Introduction

Most atoms, when they form ions, such as in a crystalline salt, achieve a closed shell configuration; either by losing their valence electrons (metallic ions) or building up an incomplete shell (negative ions). Such closed shell ions are therefore in ^1S state, which is diamagnetic, non-degenerate and generally does not give rise to interesting effects. However, the transitions and rare earth metals are exceptions to this rule because of their inner, incomplete $3d$, $4d$, $4f$, $5f$ shells as free ions of these in general have paramagnetic, degenerate ground states which in crystals get split by the electric field. In a crystalline salt, such an ion finds itself surrounded by some regular arrangement of other ions and water molecules. Now one should consider the ion and its neighbors as a big molecule, and discuss their interaction in terms of covalent and other bonds. However, it has been found a good approximation to consider the neighbors as simply giving rise to an electrostatic potential, the crystalline field, which acts on the paramagnetic ion. This field combined with the

spin-orbit coupling, splits the ground term into sequence of levels. Since 1946, paramagnetic resonance had been used to study in great detail the lowest of these energy levels and their variation in an applied magnetic field. Consequently there is considerable interest in making accurate calculations of these levels. Comparisons between the calculated and the observed levels has then determined the magnitude of various parameters such as the strength of the crystalline field, and has also brought light to some refinements that are required in the quantum theory of atoms. The use of symmetry properties may lead to very broad general results, applicable to any free atom or ion, but in this thesis, we shall use group theory in a quite different role. Group theory is used here to help calculate particular matrix elements and the splittings as required. The energy levels are determined. In detail, this involved a long and complicated calculation, so we shall show how group theory is used to calculate the type of matrix elements that are required during calculation and which kind of splitting is at each stage [Heine, 1993].

We focus mainly on the conducting fullerides, for which the 1996 Nobel Prize for Chemistry has been won by Robert F. Curl Jr., Sir

Harold W. Kroto, and Richard E. Smalley for their discovery of fullerene, in which atoms that are arranged in closed shells were found to have the structure of a truncated icosahedron C_{60} which can be derived from an icosahedron after the vertices have been cut off. The pattern of a European football (soccer ball) has exactly this structure, and the new allotrope of carbon was named Buckminsterfullerene after the architect R. Buckminster Fuller who designed geodesic domes in the 1960's [Levinovitz & Ringertz, 2001].

Endohedral fullerenes are of great interest due to their diversity and plans for numerous applications. Because of the robust carbon cage and its large hollow interior, endohedral fullerenes represent a new class of technology relevant composites as they incorporate possible metallic and fullerene like properties [R. Klingeler, G. Kann, I. Wirth, S. Eisebitt, P. S. Bechthold, M. Neeb & W. Eberhardt, 2001]. In general, two possibilities for doping are offered; either inserting a foreign atom M inside the C_{60} cage or replacing one or several carbon atoms in the C_{60} cage with atoms having different electronic structure. In the first case, M@ C_{60} endohedral

super-molecule is obtained (Fig 1.1), while in the second case, the composition $C_{59}M$ is obtained by on-site doping [Forró & Mihály, 2001].
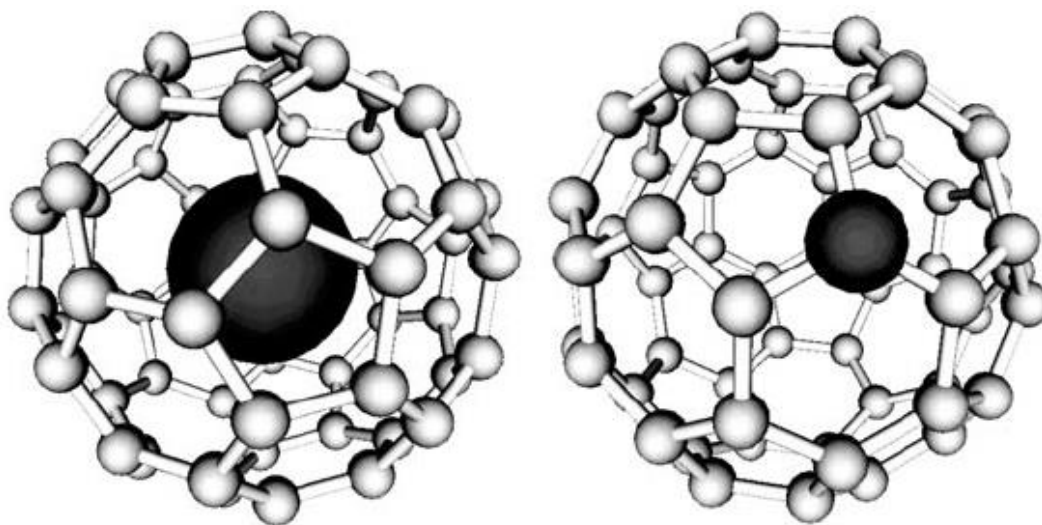

Fig 1.1:

Endohedral (left) and 'on-site' (right) doping of the fullerene molecule [Forró & Mihály, 2001].

Endohedral fullerenes, where fullerenes encapsulate additional atoms, ions, or molecular species enclosed within their inner spheres, have been an object of fascination since the first Lanthanum C_{60} complex called La@C_{60} was discovered in 1985. The "@" sign in the name reflects the notion of a small molecule trapped inside a shell. The unique carbon cages have captivated scientists with their tantalizing properties and possibilities for application; they can stabilize reactive species inside the cage, can

serve as nondissociating salts in electrochemistry and offer other exciting properties.

Endohedral C_{60} molecules can be prepared by a "brute force" method, where ions of atoms are accelerated and implanted into the C_{60} cage. The ions should have just enough energy to open up the cage and enter. Endohedral molecules of M@ C_{60} with M = N, P, Li, Ca, Na, K, Rb were produced this way in small quantities [Forró & Mihály, 2001]. A Polonium atom was the largest dopant atom to embed the C_{60} fullerene, creating the endohedral molecule Po@C_{60} [Ohtaski & Ohno, 2006].

For the quantum numbers which characterize the states, the atomic electrons can be described by eigenfunctions with the four quantum numbers n (principal quantum number), l (orbital quantum number), m_l (magnetic quantum number) and m_s (spin projection quantum number) [Haken, Wolf & Brewer, 2004].

The magnetic dipole moment of an atom, m, referred to as the orbital magnetic moment, is the resultant of all orbital and spin magnetic moments, m_l and m_s respectively, of its electrons. The resultant magnetic moment, also known as exchange force, ties the atoms together. In a

degenerate *J*-multiplet, which has a good total angular momentum quantum number *L* and a good spin quantum number *S*, if the atom is described in *LS* coupling, vector states are written in terms of the Quantum number M_J for the *x, y* and *z* components of the total angular momentum [McElhinny, 1973]. The unperturbed atomic states (eigenstates) can then be labeled by the total angular momentum (the total quantum number *J=L+S*) [Friedrich, 2006]. Spin moment is therefore largely determined by exchange interactions; an electrostatic many-body effect, caused by the Coulomb interaction between electrons [Bates & Bederson, 1990].

According to group theory, in the absence of external fields, we expect *J* to be a good quantum number and the degeneracy of the $(2J + 1)$ states in the level to be absolute. Yet, when atomic spectra are observed, one often finds that the fine-structute lines split even further into hyperfine structure. Since group theory allows no such splitting from the electronic degrees of freedom, it must result from an additional degree of freedom, Pauli (1924) suggested that, if the nucleus had a spin, it could provide this. The extra structure is then associated with the new irreducible representations (IR) of the full rotation group based on the direct product

of nuclear and electronic eigenfunctions. The energetic interaction which produces the splitting can be either electric or magnetic [Tinkham, 2003].

The magnitude of the crystal field effect in rare earth ions is relatively small. This is due to their formation, which leaves the $4f$ inside the filled $5s$ and $5d$ shells when the outermost $6s$ is removed. This means that they have a smaller radius and are partly shielded from external fields. These two factors mean that the transition metal ions are much more sensitive to the crystal field than the rare earths. Furthermore, the spin-orbit interaction is quite large because it varies with the atomic number. Therefore in treating the crystal field effects by perturbation theory, one must apply the spin-orbit interaction first. The spin-orbit interaction splits the gross structure of the free ions into fine structure terms defined by the quantum numbers (LSJ), denoted in the Russel-Saunders coupling as $^{2S+1}L_J$. The crystal field then perturbs these states, shifting their energies slightly and causing new splittings. However the size of these shift are much smaller than the spin-orbit splittings and so the dopant ions are generally fairly similar to those of the free ions [Fox, 2006].

Rare earth moments can be given by the use of Hund's rules, which predict the spin and orbital moment as a function of the number of inner shell electrons [Skomski & Zhou, 2006]. This interaction should be analyzed by means of quantum theory which strongly concerns with spin-spin interactions in the order of the atomic scale. Exchange interaction, which tends to align neighbor spins, is the appropriate treatment for analysis of many-electron systems, the f^2-electron system in this particular case.

Creating a magnetic field comes from two sources:

The first is coming from the motion of electric charges such as currents changing the electric field into magnetic field. This "Maxwell's" interaction is macroscopic, that is, it does not correspond to any characteristic length. Quantum mechanics links magnetism inextricably with the intrinsic angular momentum or "spin" of electrons. However, unlike classical angular momentum, which can take on any value, this second type of spin of an electron is a purely quantum number which can have only one of two values; "up" or "down" and atoms have a net magnetic moment, if they contain more spin-up electrons than spin-down

electrons, or vice versa. This often happens if the atom contains partially filled electron shells [Forró & Mihály, 2001], [Judd & Lo, 2004].

Rare earth elements, also known as the "4f" series, which can hold up to 14 electrons, become ferromagnetically ordered at lower temperatures, and almost have a ferromagnetic or antiferromagnetic ground state at sufficiently low temperatures. That is, below a certain temperature called the Curie temperature, the exchange interactions between the spins lead to two distinct phases in a solid depending on their sign, and the atomic magnetic moments tend to either line up in a common direction, giving a ferromagnetic phase, or form an array of spirals, yielding to an antiferromagnetic phase where alternate spins point in opposite directions [Coey & Sanvito, 2004].

We are considering two systems; each is made of a rare earth ion enclosed within the cage-like truncated icosahedron. For an f orbital, there are seven ($2 \times 3 + 1 = 7$) possible angular momentum states which are degenerate (of the same energy) under normal circumstances. Therefore, even though the angular momentum quantum number l is no longer a good quantum number, it still has a meaning; it tells the origin of a particular

atomic orbital [Haken, Wolf & Brewer, 2004]. The study of the exchange interactions of these interacting systems as they come close together is the foundation for the physics of this subject. For an endohedral fullerene, the crystalline electric field at a rare earth ion approximates to one possessing icosahedral symmetry.

Application of combinatorial methods with the IR of the icosahedral group I are made to the f-electron system by employing group representations that have no nontrivial invariant subspaces and applications. The effect of icosahedral field, a strong crystal field, on the f-orbital and how the symmetry of the crystal field can be used to write wave function of the f^2 system is discussed in this study. In order to develop a many electron theory of the exchange interactions within these ion pairs of the icosahedral symmetries, a many-body and group theoretic approach will be used to understand the system of f-electrons.

In the next chapter, the splittings of energy levels by the presence of strong crystal field is discussed in detail. Chapter 3 introduces the concepts of second quantization and perturbation theory. Many-body

operators and the exchange interactions are derived in detail in chapter 4.

Finally, a conclusion of the present work is presented in chapter 5.