J. S. GRIFFITH

THE THEORY OF TRANSITION-METAL IONS

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PREFACE

I have tried to present a unified and deductive introduction to that part of theoretical physics which is becoming known as ligand-field theory. The field of application of this theory is rapidly spreading at the present time and, because of this, it appears more suitable and more helpful to concentrate upon the methods of the theory rather than the details of applications. Hence, although a considerable survey of experimental measurements appears in chs. 10–12, it is by no means exhaustive. The exclusion of almost all reference to rare-earth or actinide ions and to chemical applications—for which the reader is referred to L. E. Orgel's book, *Transition-metal Chemistry* (London: Methuen, 1960)—stems from similar considerations.

There are a number of essential prerequisites to a proper understanding of the theory of the physical properties of ions in compounds. Chs. 1–6, together with §§8.4, 8.6 and 8.7, include those things I deem necessary. Three seem to me especially important: a detailed understanding of the selection rules and other numerical restrictions upon matrix elements implied by the classification of the behaviour of the constituent operators and functions under the elements of symmetry groups; the use of Dirac's equation to derive the spin-orbit coupling and nuclear hyperfine energy; the complex of ideas which has as particular manifestations Kramers's theorem on degeneracy, Wigner's operation of time reversal, and Frobenius and Schur's discussion of the relation between an irreducible representation and its complex conjugate. These matters play a central role in my presentation of the theory.

When deciding the contents of the book it soon became apparent to me that there were many important propositions which workers in the field regarded as 'obvious' and used in order to streamline calculations, but which had never been formally proved. A particular example is the relation between 'holes' and 'particles'. Following the work of Shortley and Racah, it is to be expected that the matrix elements of quantities of interest between hole states are simply related to those between particle states in ligand-field configurations as they are in atomic configurations. But to use this relationship with confidence in calculations it is necessary to know and prove its precise form, including the specification of relative phases. In this case and otherwise I have tried to present and prove results in the forms which are actually needed in calculations.

With a book of this size in a fast-expanding field it is inevitable that the contents should represent in the main the author's position at a time past. Most of the book was written in 1958 and it was submitted in the spring of 1959 but I have referred to later work when it has cast a genuinely new light on some topic.

Finally, it is a pleasure to acknowledge my benefit from many discussions on theoretical physics and theoretical chemistry with Professor H. C. Longuet-Higgins and members of his department, especially with L. E. Orgel on the theory of transition-metal ions. I am also indebted to C. K. Jørgensen for his kindness in preparing Table 11.3 for me and to him and C. E. Schäffer for the data in Appendix A 40.

J. S. GRIFFITH

June 1960

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CONTENTS

Preface *page* ix

Chapter 1. INTRODUCTION 1

Chapter 2. ANGULAR MOMENTUM AND RELATED MATTERS

1 The Hamiltonian for an atomic system 6
2 Orbital angular momentum 8
3 Addition of angular momenta 14
4 The spin of the electron 17
5 Wigner's formula 19
6 Permutations and the Pauli exclusion principle 24
7 The Russell–Saunders coupling scheme 30
8 Vectors, their matrix elements and selection rules 33

Chapter 3. ELECTROMAGNETIC RADIATION

1 Electromagnetic fields 41
2 Emission and absorption of radiation 52

Chapter 4. THE STRUCTURE OF FREE ATOMS AND IONS

1 One-electron atoms 58
2 Electron configurations 63
3 Evaluation of the matrix elements $\mathscr{H}_{ij}$ 68
4 Slater–Condon parameters 73
5 p^n configurations 79
6 d^n and other configurations 83
7 Fitting parameters to the observed spectrum 96
8 Radial functions and the Hartree–Fock method 102

Chapter 5. MAGNETIC EFFECTS IN ATOMIC STRUCTURE

1 Spin-orbit coupling 106
2 Examples of calculations of spin-orbit coupling energies 109
3 The nucleus in atomic structure 114
4 Dirac's linear wave-equation for the electron 116
5 Deductions from Dirac's linear wave-equation 122
6 Atoms in external magnetic fields 128

Chapter 6. GROUPS AND THEIR MATRIX REPRESENTATIONS

1 Rotations and the concept of a symmetry group 135
2 Elementary properties of groups 139
3 The symmetry groups of physics 141
4 Matrix representations of groups 146
5 The direct product of two representations 151
6 The representations of C_n, D_n, T_d, O and K 156
7 Relations between representations 161

8 Relations between functions belonging to representations *page* 164
9 Spinors and spinor groups 169
10 Some mathematical aspects of the groups R_3 and U_2 176
11 The finite spinor groups and their representations 180

Chapter 7. COMPLEX IONS

1 The concept of a complex ion 182
2 Electron configurations 183
3 Evaluation of parameters 189
4 The coupling schemes 191
5 Survey of ligand-field theory 193

Chapter 8. CRYSTAL-FIELD THEORY AND THE WEAK-FIELD COUPLING SCHEME

1 The influence of a static environment 195
2 The environment as a classical distribution of charge 199
3 Relationships between potentials for different environments 202
4 Kramers degeneracy 205
5 The Jahn–Teller effect 209
6 Real and complex representations 212
7 Various group-theoretic propositions 216
8 Examples of calculations in the weak-field scheme 219
9 Spin-orbit coupling 222
10 The method of operator equivalents 223

Chapter 9. THE STRONG-FIELD COUPLING SCHEME

1 Strong-field configurations and terms 226
2 Electrostatic matrix elements 229
3 Examples 231
4 Pairing energies 237
5 The p^n isomorphism 238
6 Spin-orbit coupling energies 240
7 Holes and particles 245
8 Fractional parentage 256

Chapter 10. PARAMAGNETIC SUSCEPTIBILITIES

1 Van Vleck's theorem 265
2 Susceptibilities of ground terms of d^n configurations 269
3 Residual paramagnetism 278
4 More accurate treatments 279

Chapter 11. OPTICAL SPECTRA AND THERMODYNAMIC PROPERTIES

1 Introduction to d^n spectra 286
2 Intensities 288
3 Coupling of nuclear and electronic motions 292
4 Spectra of the aqueous aquo-ions 301
5 Further examples of spectra 305
6 The cobaltic ion 312
7 Thermodynamic properties 315

Chapter 12. PARAMAGNETIC RESONANCE

1 Electron resonance page 320
2 Refinements to the Hamiltonian 322
3 The spin-Hamiltonian 330
4 Survey of electron resonance measurements 340
5 Nuclear magnetic resonance in cobaltic compounds 374

APPENDICES

1 The elements 378
2 Tables 382
3 Summary of relevant parts of perturbation theory 428
4 The Hamiltonian for a charged particle in an electromagnetic field 432
5 Gauge invariance in perturbation theory 434
6 Atomic spectral parameters 437
7 Deductions from Wigner's formula 440
8 L.C.A.O. theory 443
9 Symmetry of the coupling coefficients for the octahedral group 446

BIBLIOGRAPHY 447

INDEX OF SYMBOLS 451

SUBJECT INDEX 453

CHAPTER 1

INTRODUCTION

1.1. Transition metals and their compounds

The transition metals are those which have partly filled shells of *d*-electrons in some, at least, of their compounds. In a similar way, the rare-earth metals have partly filled shells of *f*-electrons. Among the stable elements there are three series of transition metals and one of rare-earth metals. We are concerned in this book with the three stable series of transition metals. In order of increasing atomic number, they are called the first, second and third transition series. (See Appendix 1 for an enumeration of the elements in the three series.) The theory we shall develop is applicable, with minor modifications, to rare-earth metal compounds and to those compounds of the unstable elements at the end of the periodic table which contain partly filled shells.

Two extreme classes of transition-metal compound are conveniently distinguished—the metallic and the non-metallic. The former class includes the alloys, interstitial hydrides, borides, carbides and, stretching the use of the word compound slightly, the metals themselves. Typical members of the latter class are inorganic salts such as copper sulphate or potassium ferricyanide. From a theoretical standpoint the essential distinction between the two classes is that in the latter the *d*-electrons of the partly filled shells may be assigned individually to particular metal atoms. Each metal atom (or ion) has its own set of *d*-electrons localized near it and having little interaction with the sets belonging to neighbouring metal atoms. In a metallic compound the *d*-electrons are owned collectively by all the metal atoms and they cannot be separated into nearly non-interacting sets.

In this book we are concerned only with the non-metallic type of compound. The implied division of the electrons into localized groups is strictly never more than an approximation to the truth but it turns out to be a good approximation for a wide range of compounds which may, therefore, be called non-metallic.

It is usually possible to decide unambiguously how many *d*-electrons are localized near a particular transition-metal atom in a compound. There are transition-metal compounds, $KMnO_4$ or CrO_2Cl_2 are examples, in which there are no *d*-electrons. Our theory says little about such compounds although it can compare them with similar compounds which do contain *d*-electrons.

Finally, what is a *d*-electron in an atom, an ion or a compound? This will emerge slowly as we pass through the book. The main general discussion of the meaning of a *d*-electron in a compound is in ch. 7 and there the sense in which we may say that $KMnO_4$ contains no *d*-electrons will become apparent.

1.2. Stereochemistry

X-ray crystallographic determinations of the structures of a great number of transition-metal compounds have been made. A survey of all the data available on the class of compounds in which we are interested shows that the most common arrangement of nearest neighbours about the metal ion is that of a more or less distorted octahedron. Thus the anhydrous fluorides of Mn^{++}, Fe^{++}, Co^{++} and Ni^{++} crystallize in the rutile structure, each metal atom being surrounded by an almost regular octahedron of fluoride ions (as shown in Fig. 12.8). The hydrated ions $Mn(H_2O)_6{}^{++}$, $Fe(H_2O)_6{}^{++}$, $Co(H_2O)_6{}^{++}$, $Ni(H_2O)_6{}^{++}$ in crystals all have almost regular octahedral symmetry. An ion such as $Co(NH_3)_5Cl^{++}$ has the five ammonia molecules at the vertices of an octahedron and the chloride ion at a slightly greater distance from the metal atom along the line joining the latter to the sixth vertex.

Two other important types of stereochemical arrangement must be mentioned. Tetrahedral coordination of the metal ion is fairly common, particularly among the Co^{++} compounds. Some examples are $CoCl_4{}^{--}$, $ReCl_4{}^{-}$ and the blue form of $CoCl_2(NH_3)_2$. Planar complexes in which the metal is surrounded by a square of four molecules or ions are very common for metal ions with eight *d*-electrons and occur also for those with seven and nine. The Cu^{++} ion with nine *d*-electrons exhibits the whole range of stereochemistries from slightly distorted octahedral to planar. Sometimes there are four close neighbours of the Cu^{++} ion in a plane and two more distant ones completing a distorted octahedron. Other stereochemical arrangements are found, but not nearly as commonly as the three types already mentioned.

The more distant environment of the metal ion, namely the environment of the central octahedral, tetrahedral or planar group, is extremely variable. Fortunately groups other than nearest neighbours are relatively unimportant in determining at least the coarse chemical and physical properties of the ion. Consequently we can often neglect all but the nearest neighbours of the metal ion. These latter we shall usually refer to as the ligands.

Many of our detailed spectroscopic and magnetic data refer to ions in solution. The few detailed comparisons which can be made between the properties of ions in solids of known structure and those of the corresponding ions in solution show that the inner coordination group is usually maintained almost unchanged in solution. For example, the optical spectra of hydrated transition-metal ions in aqueous solution are almost identical with those of the same hydrated ions in crystalline solids. It will appear in due course that this usually implies that the stereochemistry is the same in the two situations. The physicist, however, must be warned that solutions of transition-metal compounds often contain unexpected molecular species. In general, solutions of transition-metal ions may contain equilibrium mixtures of different complexes, that is, the metal may occur in association with different sets of ligands. Nevertheless, many different types of evidence show that each species maintains its own particular stereochemistry with regard to the orientation of nearest neighbours about the metal ion.

In textbooks dealing with transition-metal chemistry it is usual to distinguish between compounds and complex ions. This particular type of classification, while it may be useful in certain contexts, tends to hide the important features common to both classes. In general, the electronic properties of a metal ion will be determined by its nearest neighbours, and it makes little difference whether these are part of a binary solid or of a discrete complex ion. In fact it is even true that the optical absorption spectrum of the 'compound' MnF_2 is very similar to that of the 'complex ion' $Mn(H_2O)_6^{++}$ in aqueous solution.

1.3. The valencies of the transition metals

The concept of valency as used by the chemist in connexion with transition-metal compounds will be regarded as a purely formal one. The molecular species under consideration is supposed to be made up of metal ions and other molecules or ions. To each of the latter a certain characteristic charge is assigned, usually that necessary to give it a closed shell, e.g. zero for a molecule such as water or ammonia, minus one for a halide or nitrate ion, minus two for an oxide, sulphide or sulphate ion, and so on. (See ch. 7 for a discussion of closed shells.) The charge which must then be assigned to the metal ion in order to give the correct charge for the molecular species is termed its valency. To take an example, we consider CrO_4^{--}, which is said to be a compound of hexavalent chromium, since a charge of $+6$ on the chromium, together with four charges of -2 on the oxygens, add up to give a charge of -2 on the species CrO_4. It must be emphasized that there is no implication that anything like a Cr^{+6} ion is present in the CrO_4^{--} anion. The term 'valency' is also used in many other, usually imprecisely defined, ways. For the purposes of the present book the formal definition given above is almost always unambiguous and then has the advantage that it involves no preconceptions about the electronic structure of particular transition-metal compounds. In other contexts a different definition might be more convenient.

It is next interesting to ask whether there is ever a direct correspondence between the formal valency and the electronic distribution in the region near the metal ion. Since the second and subsequent ionization potentials of the metals are larger than the ionization potential of any other molecule or ion in the environment, it is clear that the consequent electron-attracting tendency of the metal ions in high valencies must be neutralized in one way or another by their nearest neighbours. The manner of this neutralization will appear in ch. 7; for the present we note that as the formal valency of the metal ion increases, the degree of its correspondence with the actual electronic structure usually decreases. It is for this reason that the compounds discussed in this book are nearly all formally of low valency.

The valencies of a metal ion which are stable will of course depend on the nature of the ligands. Manganese, for example, forms hexa- and heptavalent compounds with oxygen, MnO_4^{--}, MnO_4^{-}; di- and trivalent compounds with water; and zerovalent compounds with carbon monoxide. A full discussion of the stabilization of valencies by different ligands would take us too far into general

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chemistry. The reader is referred to works on inorganic chemistry for further details.

The valencies exhibited by different metals in the presence of the same ligand also depend on a number of factors. One of these is very simple and of great importance. The ease of oxidation from the nth to the $n+1$th valency is closely related to the $n+1$th ionization potential, particularly for the lower valencies of the transition metals. The observed ionization potentials for the three lowest valencies of the transition metals are given in Appendix 1.

In the first transition series only copper can exist as an aqueous monovalent ion. This is presumably to be correlated with the high second ionization potential of copper, which is more than 2 eV larger than that of any other of these elements. In a similar way the trivalent compounds of Sc, Ti, V, Cr, Mn, Fe, Co are obtained more easily than those of Ni, Cu, Zn; that is, the metals with lower third ionization potentials are more easily obtained in the trivalent state. Many other examples of this sort could be given, but it must also be emphasized that a number of other factors are involved which depend on the interaction of the metal with its environment. The chemist describes this situation by saying that the oxidation-reduction potential of a metal ion depends on the nature of the ligands.

1.4. Theories of chemical bonding

A few remarks on the more important contemporary theories of the electronic structure of transition-metal compounds may help to clarify our approach to the subject.

The simplest possible picture of the electronic structure of transition-metal compounds is the purely ionic one. Here the formal valencies of the different ions in the structure are interpreted literally to imply the presence of the corresponding ions. This theory, which was adequate for the description of the stoichiometric properties of most compounds, has been more or less abandoned by chemists, since it is clearly unable to account for many experimental observations and is, in any case, quite unrealistic in the light of our present knowledge of the ionization potentials and electron affinities of atoms, ions and molecules.

The most influential 'chemical' theory of transition-metal structure has undoubtedly been the valence-bond theory, as developed by Pauling. Here an attempt is made to distinguish between 'ionic' compounds which are held together by electrostatic forces, much as in alkali halide crystals, and 'covalent' compounds which are held together by directed bonds. Conceptually this theory has proved so attractive to chemists that it has been the basis of most recent chemical thinking on the subject. Despite its usefulness in this direction it has not proved fruitful in the field of quantitative calculation. It now seems certain that some of the postulates of the scheme require revision, but its simplicity guarantees it a central importance in qualitative chemical discussions of the theory of valency.

While chemists were developing the valence-bond theory, the ionic theory was being adapted for use in a more quantitative way. Largely through the influence of Bethe and Van Vleck, a detailed understanding of the magnetic properties of divalent and trivalent ions in certain types of environment was built up. This theory was restricted in its range of application since failure to include 'chemical' interactions excluded most metal compounds of high valency and also many others. Within its range, by applying perturbation theory to the quantum mechanical description of the free ions, it achieved many notable quantitative successes. For reasons which it is now difficult to understand no chemical applications of the theory were made before 1950. In other fields of theoretical chemistry the molecular-orbital method had, by 1950, achieved a central position. It was natural, therefore, that when certain experimental observations demanded an explanation in terms of electron-sharing between atoms the electrostatic theory was extended in the direction suggested by the molecular-orbital method. The theory which has resulted is a hybrid which still depends heavily on the simple electrostatic theory, but which can be justified as an approximation to a more complete molecular-orbital treatment.

CHAPTER 2

ANGULAR MOMENTUM AND RELATED MATTERS

2.1. The Hamiltonian for an atomic system

In order to understand the behaviour of a metal ion in the environment imposed upon it in a compound, it is necessary first to understand the electronic structure of free atoms and ions. This is obvious for compounds in which one believes that the environment represents a rather small disturbance of this electronic structure. However, it is also very useful to be able to refer to the theory of the structure of free atoms even when the disturbance is large. This is especially true of the sort of compounds that we consider in this book, namely those in which unpaired metal electrons are localized on or at least near to their parent metal ions. In this chapter and the next three, therefore, I describe those features of the theory of atomic structure which are most relevant to our later treatment of metal compounds. I start from the beginning, but it is rather desirable that the reader should possess already a little knowledge of quantum mechanics: §§ 1–22, 27, 42 and 43 of Professor Dirac's book *Quantum Mechanics* probably cover all that is really necessary.[1] I use the bra and ket notation almost exclusively throughout the book because I feel that, as with vectors in classical mechanics, it makes the intuitive significance of equations and results much easier to grasp.[2]

An atom or ion consists of a relatively massive positively charged nucleus together with a number of electrons. The electrons are held near the nucleus by their electrostatic attraction to the latter and to some extent apart from each other by their mutual electrostatic repulsions. Because of its relatively large mass it is a good approximation to regard the nucleus as being at rest. This means, then, that we have a classical Hamiltonian

$$\mathscr{H} = \sum_{\kappa=1}^{n}\left(\frac{1}{2m}\mathbf{p}_{\kappa}^{2} - \frac{Ze^{2}}{r_{\kappa}}\right) + \sum_{\kappa<\lambda}^{n}\frac{e^{2}}{r_{\kappa\lambda}}, \tag{2.1}$$

for the system. In (2.1) $\mathbf{p}_\kappa$ is the momentum vector of the κth electron and r_κ its distance from the nucleus, m the mass of the electron, $-e$ its charge, $+Ze$ the charge on the nucleus and $r_{\kappa\lambda}$ the distance from the κth to the λth electron. There are n electrons and the whole system has a charge $(Z-n)e$, so for a neutral atom $n = Z$ and for a positive ion $n < Z$.

---

[1] Dirac (1947). §§ 42 and 43 are perturbation theory. A summary of parts of this, together with some further developments, is in Appendix 3.

[2] I quite often use single symbols to stand for kets or bras and may write, for example, $\psi = |\psi\rangle$. I do not apologize for this apparent confusion of types because it does not occur in places where it could lead to difficulty.

Naturally (2.1) is not a complete and accurate Hamiltonian for the system. The effect of regarding the nucleus as being at rest is truly a small one and the whole part of it which is relevant to us can be taken into account by interpreting m in (2.1) as the reduced mass $\mu M/(\mu+M)$, where μ is the true mass of an electron and M the mass of the nucleus. This result is obtained by referring all distances in the more exact theory to the centre of mass of the system whereupon one obtains (2.1) to an approximation quite sufficient for our purposes. There are other ways in which (2.1) is incomplete which will prove important in our theory. The electron has a magnetic moment and so, quite often, does the nucleus. This introduces extra terms into (2.1) which represent magnetic interactions between the various particles of the system. These we consider in ch. 5, but until the end of ch. 4 we derive only the consequences of the Hamiltonian (2.1). The main reason for this particular division of labour is that we find later that the effect of the environment of a metal ion is usually larger, in terms of the energies associated with it, than most or all of the magnetic interactions but usually a little smaller than the electrostatic interactions arising from (2.1). As a consequence of this, the electronic structure of atoms or ions having the Hamiltonian (2.1) is specially important and so we now pass on to consider this.

In quantum theory the classical Hamiltonian $\mathscr{H}$ is taken over directly, but $\mathbf{p}_\kappa$ and $\mathbf{r}_\kappa$ are now regarded as operators, the components of which do not all commute. If we write q and q' for typical, but not necessarily different, coordinates x, y or z then

$$\left.\begin{aligned} p_{\kappa q}p_{\lambda q'} &= p_{\lambda q'}p_{\kappa q} \quad \text{for all} \quad \kappa, \lambda,\\ q_\kappa q'_\lambda &= q'_\lambda q_\kappa \quad \text{for all} \quad \kappa, \lambda,\\ q_\kappa p_{\lambda q'} - p_{\lambda q'} q_\kappa &= i\hbar\delta_{qq'}\delta_{\kappa\lambda}, \end{aligned}\right\} \tag{2.2}$$

where the Kronecker delta symbol is defined by the equations $\delta_{ab} = 0$, unless $a = b$ when $\delta_{ab} = 1$. In (2.2) $p_{\kappa q}$ represents the q component of $\mathbf{p}_\kappa$ and similarly for the others. Any pair of components of the same or different momenta commute with each other and the corresponding statement is true for coordinates. The only non-commuting pairs of components are those referring to a coordinate of a single particle and its conjugate momentum.

Schrödinger's form for the equations of motion is

$$i\hbar\frac{d}{dt}|X\rangle = \mathscr{H}|X\rangle, \tag{2.3}$$

and, if we express the ket $|X\rangle$ in terms of the coordinates of the electrons and the time, the $\mathbf{p}_\kappa$ may be equated to differential operators

$$\mathbf{p}_\kappa = -i\hbar\nabla_\kappa = -i\hbar\left(\frac{\partial}{\partial x_\kappa}, \frac{\partial}{\partial y_\kappa}, \frac{\partial}{\partial z_\kappa}\right). \tag{2.4}$$

It is immediate that these $\mathbf{p}_\kappa$ satisfy (2.2). Equation (2.3) then becomes Schrödinger's wave-equation for the system

$$\mathscr{H}(-i\hbar\nabla_\kappa, \mathbf{r}_\kappa)\,\phi(\mathbf{r}_\kappa, t)\rangle = i\hbar\frac{\partial}{\partial t}\phi(\mathbf{r}_\kappa, t)\rangle. \tag{2.5}$$

The Hamiltonian $\mathscr{H}$ represents the total energy of the system. Since it does not involve the time explicitly we may find stationary states which are eigenfunctions of $\mathscr{H}$. In fact we write

$$\phi(\mathbf{r}_\kappa, t)\rangle = e^{-iEt/\hbar}\,\psi(\mathbf{r}_\kappa)\rangle, \tag{2.6}$$

and

$$\mathscr{H}\psi\rangle = E\psi\rangle, \tag{2.7}$$

where ψ is independent of time and ϕ then satisfies (2.5). We shall be interested in these stationary states for atomic systems and when discussing them shall sometimes drop the ket symbols in equations such as (2.7). We always retain the symbols to express average values and for matrix elements between different states, e.g. $\langle\bar{\psi}|\, \mathbf{p}_\kappa^2\, |\psi\rangle$ is the average value of the square of the momentum of the κth electron for the state ψ and $\langle\bar{\psi}_1|\, x_\lambda\, |\psi_2\rangle$ is the matrix element of x_λ between the states ψ_1 and ψ_2. We now have the wave equation

$$\left\{\sum_{\kappa=1}^{n}\left(-\frac{\hbar^2}{2m}\nabla_\kappa^2-\frac{Ze^2}{r_\kappa}\right)+\sum_{\kappa<\lambda}^{n}\frac{e^2}{r_{\kappa\lambda}}\right\}\psi = E\psi, \tag{2.8}$$

corresponding to (2.1).

It is an experimental fact that electrons obey Fermi–Dirac statistics and this appears in the theory as an assertion that electronic systems can only be represented by solutions of (2.8) which are fully antisymmetric with respect to interchange of electrons. We shall see precisely what this means in § 2.6. It is also an experimental fact that an electron has a magnetic moment and that there are two independent internal states for the electron, called states of spin, which are associated with different orientations of the magnetic moment. The extra terms in the Hamiltonian due to the magnetic moment of the electron are usually small and as already remarked are not considered until ch. 5.

Because of the requirement of Fermi–Dirac statistics it turns out that the existence of two independent spin states for the electron actually has a very large influence upon the energy of many-electron systems even though the terms in the Hamiltonian which involve the spin are small. In § 2.4 we shall consider the algebraic techniques for dealing with the spin and then discuss its influence on the electronic energy. First, however, we must discuss the properties of orbital angular momentum.

2.2. Orbital angular momentum

In classical mechanics there are always two important constants of the motion for an isolated system. The first is the total energy and we recognize this in quantum theory by taking it for our Hamiltonian. The second is the total angular momentum. This is also important in quantum theory and, as we shall see shortly, it commutes with the Hamiltonian (2.1) and so can still be taken as a constant of the motion. Because of this it is very useful to examine its properties, eigenstates and eigenvalues in considerable detail. We shall find actually that if we use (2.1) there are two kinds of angular momentum which are constants of the motion in quantum theory. The first corresponds most closely to the total angular momentum in classical mechanics. We now call it the total orbital angular momentum to distinguish it from the second kind, the spin angular momentum. Then we shall find later that if magnetic interactions between the particles are included, only the sum of the orbital and spin momentum is a constant of the motion. This, in quantum mechanics, is called the total angular momentum. The third common constant of the motion for a classical system is the total linear momentum. This is not relevant for us because our system is not really isolated; it is congregated round the fixed nucleus. In the words of Weyl, we have transformed space from a homogeneous space to a centred space. The centre is the nucleus and so long as we regard it as a fixed point charge we have full rotational symmetry about it but no longer translational symmetry. This is why angular but not linear momentum is useful as a tool in the analysis of structure.

Just as in the classical theory, then, the orbital angular momentum of a particle about the origin is defined as the vector $\mathbf{l} = \mathbf{r} \wedge \mathbf{p}$. Using the commutation relations (2.2) we find readily that

$$\mathbf{r} \wedge \mathbf{p} = -\mathbf{p} \wedge \mathbf{r}, \tag{2.9}$$

as in the classical theory, but that

$$l_x l_y - l_y l_x = i\hbar l_z, \tag{2.10}$$

and similarly for cyclic permutations of x, y, z. The three relations of the type (2.10) may be abbreviated in vector notation to the equivalent single equation $\mathbf{l} \wedge \mathbf{l} = i\hbar\mathbf{l}$ showing that in quantum theory, unlike the classical theory, the vector product of a vector with itself is not necessarily zero.

It is convenient to introduce a notation for the commutator of two quantities a and b, of which one may be a vector:

$$[a, b] \equiv ab - ba. \tag{2.11}$$

The reader should note that we are following here the normal mathematical usage rather than the Poisson bracket notation of Dirac. The two notations differ, of course, only by a factor $i\hbar$. A number of useful relations follow immediately from (2.11). We have the anticommutation relations for the commutator:

$$[b, a] = -[a, b] \quad \text{and} \quad [a, a] = 0,$$

and the distributive laws

$$[a, b+c] = [a, b] + [a, c],$$

$$[b+c, a] = [b, a] + [c, a].$$

Then there is also a pair of relationships which are rather like the rule for differentiating a product

$$\left.\begin{aligned} [ab, c] &= a[b, c] + [a, c]b, \\ [c, ab] &= a[c, b] + [c, a]b. \end{aligned}\right\} \tag{2.12}$$

We shall refer to all these relations collectively as (2.12). In the new notation, (2.10) becomes $[l_x, l_y] = i\hbar l_z$

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