0 \leqslant l < n$ and $-l \leqslant m \leqslant l$, and that the energy of these solutions is given by:

$$E_{\mathrm{nlm}} = \int_{\text{all space}} \psi^*_{nlm}(\mathrm{r}, \theta, \phi)\,\mathscr{H}\,\psi_{nlm}(\mathrm{r}, \theta, \phi) = \mathrm{K}/\mathrm{n}^2 \tag{1.10}$$

Dirac introduced a very elegant system of notation which avoids the continual use of subscripts and integral signs:

(i) ψ_a is denoted by $| a >$

(ii) ψ^*_a is denoted by $< a |$

(iii) $\int_{\text{all space}} \psi^*_a \psi_b$ is denoted by $< a | b >$

Thus we may rewrite Eq. (1.10) as:

$$E_{nlm} = < nlm |\; \mathscr{H} \;| nlm > = \mathrm{K}/n^2 \tag{1.10a}$$

---

[1] For example, see Murrell, Kettle, and Tedder (see Bibliography, page 37).

This 'bracket' notation is extremely convenient and we shall use it extensively.

Following Eq. (1.4), it is found that $< nlm \mid nlm > = 1$; this is the normalisation condition. If a wave function ψ_a is not normalised, so that $< a \mid a > = \alpha$ (for example), then the wave function $\psi_b = (1/\sqrt{\alpha})\ \psi_a$ will be normalised ($< b \mid b > = 1$). This is clearly a trivial alteration, and we shall henceforth assume all wave functions to be normalised.

Another property of the wave functions ψ_{nlm} is that the integral

$$\int_{\text{all space}} \psi^*_{nlm}\ \psi_{n'l'm'} = < nlm \mid n'l'm' > = 0$$

unless $n = n'$, $l = l'$, $m = m'$. This is a fundamental property of eigenfunctions, known as *orthogonality*. Any eigenfunction corresponding to a given eigenvalue will be *orthogonal* to all others corresponding to a different eigenvalue. For degenerate eigenfunctions, the problem is a little more complicated if two eigenfunctions ψ_a and ψ_b correspond to the same energy E, then, even if $< a \mid b > = 0$, the wave function $\psi_a \cos\alpha + \psi_b \sin\alpha$ will be an eigenfunction of the Hamiltonian for all α, and will not be orthogonal to ψ_a or ψ_b. This might appear to imply an infinite number of eigenfunctions corresponding to an infinite number of values for α. In fact, this is not the case and we require of all eigenfunctions that they are orthogonal to all other eigenfunctions, and we shall assume that all eigenfunctions have been orthogonalised.

A set of eigenfunctions which are orthogonal to each other, and are normalised are said to be *orthonormal.* This relationship may be summarised as

$$< \alpha\beta\gamma \ldots\ldots \mid abc \ldots\ldots > = \delta_{\alpha a}\ \delta_{\beta b}\ \delta_{\gamma c} \ldots\ldots \tag{1.11}$$

where δ_{ij} is the Kronecker delta symbol such that $\delta_{ij} = 0$ unless $i = j$, when $\delta_{ij} = \delta_{ji} = 1$. All wave functions we discuss will be assumed to be orthonormal.

We have now discussed the general properties of our wave functions – their orthonormality and degeneracy, and such remarks apply to all wave functions, although the form of the solutions will be very different, and the degeneracy is usually much lower than that of the hydrogen atom. We now turn to the actual solutions ψ (r, θ, ϕ). It will be recalled that the wave function could be separated into the product of a radial function of r only, and an angular function of θ and ϕ only. We will discuss these two parts separately. Good discussions and diagrams are given in many physical and theoretical chemistry texts[2] – we discuss here only the fundamentals.

(i) The radial function R (r). We may notice immediately that, since the functions $Y_{lm}(\theta, \phi)$, $Y_{l'm'}(\theta, \phi)$ are orthogonal only if $l \neq l'$, $m \neq m'$, then for orthogonality, we require that the functions R_{nl} (r), $R_{n'l'}$ (r) should be orthogonal for $n \neq n'$. The general form of R_{nl}(r) for a series of n, l is shown in Fig. 1.1, together with the function $R^2{}_{nl}$ (r) $\cdot$ 4 π r^2, the total electron density at a distance r from the nucleus. It will be seen that there are points where the wave function changes sign; these points are known as nodes, and, for the radial function R (r) form spheres.[3] A function R_{nl}(r) will have $(n-l-1)$ nodes. We label radial wave functions by the convenient (if not logical) notation in which the l value is represented by the letters s, p, d, f, g, ... as $l = 0, 1, 2, 3, 4, \ldots$ The radial function for $n = 4$, $l = 3$ is thus labelled 4f, for $n = 2$, $l = 0$ it is labelled 2s. There are three general features to note about the radial function:

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[2] E.g. Atkins; Coulson; Murrell, Kettle, and Tedder (see Bibliography, page 37).

[3] Note that the electron has zero probability density at a node.

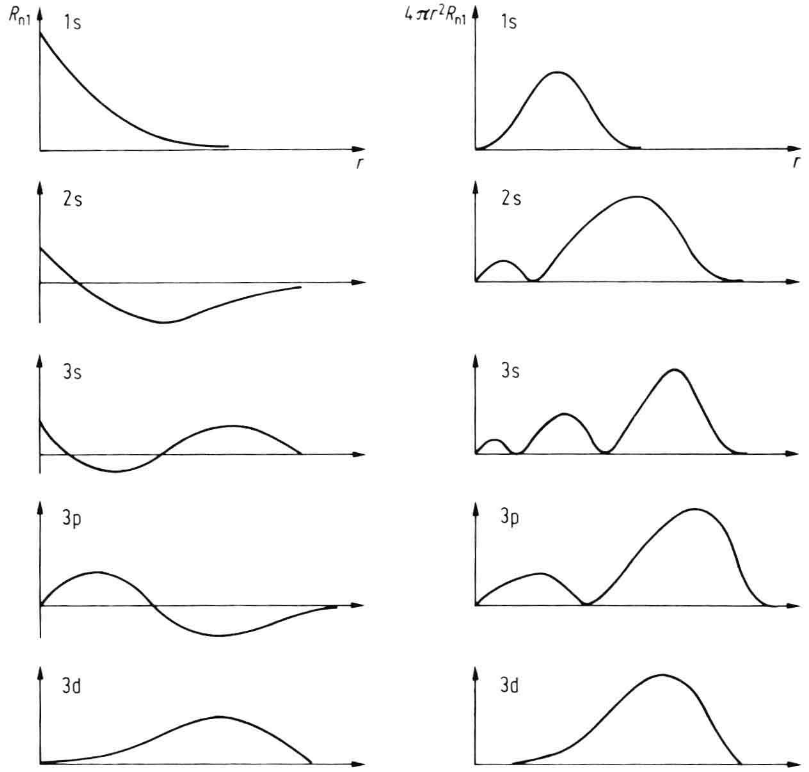

Fig. 1.1. The forms of the radial function R_{nl} (r) and radial distribution function $4\pi\,r^2R_{nl}$ (r) for various nl values of the hydrogen atom

a) As the value of n increases, the electron density moves away from the nucleus. This corresponds to a higher potential energy, and consequently a higher total energy (to be expected from the variation of E with n).

b) As the value of n increases, the wave function becomes more spread out for a given value of l. Thus the 6p radial function will have $6-1-1 = 4$ nodes, five regions of non-zero electron density, the smallest closest to the nucleus, the largest furthest away from the nucleus.

c) All the radial functions have a vanishing electron density at the nucleus, with the exception of s-type functions ($l = 0$).

(ii) The angular function Y_{lm} (θ, ϕ). The angular functions Y_{lm} (θ, ϕ) are a class of functions well known in mathematics: the spherical harmonics. They have the particular property that the wave function f (r) $\cdot$ Y_{lm} (θ, ϕ) will be an eigenfunction of certain angular momentum operators. The two angular momentum operators $\mathscr{L}^2$ (giving the square of the total electronic angular momentum) and $\mathscr{L}_z$ (giving the value of the component of the angular momentum along one axis, arbitrarily denoted as the z axis) both commute with the Hamiltonian operator. This means that the eigenfunctions of $\mathscr{H}$ are also eigenfunctions of $\mathscr{L}^2$ and $\mathscr{L}_z$ however, unlike the Hamiltonian operator,