Chapter 1. Introduction

1.1. Group-IVB Metal Oxides:

In the Periodic Table, Group-IVB contains Titanium (Ti), Zirconium (Zr) and Hafnium (Hf) as naturally-occurring elements. William Gregor, Franz Joseph Muller and Martin Heinrich Klaproth independently discovered titanium between 1791 and 1795. Klaproth named it for the Titans of Greek mythology [1]. Klaproth also discovered zirconium in the mineral zircon in 1789 and named it after the already known Zirkonerde (zirconia). Hafnium was discovered by Dirk Coster and Georg von Hevesy in 1923 in Copenhagen, Denmark, validating the original 1869 prediction of Mendeleev [2]. The properties of these elements are summarized in Table 1.1.

Table 1.1: Some properties of Ti, Zr and Hf (Taken from “Chemistry of the Elements” by N. N.Greenwood and A. Earnshaw)

<table>
<thead>
<tr>
<th>Properties</th>
<th>Ti</th>
<th>Zr</th>
<th>Hf</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number</td>
<td>22</td>
<td>40</td>
<td>72</td>
</tr>
<tr>
<td>Number of naturally occurring isotopes</td>
<td>5</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>Atomic weight</td>
<td>47.867(1)</td>
<td>91.224(2)</td>
<td>178.49(2)</td>
</tr>
<tr>
<td>Electronic configuration</td>
<td>[Ar]3d²4s²</td>
<td>[Kr]4d²5s²</td>
<td>[Xe]4f¹4d²6s²</td>
</tr>
<tr>
<td>Electronegativity</td>
<td>1.5</td>
<td>1.4</td>
<td>1.3</td>
</tr>
<tr>
<td>Metal radius (pm)</td>
<td>147</td>
<td>160</td>
<td>159</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>1667</td>
<td>1857</td>
<td>2222</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>3285</td>
<td>4200</td>
<td>4450</td>
</tr>
<tr>
<td>Density at 25°C (g/cc)</td>
<td>4.50</td>
<td>6.51</td>
<td>13.28</td>
</tr>
</tbody>
</table>

All these elements have typically hcp structure which gets transformed to bcc structure at high temperatures (882°, 870° and 1760°C for Ti, Zr and Hf respectively). These metals are highly
resistant to corrosion due to the formation of a dense, adherent, self-healing oxide film. The most common oxidation state for these elements is +4. The oxides of these three elements have recently attracted the attention to a great extent because of their different applications.

**Titanium dioxide**, also known as titanium(IV) oxide or titania, is the naturally occurring oxide of titanium with chemical formula TiO₂. Generally, it is sourced from ilmenite, rutile and anatase. **Hafnium(IV) oxide** is the inorganic compound with the formula HfO₂. Also known as hafnia, this colourless solid is one of the most common and stable compounds of hafnium. **Zirconium dioxide** (ZrO₂), sometimes known as zirconia (not to be confused with zircon), is a white crystalline oxide of zirconium.

1.1.1 Crystal Structure:

TiO₂, among several natural polymorphs, exists in three main crystalline modifications—rutile, anatase, and brookite, each of which occurs naturally. Of these, rutile is the most stable form. Other forms are converted into rutile on heating. Each contains 6 coordinate Ti but rutile is the most common form, both in nature and as produced commercially. The rutile structure is based on slightly distorted hcp of oxygen atoms with half the octahedral interstices being occupied by Ti atoms. Anatase and brookite are both based on cubic rather than hexagonal close packing of oxygen atoms, but again the Ti atoms occupy half the octahedral interstices. Anatase and Rutile, both have tetragonal lattice structure with different lattice parameters (\(a = b = 4.5845 \ \text{Å}; \ c = 2.9533 \ \text{Å} \) for Rutile and \(a = b = 3.7842 \ \text{Å}; \ c = 9.5146 \ \text{Å} \) for Anatase). The structures of rutile and anatase crystalline forms are shown in Fig.1.1. The titanium cations have a coordination number of 6 meaning they are surrounded by an octahedron of 6 oxygen atoms. The oxygen anions have a co-ordination number of 3 resulting in a trigonal planar co-ordination.
In 1959 Adam and Rogers [3] first suggested the similarity between the crystal structures of monoclinic HfO$_2$ and ZrO$_2$ [4]. It is explained on the basis of similarity between the Hf$^{4+}$ and Zr$^{4+}$ ions. Both the elements belong to the same Group-IVB in the periodic table with similar valence electrons ($4f^{14}5d^{2}6s^{2}$ for Hf and $4d^{2}5s^{2}$ for Zr). Due to lanthanide contraction, the ionic size of Hf$^{4+}$ and Zr$^{4+}$ are very similar (~0.8 Å). At room temperature, ZrO$_2$ (baddeleyite) and isomorphous HfO$_2$ have a structure in which the metal is 7-coordinate as shown in Fig. 1.2. The unit cell dimensions for HfO$_2$ and ZrO$_2$ are $a = 5.1156$ Å, $b = 5.1722$ Å, $c = 5.2948$ Å and $a = 5.1454$ Å, $b = 5.2075$ Å, $c = 5.3107$ Å respectively.

The monoclinic phase of ZrO$_2$ is a distortion of fluorite (CaF$_2$) structure with Zr atom in seven coordination. The baddeleyite structure was determined by McCullough and Trueblood in 1959.
It has space group symmetry of P2₁/c with four ZrO₂ in the unit cell. The coordination polyhedron around Zr-atom might be ideally visualized as being derived from a cube. In this view, four oxide ions are at the four corners of the base of the cube (designated as O_{II}). Among the other three (designated as O_{I}), one at one of the upper corners of the cube and the remaining two are at the midpoints of the cube-edges connecting the unoccupied corners. Another interesting feature of this structure is the alternation of fluorite-like layers containing O_{II} ions in tetrahedral coordination with layers which contain O_{I} ions in triangular coordination. In the O_{II} coordination tetrahedron, the Zr-O_{II} distances range from 2.16 Å to 2.26 Å and in O_{I} coordination triangle, Zr-O_{I} distances are 2.04 Å, 2.10 Å and 2.15 Å. At higher temperatures the oxides get transformed into tetragonal and cubic phases. In tetragonal and cubic phases, the metal ions have 8-fold oxygen atom coordination as in fluorite structure.

### 1.1.2. Phase Transformation:

Anatase is kinetically while rutile is thermodynamically stable [6]. However, thermodynamic stability depends on its particle-size, and at particle diameters below ~14 nm, anatase is more stable than rutile [6]. The transformation sequence among the three titania polymorphs anatase, brookite, and rutile is size dependent, because the energies of the three polymorphs are sufficiently close that they can be reversed by small differences in surface energy [7]. The temperature range at which the phase transition from anatase to rutile takes place is 673K - 1473K [8] for bulk TiO₂. The transformation from rutile to anatase for the bulk is forbidden. But at nano dimension (<16nm) phase transformation reverses from rutile to anatase [6]. This is attributed to a higher surface energy of rutile than that of anatase (1.32 J.m⁻² for anatase and 1.91 J.m⁻² for rutile). Therefore, the stability of either polymorph has an important dependence on the size of the crystallite. This aspect of the average size dependence on the anatase to rutile phase
transformation has been studied by several authors [9-12]. If particle sizes of the three nanocrystalline phases are equal, anatase is the most thermodynamically stable at sizes less than 11 nm, brookite is most stable for crystal sizes between 11 and 35 nm, and rutile is most stable at sizes greater than 35 nm [7]. The activation energy of the anatase to brookite transformation is small (11.9 kJ mol⁻¹), thus the transformation can proceed at lower temperatures. The activation energy of the brookite to rutile transformation is higher (163.8 kJ mol⁻¹), thus the transformation proceeds rapidly only at higher temperatures. Recently, in the review article by Dorian et al. [13], the anatase to rutile phase transformation has been examined followed by a discussion on the thermodynamics of the phase transformation and the factors affecting its observation. The conditions affecting the kinetics to control the anatase to rutile phase transformation is of considerable importance. This is particularly important in case of high-temperature applications, such as gas sensors and porous gas separation membranes [14-16], where the phase transformation may occur. Therefore, the kinetics of their phase transformation along with the parameters affecting them has to be understood properly in order to obtain different polymorphs for different applications. Both anatase, space group I₄₁/amd, and rutile, space group P₄₂/mnm, are tetragonal in structure. Both crystal structures consist of TiO₆ octahedra, sharing four edges in anatase and two in rutile [17-18]. The anatase to rutile transformation is reconstructive involving the breaking and reforming of bonds [19]. This is in contrast to a displacive transformation, in which the original bonds are distorted but retained. The reconstructive anatase to rutile transformation involves a contraction of the c-axis and an overall volume contraction of ~8% [20]. This volume contraction explains the higher density of rutile relative to anatase. Shannon and Pask (1964) proposed a mechanism in which the (112) nearly close-packed oxygen planes of anatase are retained as the (100) nearly close-packed oxygen planes of rutile. Within
these planes a cooperative rearrangement of Ti\(^{4+}\) and O\(^{2-}\) ions is thought to occur in which the Ti\(^{4+}\) ions need break only two of their six Ti-O bonds in order to reach their new sites [21-22]. The c-axis of anatase appears to be significantly longer than that of rutile only because anatase has more atoms per unit cell than rutile. There have been a number of kinetic studies on this phase transition. Using spectroscopically pure anatase, Czanderna, Rao and Honig (1957) found the transition fits "second order kinetics" in which a plot of \(1/ (1 - \alpha)\) is linear, where, \(\alpha\) is the extent of reaction [23]. Rao (1961) later re-investigated their results in a more accurate way and concluded that the reaction was “first order” in which a plot of \(\log (1 - \alpha)\) vs. time is linear [24]. However, this phase transformation is affected by several factors, namely defects in oxygen sub-lattice, dopants etc. The impurities or conditions which increase the number of oxygen vacancies accelerate the reaction and those which form interstitial oxygen ions would slow it down [20]. HfO\(_2\) and ZrO\(_2\) have three polymorphs: Monoclinic, Tetragonal and Cubic. The room temperature polymorph, known as the baddeleyite structure, has monoclinic space group \(P2_1/c\). The monoclinic phase is converted to tetragonal at 1720°C for HfO\(_2\) and at 1170°C for ZrO\(_2\) [25]. The cubic phase is attained at 2600°C for HfO\(_2\) and at 2370°C for ZrO\(_2\) shown in Fig. 1.3.

**Figure 1.3:** Phase transformation of ZrO\(_2\) at different temperatures (Wikipedia).

The oxides in the tetragonal fluorite structure have the \(P4_2/nmc\) space group symmetry. This crystal structure was first accurately described by Teufer in 1962 using high temperature x-ray
The highest temperature polymorph of HfO$_2$ and ZrO$_2$ has the cubic fluorite structure with the $Fm\bar{3}m$ space group symmetry. In the tetragonal and cubic phases the metal ions have 8-fold oxygen atom coordination and oxygen is 4-fold coordinated with metal ions. The lattice parameters of the monoclinic cell in HfO$_2$ at 1700$^\circ$C would be similar to the lattice parameters of ZrO$_2$ at 1100$^\circ$C. This provided evidence for a critical metal oxygen bond length, above which the monoclinic structure is no longer stable. It has been proposed that the difference in transformation temperature is hence due to a critical bond length, between metal ion and oxygen that must be reached in the monoclinic phase before the tetragonal phase becomes stable [27]. The high temperature phases cannot be quenched at room temperature. However, these high temperature modifications, when stabilized by proper dopant, have different technical applications. By incorporating suitable cation dopants and hence, introducing oxygen-vacancies, tetragonal or cubic phase can be stabilized. Again, metastable phases can be stabilized by controlling the particle-sizes due to the difference in surface-energies for different polymorphs.

Bulk crystalline hafnia and zirconia both undergo a similar sequence of phase transitions from monoclinic to tetragonal to high symmetry cubic phase. The structures of each phase have been depicted in Fig. 1.4. Hf/Zr-atoms are shown by smaller ‘red’ spheres while O-atoms are shown by bigger spheres.

**Figure 1.4:** Three phases of hafnia and zirconia; a: cubic, b: tetragonal, c: monoclinic (Wikipedia).
Martensitic transformations are well-observed in case of bulk solid materials [28]. Martensite was the name originally given to the hard material obtained during the quenching of steels. Martensite is formed in carbon steels by the quenching of austenite at such a high rate that carbon atoms do not have time to diffuse out of the crystal structure in large enough quantities to form cementite (Fe₃C). As a result, the face centered cubic austenite transforms to a highly strained body centered cubic form of ferrite that is supersaturated with carbon. The shear deformations that result produce large numbers of dislocations, which is a primary strengthening mechanism of steels. This type of transformation occurs by a *diffusionless shearing* mechanism.

A diffusionless transformation is a phase change that occurs without the long-range diffusion of atoms but rather by some form of cooperative, homogeneous movement of many atoms that results in a change in crystal structure. These movements are small, usually less than the inter-atomic distances, and the atoms maintain their relative relationships. When a structural change occurs by the coordinated movement of atoms (or groups of atoms) relative to their neighbors then the change is termed *displacive* transformation. This covers a broad range of transformations and so further classifications have been developed [Cohen 1979]. The first distinction can be drawn between transformations dominated by *lattice-distortive strains* and those where *shuffles* are of greater importance as shown in Fig. 1.5.

![Figure 1.5: Types of displacive transformation (Wikipedia).](image-url)
In martensitic transformation, the parent and the product phases have the same composition and their crystal structures are closely related. This transformation does not involve diffusion and because there is no activation energy of diffusion is involved; the rate of this transformation is very high. Unlike other phase transitions, the martensitic transformations do not take place at a particular temperature, but over a wide range of temperatures. The monoclinic-tetragonal phase transformation is a kind of martensitic transformation. Both these polymorphs have distorted fluorite structure and transformation takes place by a diffusionless shear mechanism over a range of temperatures [29] as shown in Fig 1.6.

![Figure 1.6: Pictorial representation of the two phases in zirconia (Wikipedia).](image)

On heating, the transformation to the tetragonal phase starts above ~ 1000°C but is not complete until ≥ 1120°C. The transformation exhibits a hysteresis (shown in Fig. 1.7) of about 200°C and the reverse transformation on cooling begins at only ≤ 930°C. Hence, the high temperature tetragonal phase is formed from the low temperature monoclinic phase at a higher temperature that that at which tetragonal phase is formed from monoclinic phase.
Figure 1.7: Hysteresis in martensitic transformation (Wikipedia).

The transformation is classified as athermal because it takes place over a range of temperatures and the percentage transformation within that range does not change with time as long as temperature remains constant. The details of the monoclinic-tetragonal-cubic phase transition series and its relation to the stabilization of the cubic phase of ZrO$_2$ has increasingly gained interest due to the rapidly growing applications of the ZrO$_2$ ceramics in different fields.

1.1.3. Applications in Bulk and Lower Dimensions:

TiO$_2$ has high refractive index which gives it the quality of an opacifier and its whiteness makes it very useful as white paint. It is transparent in the visible light but absorbs in the UV range. The primary application of titanium dioxide is as a white pigment in paints, food coloring, cosmetics, toothpastes, polymers, and other fields where white coloration is required [30]. This is attributed to the high refractive indices of rutile (2.79) and anatase (2.54) resulting in high reflectivity from the surfaces. Hence, TiO$_2$ of smaller particle size with higher surface areas is used for this purpose due to its enhanced opacifying power and brightness. However, paints utilize polymeric binders to fix the pigment and while in contact with titania, the polymer may oxidize when exposed to sunlight. This effect is known as chalking and, in addition to the direct degrading effect of ultraviolet (UV) radiation, is accelerated by the photocatalytic activity of TiO$_2$, which
also is enhanced by the high surface area of this material [31]. The potential for the application of the photocatalytic effect in TiO$_2$ has attracted considerable interest over the last few decades. Titania as photocatalyst is known to be applicable in a range of important technological areas, viz., electrolysis of water to generate hydrogen [32-33], dye-sensitized solar cells [34-35], air purification [36-37], water treatments [38-40] etc.

TiO$_2$ is a large band gap [41] semiconductor with 3.2 eV for anatase and 3.06 eV for rutile and these have absorption in the UV region ($\lambda \leq 380$ nm). TiO$_2$ is a compound semiconductor whose valence band and the conduction comprise of the 2p electrons of oxygen and the 3d & 4s electrons of Ti respectively. Excitation of electrons from the valence band causes equivalent number of holes in the valence band. This is equivalent to the movement of electrons from bonding orbitals to the antibonding orbitals. Therefore photo-excitation leaves the material in an unstable state and the semiconductor breaks down in many cases. However TiO$_2$ is very stable in this respect making TiO$_2$ an excellent photocatalyst. The photo-catalyzed reactions for the above applications are facilitated by the presence of adsorbed radicals (from air or water) on the TiO$_2$ surface [42-43]. These radicals, which are atomic species with a free unpaired electron, are formed upon reaction of an adsorbed molecule (such as O$_2$ or H$_2$O) with a photo-generated charge carrier (electron–hole pair or exciton) when TiO$_2$ is exposed to radiation exceeding its band gap; this radiation normally is in the UV wavelength region (290–380 nm). These electron–hole pairs are formed when an electron is elevated from the valence to the conducting band, leaving behind an electron hole, as shown in Fig. 1.8. The holes produced in the valence band cleaves the water molecule to produce OH$^-$ radical which is a strong oxidizing agent (oxidation potential is 2.8 V) to cause damage to other molecules in the surrounding. In some cases the holes directly oxidize the molecules surrounding it. The electrons in the conduction band
facilitate reduction of electron acceptors and the holes facilitate oxidation of electron donors [44].

![Figure 1.8: Mechanism of Photo-oxidation by charge-carriers for TiO$_2$.](image)

It must be noted that during the photocatalytic reaction, at least two events must occur simultaneously in order for the successful production of reactive oxidizing species to occur. Typically, the first involves the oxidation of dissociatively adsorbed H$_2$O by photo-generated holes, the second involves reduction of an electron acceptor by photoexcited electrons; these reactions lead to the production of a hydroxyl (OH$^-$) and superoxide (O$_2^-$) radical anion, respectively [45]. Charge carriers can be trapped as Ti$^{3+}$ and O$^-$ defect sites in the TiO$_2$ lattice, or they can recombine, dissipating energy [46]. Alternatively, the charge carriers can migrate to the catalyst surface and initiate redox reactions with adsorbates [47]. Positive holes can oxidize OH$^-$ or water at the surface to produce OH radicals as mentioned above. Electrons in the conduction band can be rapidly trapped by molecular oxygen adsorbed on the titania particle, which is reduced to form superoxide radical anion (O$_2^-$) that may further react with H$^+$ to generate hydro-
peroxyl radical (’OOH) and further electrochemical reduction yields H₂O₂ [48-49]. The reactions involved in the photocatalytic mechanism of TiO₂ are furnished below:

\[ TiO₂ + h\nu \rightarrow h_{VB}^+ + e_{CB}^- \]  \hspace{1cm} (1.1)
\[ e_{CB}^- + h_{VB}^+ \rightarrow \text{Energy} \]  \hspace{1cm} (1.2)
\[ O₂ + e_{CB}^- \rightarrow O₂^- \]  \hspace{1cm} (1.3)
\[ H₂O + h_{VB}^+ \rightarrow OH^- + H^+ \]  \hspace{1cm} (1.4)
\[ O₂^- + H^+ \rightarrow HOO^- \]  \hspace{1cm} (1.5)
\[ HOO^- + HOO^- \rightarrow H₂O₂ + O₂ \]  \hspace{1cm} (1.6)

Recombination of photogenerated charge carriers is the major limitation in semiconductor photocatalysis as it reduces the overall quantum efficiency [49]. When recombination occurs, the excited electron reverts to the valence band without reacting with adsorbed species (Eq. 1.2) [50] non-radiatively or radiatively, dissipating the energy as light or heat. A key factor of the photocatalytic ability of titania is its high surface area, the same property that contributes to its optical properties. A high surface area leads to a higher density of localised states, which involve electrons with energies between the conduction band and valence band [51]. Titania has a relatively slow rate of charge carrier recombination in comparison with that for other semiconductors [52]. In spite of the larger band gap of anatase (~3.2 eV), compared with that of rutile (~3.0 eV), the photocatalytic performance of anatase generally is considered superior to that of rutile. This is attributed to a higher density of localized states and consequent surface-adsorbed hydroxyl radicals and slower charge carrier recombination in anatase relative to rutile [53-54], parameters that contribute to an improved performance. The higher rate of electron–hole recombination in rutile is explained in terms of its larger grain-size leading to a lower capacity to absorb species. In some cases, rutile may be advantageous for certain applications, viz., rutile containing residual anatase [55], Iron-doped rutile [56] etc. It is possible that electron transfer
between rutile and a residual quantity of anatase [55] may deliver improved photo-oxidative reactions. For example, the TiO₂ crystallites of Evonik (Degussa) P25 contain a combination of anatase (~80%) and rutile (~20%). The conduction band potential of rutile is more positive than that of anatase and hence, the rutile phase may act as an electron sink for photogenerated electrons from the conduction band of the anatase phase. Many researchers attribute the high photocatalytic activity of this preparation to the intimate contact between two phases, enhancing separation of photogenerated electrons and holes and resulting in reduced recombination [57]. Therefore, in the field of surface area, morphology, and doping, an insight of the titania polymorphs, their transformation, and the methods by which they can be controlled is to be achieved in order to optimize its photocatalytic efficacy.

Two ceramics, zirconia (ZrO₂) and hafnia (HfO₂), are known for their similar behaviour, and are important for several advanced applications. ZrO₂ is mostly used for its structural properties. The strengthening afforded by its martensitic phase transformation has made it the material of choice for high-temperature applications. Other common applications include fuel cell electrodes [58], thermal barrier coatings [59], cutlery and jewelry etc. HfO₂ is often thought to be a higher temperature substitute for ZrO₂. This is mostly due to the similarities in their chemical properties. HfO₂ has uses in nuclear applications also due to its high neutron absorption efficiency. More recently it has found application as high-κ dielectric materials and has proved to be a promising candidate to replace SiO₂ as the gate oxide in transistors, to obtain electronics with smaller feature sizes. It is well known that the cubic phase of ZrO₂ can be stabilized by incorporating another oxide such as MgO, CeO₂, or Y₂O₃. At high temperatures, phase transformation has been reported with a significant concomitant change in the electrical conductivity [60-61]. ZrO₂ has a high dielectric constant (22–24), a high breakdown field (3.3–
5.7 MV/cm) and a large band gap (5-7 eV) [62]. Regarding electrical property, ZrO$_2$ is oxygen deficient when non-stoichiometric therefore the predominant defects have been proposed to be oxygen ion vacancies. A recent review article [63] furnishes the development of hafnium-based high-κ materials. For the complementary metaloxide-semiconductor field effect transistor (CMOSFET) application, an amorphous ZrO$_2$ film is preferred to prevent leakage current through crystalline grain boundaries. TiO$_2$ has the highest dielectric constants (80–110) among these three IV-B oxides due to its high polarizability resulting in the smallest band-gap (~3eV). Although, the high dielectric constant of TiO$_2$ makes it a potential gate oxide candidate in MOSFET, small band-gap and other limitations such as multiple oxidation states, Ti$^{3+}$ and Ti$^{4+}$, leading to various Ti–O bonds that provide leakage paths [64-66] restricts its application in this field. Among all IV-B oxides and other transition metal oxides, HfO$_2$ is the most promising candidate due to its large band-gap (5.5–6.0), relatively high dielectric constant (22–25), high breakdown field (3.9-6.7 MV/cm), high thermal stability and large heat of formation (271 kcal/mol). Thin HfO$_2$ films deposited on silicon substrate exhibit favorable parameters, such as high thermal stability and low leakage current [67-69]. The performance of these thin films as gate-dielectrics is affected by the presence of lattice defects, particularly oxygen defects. The presence of interstitial oxygen may trap the electrons and holes while the oxygen-defects may affect the leakage current. Hafnia is used in optical coatings. Because of its very high melting point, hafnia is also used as a refractory material in the insulation of such devices as thermocouples, where it can operate at temperatures up to 2500 °C. Zirconia is often more useful in its phase 'stabilized' state. Upon heating, zirconia undergoes disruptive phase changes. By adding small percentages of yttria, these phase changes are
eliminated and the resulting material has superior thermal, mechanical, and electrical properties. A special case of zirconia is that of tetragonal zirconia polycrystal, or TZP, which is indicative of polycrystalline zirconia composed of only the metastable tetragonal phase. **Yttria-stabilized zirconia (YSZ)** is a zirconium-oxide based ceramic, in which the particular crystal structure of zirconium oxide is made stable at room temperature by an addition of yttrium oxide. As discussed above, pure zirconium dioxide undergoes a phase transformations from monoclinic (stable at the room temperature) to tetragonal and then to cubic, according to the scheme:

\[
\text{monoclinic (1173 °C)} \leftrightarrow \text{tetragonal (2370 °C)} \leftrightarrow \text{cubic (2690 °C)} \leftrightarrow \text{melt}
\]

The ionic radius of \(\text{Zr}^{4+}\) (0.82 Å) is too small for ideal lattice of fluorite nature for the tetragonal zirconia. The stabilization of the tetragonal zirconia over wider range of temperatures is accomplished by substitution of some of the \(\text{Zr}^{4+}\) ions in the zirconia crystal lattice with slightly larger ions, e.g., those of \(\text{Y}^{3+}\) (ionic radius of 0.96 Å) as depicted in Fig. 1.9. The resulting doped zirconia materials are termed as *stabilized zirconia* [70]. The addition of yttria to pure zirconia replaces some of the \(\text{Zr}^{4+}\) ions in the zirconia lattice with \(\text{Y}^{3+}\) ions. This produces oxygen vacancies, as three \(\text{O}^2-\) ions replace four \(\text{O}^2-\) ions. It also permits yttrium stabilized zirconia to conduct \(\text{O}^2-\) ions (and thus conduct an electrical current), provided there is sufficient vacancy site mobility, a property that increases with temperature. This ability to conduct \(\text{O}^2-\) ions makes yttria-stabilized zirconia well suited to use in solid oxide fuel cells, although it requires that they operate at high enough temperatures. The ionic conductivity of the stabilized zirconias increases with increasing dopant concentration (linearly for low dopant concentrations), then saturates, and then starts to decrease.
The very low thermal conductivity of cubic phase of zirconia also has led to its use as a thermal barrier coating, or TBC, in jet and diesel engines to allow operation at higher temperatures. This material is also used in dentistry. Single crystals of the cubic phase of zirconia are commonly used as diamond simulant in jewellery. Like diamond, cubic zirconia has a cubic crystal structure and a high index of refraction. Visually discerning a good quality cubic zirconia gem from a diamond is difficult, and most jewellers will have a thermal conductivity tester to identify cubic zirconia by its low thermal conductivity (diamond is a very good thermal conductor). This state of zirconia is commonly called "cubic zirconia," (CZ).

1.1.4. Doped Oxides:

The versatile applications of anatase and rutile TiO₂ polymorphs utilize its optical properties. TiO₂ has a band gap of ~3eV and absorbs UV photons. But the solar radiation that reaches the earth’s surface lies in the range of 1.0-1.9 eV. Again, it would be desirable to decrease the
photocatalytic efficiency of TiO$_2$ to be used as a paint opacifier since it causes the radical-formation resulting in the degradation of the organic binders in paint. Hence, the optical properties of TiO$_2$ are to be tuned properly for its use in different applications. Again, for another important application of the photocatalytic property of TiO$_2$ towards the hydrogen production, it is required to adjust band-gap of TiO$_2$. For hydrogen production, the energy of the CB of TiO$_2$ should be such that it becomes more negative than hydrogen production level ($E_{H_2/H_2O}$) while that of VB of TiO$_2$ should be more positive than water oxidation level ($E_{O_2/H_2O}$) to ensure the efficient photocatalytic oxygen production from water. A recent review article [71] provides information about the methods of preparation of doped-TiO$_2$ with metallic and nonmetallic species, including various types of dopants and doping methods. Again the effect of doping on the optical and photocatalytic properties of TiO$_2$ has also been furnished [72] with possible explanation of those effects. For this purpose, TiO$_2$ is doped with transition metal ions (Fe, Mn, Ni, Cr etc.) and non-metals (N, S, C, B etc.). First non-metal doped TiO$_2$ was described in 1986 by Sato, et al. [73]. After the success of Asahi et al. [74], nitrogen-doped TiO$_2$ has been studied quite extensively in order to tune the band-gap and photocatalytic activity of titania so that it absorbs photons in the visible region. It was suggested that the 2p state of N atom hybrids with the 2p states O atom in anatase TiO$_2$ doped with nitrogen because their energies are very close, and thus the band gap of N-TiO$_2$ is narrowed and able to absorb visible light. It was also suggested [75] that in TiO$_2$ the oxygen sites substituted by nitrogen atom form isolated impurity energy levels above the valence band. Irradiation with UV light excites electrons in both the VB and the impurity energy levels, but illumination with visible light only excites electrons in the impurity energy level. Although S can decrease the band-gap of TiO$_2$, its use is restricted due to the incompatible ionic size of S for its incorporation into the titania matrix. The energy states
introduced by the C and P dopants are so deep that the photo-generated charge carriers are difficult to get transferred to the surface of the catalyst. Hence, these are inefficient anion-dopants for the present purpose. In addition to the above observations, Umebayashi et al. [76] also reported the preparation of S doped TiO\textsubscript{2} by the oxidation annealing of TiS\textsubscript{2} followed by its annealing at 600°C. On annealing, TiS\textsubscript{2} gets partly converted to anatase TiO\textsubscript{2} and the residual S atoms in the anatase TiO\textsubscript{2} form S-doped TiO\textsubscript{2} by Ti-S bond-formation. The calculation for band structures of S-doped TiO\textsubscript{2} based on the super cell approach revealed the mixing of S 3p states with the VB of TiO\textsubscript{2} increased the width of VB resulting in narrowing of band gap. Ohno et al. developed a new method to prepare S-doped TiO\textsubscript{2} powder [77]. Titanium isopropoxide was mixed with thiourea and the mixture was stirred in ethanol. After subsequent evaporation, aging and calcination, S-doped TiO\textsubscript{2} powder was obtained. The S-ions were incorporated to replace some of the Ti atoms in the form of S\textsuperscript{4+}. The photocatalytic activity of S-doped TiO\textsubscript{2} was then evaluated by photodecomposition of 2-propanol and methylene blue. It was found that S-doped TiO\textsubscript{2} has better photocatalytic efficiency than the pure TiO\textsubscript{2} under visible light irradiation. The oxidation ability of S-doped TiO\textsubscript{2} was found to be still high even after the VB was shifted upwards. There have been reports on C and F ion doped TiO\textsubscript{2} also and it was found that they can also expand the photo-response in visible spectrum [78-80].

There has been an extensive study on the effect of transitional metal ion doping and rare earth metal ion doping for enhancing the photocatalytic efficiency of titania. Choi et al. [81] extensively studied the effect of doping by 21 metal ions on the photocatalytic activity of TiO\textsubscript{2}. The study revealed that the impurity energy levels are generated within the band-gap of TiO\textsubscript{2} after the incorporation of metal ion \((M^{n+})\) within the TiO\textsubscript{2} matrix as indicated below:

\[
M^{n+} + h\nu \rightarrow M^{(n+1)+} + e_{CB}^- \tag{1.7}
\]
The metal-ion can then act as electron trap as well as hole trap. Thus the electron-hole recombination is thus modified by the electron (hole) transfer between metal-ion and TiO$_2$ as below:

\[
M^{n+} + h\nu \rightarrow M^{(n-1)+} + h_{VB}^+
\]  (1.8)

Electron trap: \[
M^{n+} + e_{CB}^- \rightarrow M^{(n-1)+}
\]  (1.9)

Hole trap: \[
M^{n+} + h_{VB}^+ \rightarrow M^{(n+1)+}
\]  (1.10)

The energy level of $M^{n+}/M^{(n-1)+}$ should be less negative than that of the CB edge of TiO$_2$, while the energy level of $M^{n+}/M^{(n+1)+}$ should be less positive than that of the VB edge of TiO$_2$. Again the photocatalytic reaction will take place only if the trapped charge-carriers are transferred to the surface of the photocatalyst. Therefore, metal ions should be doped near the surface of TiO$_2$ particles for a better transfer of charge-carriers to the surface. In case of deep doping, such transfer of charge-carriers becomes difficult and hence, metal ions behave as recombination centers. Furthermore, there exists an optimum concentration for the doped metal ion above which the photocatalytic activity decreases due to the increase in recombination of charge-carriers. Among the 21 metal ions studied by Choi et al., V, Fe, Mo, Ru, Os, Re and Rh ions can increase photocatalytic activity, while dopants Co and Al ions cause detrimental effects. The metal-ions which can trap both the electrons and holes, are generally recommended for enhancing the photocatalytic efficiency. Wu et al. [82] qualitatively investigated the effect of doping with transitional metal ions (Cr, Mn, Fe, Co, Ni & Cu) on photocatalytic activity of TiO$_2$. The Mn, Fe and Cu metal-ions can trap both electrons and holes while Cr, Co and Ni metal-ions can only trap one type of charge carrier. Hence, the doping with the first three metal-ions (Mn, Fe & Cu) is expected to work better than the later three metal-ions (Cr, Co & Ni) for the present
purpose. The similar study on different rare earth metal ions (La, Ce, Er, Pr, Gd, Nd and Sm) by Xu et al. [83] revealed the fact that the Gd metal-ion most is the most effective one in enhancing the photocatalytic activity due to its highest ability to transfer charge carriers to the surface of TiO$_2$. Noble metals, including Pt, Au, Pd, Rh, Ni, Cu and Ag, have also been found to be very effective for enhancing the photocatalytic efficiency of TiO$_2$. Due to the fact that the Fermi levels of these noble metals are lower than that of TiO$_2$, the photo-excited electrons can be transferred from CB of TiO$_2$ to metal particles deposited on the surface of TiO$_2$. However, the photo-generated holes still remain in the VB of TiO$_2$ and hence, the probability of electron-hole recombination is greatly reduced resulting in a better photocatalytic effect. A comprehensive review by M. Ni et al. [84] provides information about the recent developments in the different methods to improve the photocatalytic ability of TiO$_2$.

The other two oxides, namely HfO$_2$ and ZrO$_2$ have found their applications in different phase including high-temperature phases. At room temperature, they both exist in the monoclinic phase. The monoclinic phase is converted to tetragonal at 1720ºC for HfO$_2$ and at 1170ºC for ZrO$_2$. The cubic phase is attained at 2600ºC for HfO$_2$ and at 2370ºC for ZrO$_2$. These high temperature phases have found different applications in different fields. Zhao et al. [85] employed density functional theory to model the undoped HfO$_2$ and predicted a higher permittivity in the cubic ($\kappa$~29) or in the tetragonal ($\kappa$~70) structures than that in the monoclinic phase. There have been a number of studies on the stabilization of high-temperature phases by doping with suitable elements. The doping with a tetravalent cation (same valence as of Hf$^{4+}$ and Zr$^{4+}$) with a larger ionic radius that Hf$^{4+}$ or Zr$^{4+}$ ions leads to an enlargement of the crystal system in order to accommodate the larger resulting in the stabilization of the high temperature phases. Again, the doping with a cation having a lower valence than the Hf$^{4+}$ or Zr$^{4+}$ ions
introduces oxygen vacancies which play a key role in the stabilization of the high temperature phases. For Y-stabilized hafnia [86], a phase boundary between the monoclinic and cubic structures exists between 6 and 8 atom % of Y_2O_3, while a single cubic phase exists above 8 atom % Y_2O_3 at 1500°C. The study on the cubic HfO_2-R_2O_3 (R=Lu, Ho, Gd, Sm, Yb, Y and Sc) with R^+3 ions has revealed that the deep vacancy trapping leads to the decrease in the ionic conductivity at high dopant concentrations [87]. A recent study on the Mn-doped HfO_2 [88] reveals the fact that the Mn-dopant stabilizes the cubic phase of hafnia. The variable valences of Mn leading to the different ionic-sizes of Mn and the oxygen vacancies play an important role to stabilize the cubic phase. Tetragonal Zirconia Polycrystal (TZP) is a new type of zirconia-based engineering ceramics. A comprehensive review article [89] provides the information about the microstructural development and mechanical properties of TZP. The metastable TZP materials are usually fabricated in ZrO_2-Y_2O_3 system due to the wide-range of yttria solubility in tetragonal zirconia. This ZrO_2-Y_2O_3 system is also believed to have a comparatively large critical particle-size below which the tetragonal phase can be stabilized at room temperature. Recently interest has also been shown in the potentially more economic ZrO_2-CeO_2 system. The high strength and toughness of TZP is considered to be largely due to the stress-induced martensitic transformation of the metastable tetragonal phase to the stable monoclinic phase. The common notation used in TZP literature involves placing the cation symbol of the stabilising oxide before the TZP abbreviation. In some cases the molarity of the stabilising oxide will be indicated by a number before the cation symbol, e.g. ZrO_2-3 mol% Y_2O_3 = 3Y-TZP. When heated to about 1170°C, zirconia undergoes a phase transformation from monoclinic to tetragonal and volume shrinkage of more than 3-5%. Further heating produces another change to cubic at 2370°C. The cubic phase is maintained until the melting point of zirconia is reached (~2680°C). On cooling
from sintering temperatures and/or high temperature exposure, zirconia undergoes the tetragonal to monoclinic transformation at 950°C and an expansion similar in magnitude of the shrinkage during heat up. The large volumetric change associated with this phase transformation is large enough to affect the structural integrity of the material. Repeated heating and cooling cycles would result in further erosion of mechanical integrity and properties. In partially stabilized zirconias, similar additions are made but not enough to stabilize all of the material and hence the name “partially stabilized zirconia” or “PSZ”. These materials typically consist of two or more of the phases cubic, tetragonal and monoclinic. If produced properly, the resultant microstructure consists of lens or elliptical-shaped precipitates of tetragonal zirconia within the cubic grains. Normally the tetragonal phase would transform into the monoclinic phase at low enough temperatures, but the high strength of the cubic phase prevents the required expansion from happening, freezing in the tetragonal precipitates. Monoclinic zirconia may also be present in the cubic grains and at the grain boundaries. Normally the tetragonal phase would transform into the monoclinic phase at low enough temperatures, but the high strength of the cubic phase prevents the required expansion from happening, freezing in the tetragonal precipitates. Monoclinic zirconia may also be present in the cubic grains and at the grain boundaries. This is called “Transformation Toughening” and is a stress induced martensitic transformation to the monoclinic phase [90]. The PSZ materials have got excellent fracture toughness, wear resistance, impact resistance, resistance to thermal shock, chemical resistance and corrosion resistance. The PSZ materials have found several applications as dies and tooling, knives, scissors and blades, wear resistant components including bearings and linings, pump parts etc. Hence, zirconia based ceramic materials have received extensive interest as important structural ceramic and biomedical materials [91] due to its excellent mechanical properties. Zirconia in tetragonal phase
has got a long-term biocompatibility which makes it possible to be used in prosthetic hip, knee-bearings, dental material for crown etc. So the tetragonal phase has to be stabilized for these kinds of applications. Now, as discussed earlier, the transformation from tetragonal to monoclinic phase is diffusionless and requires only shear of the parent structure to obtain the daughter phase, and the transformation at any temperature is almost instantaneous. There have been a number of attempts to get an explanation of these low-temperature degradation phenomena [92]. The postulated degradation mechanism states that a tetragonal surface grain transforms to the monoclinic structure when the water vapor draws sufficient yttria from a small volume element on the surface of the tetragonal grain. As the monoclinic nucleus grows by further depletion of yttria, it will eventually attain a critical size. At this critical size, growth-process becomes so spontaneous it does not require any further diffusion of yttria to complete transformation of the tetragonal grain on which the nucleus was growing. If the grain is sufficiently large, the transformation will be accompanied by microcracking of the matrix. The microcracks will open up new surfaces on the subgrains which initiate further diffusion of yttria and subsequent transformation. The kinetics of this degradation process has also been studied [93] for 3Y-TZP. The study reveals that the kinetics of transformation of 3Y-TZP is of first order, with time exponent approaching unity, which indicates that a nucleation and growth mechanism dominated on the specimen surface.

1.2 Perturbed Angular Correlation Spectroscopy:

The origin of the different nuclear probe techniques relies on those nuclear properties which are sensitive to the chemical state of the radioactive probe atoms and to the chemical properties of the environment surrounding the probe atom. Radioactive decay processes are, in general, independent of the chemical state of the atom undergoing radioactive disintegration. However,
there are certain decay processes where the extra-nuclear electrons are involved (e.g., in case of internal conversion and electron capture decay) and the decay rate in those processes has been found to depend on the chemical state of the atom. Nuclear probe techniques, such as, Perturbed Angular Correlation (PAC), Positron Annihilation Spectroscopy (PAS), Nuclear Magnetic Resonance (NMR), Mossbauer Spectroscopy (MS), Nuclear Quadrupole Resonance (NQR) etc. are also based on the effect of chemical environment on the nuclear phenomenon. In the case of PAS, the extent of Doppler broadening in the gamma ray peak of 511 keV annihilation gamma ray is dependent upon the momentum of the electron with which the positron annihilates, and hence on the chemical state of the atom in the medium. Similarly the formation probability of the ortho-positronium (Ps), depends upon the electron density in the medium in which the positron is stopped. In the case of Mossbauer spectroscopy the hyperfine interaction between the electric field gradient and the quadrupole moment of the absorbing nucleus leads to splitting in the gamma-absorption spectrum. A relatively slow development of PAC technique in chemistry in comparison with NMR or MS techniques originates from the lack of complete rigorous theory and availability of commercial “Push Button” instrument. The PAC instrument has to be fabricated by the experimenter and a chemist may not be so familiar with the complicated electronic circuit-diagrams required for nuclear experiments. Although the number of suitable isotopes for PAC seems to exceed that of MS, most of the chemical applications are limited to compounds of a few elements. Again data-acquisition in PAC is more time-consuming and data-analysis is also more intricate than that in MS. However, the same probe can be used for the study of various matrices and the number of probe-atoms present in the matrix under study is so diluted (~10^{-3}-10^{-4} atom %) that it does not affect the crystal structure of the matrix. Again, PAC permits the removal of temperature and solid-state restrictions. Hence, high-temperature phase
transition, solution chemistry of metal complexes, rotational diffusion of macromolecules etc. are some of the special topics of investigation in the field of PAC. Besides, PAC has certain subtle edges over the other complementary methods NMR or MS, viz., it requires no external RF field or magnetic field, sensitivity is independent of vibration (hence, stirred bath can be used) and temperature etc. Again PAC can be applied to a trace quantity of sample while the other resonance techniques require at least ~mg quantity of material. In solid state chemistry, PAC cannot be a competitive but a complimentary technique with MS for those elements lacking isotopes with suitable transitions for γ-resonance.

The method relies on the fact that when a nucleus emits two or more radiations in cascade, they have a spatial distribution with respect to each other depending on the spins of the nuclear levels and multi-polarities of the radiations involved in the cascade. This angular correlation is the manifestation of the population of the m-states in the intermediate level. However, if the intermediate state, after the emission of first radiation, interacts with the extranuclear field, then the population of the m-states in the intermediate level gets altered and thereby changing the angular correlation pattern. This is called the perturbation of the angular correlation which depends on the chemical environment surrounding the probe atom. This interaction can be either static or time-dependant depending on whether the interaction Hamiltonian is independent of time or fluctuates with time respectively. The unperturbed angular correlation is represented by the sum of the even order Legendre polynomials multiplied by the radiation parameters. However, when the perturbation takes place, the above product contains another term called perturbation or attenuation factor. This factor provides all the information about the electronic structure and hence the chemical environment at the site of the probe.
In actual experiment, one measures the coincidence between cascade radiations at least at two different angles (viz. 90° and 180°) and after fitting the experimental values with the theoretical expression, one gets the perturbation factor. Depending on the resolving time ($\tau_R$) of the instrument, two different methodologies are followed. If the resolving time ($\tau_R$) of the instrument is more than the life time of the intermediate level, integral PAC (IPAC) method is followed and if it is less, Time Differential PAC (TDPAC) method is followed. IPAC is an average process and one looses the detailed information about the mechanism of interaction. Although the information obtained from TDPAC method is more useful than that obtained from IPAC, later method becomes the only choice in certain cases. With the advent of accelerators, other PAC methods, viz., Time Differential Perturbed Angular Distribution (TDPAD), In Beam PAC study have also been possible. However, present thesis deals with TDPAC with the $\gamma-\gamma$ angular correlation being perturbed by the electric field gradient (EFG).

1.2.1. Historical Background on PAC:

The pioneer work on the theory of directional correlation was done in 1940 by Hamilton [94]. After that, some attempts were made to experimentally verify the predictions of Hamilton’s theory but without any remarkable success. The theoretical investigation of the influence of extranuclear fields on the directional correlation was performed by Goertzel [95] in 1946. The first successful experiment was carried out by Brady and Deutsch [96] in 1947 with Geiger counters. Subsequently, the angular correlation works were improved by scintillation counters. A typical run that takes a day with scintillation counters would require more than a thousand years of continuous work with Geiger counters. A scintillation counter has a high counting efficiency, speed and energy sensitivity and hence, with the development of fast electronics, angular correlation technique gradually became a well-established tool in nuclear spectroscopy. At first,
the angular correlation measurements were utilized for the measurement of spin and parities of nuclear levels and radiations. As soon as the sensitivity of the correlation pattern to the extranuclear fields with a specified life time of the intermediate state was realized, the technique was used in the determination of g-factor [97] and quadrupole moment [98] of the excited nuclear states. After the discovery of parity non-conservation, the angular correlation experiments were also used in the field of β-decay. In 1960’s and 1970’s, the angular correlation experiments were mainly motivated towards the hyperfine interaction of the magnetic and electric fields between the host-matrix and the probe nucleus. After the discovery of ion-implantation, the angular correlation experiments were also used in the study of point defects including geometric arrangement of vacancies and interstitials inside the host matrix [99]. From 1980’s, PAC technique started to get applied in the field of materials science. After that, PAC Spectroscopy was extensively used in Chemistry, Materials Science and Biology [100] for the last few decades. However, this is still being used in the study of defects and diffusion. The defect formation energy, association energy and migration barriers can also be extracted from the analysis of the PAC spectra [101]. With this formal background of PAC, general theory of angular correlation and the effect of the external magnetic or electric field on this correlation pattern will be discussed. However, a brief overview of electric quadrupole moment and the electric field gradient (EFG) will be provided before discussing the detailed theory of angular correlation technique. The basic background theory required for the development of the above theory will not be discussed separately but be referred in a proper manner.

1.2.2. Electric Quadrupole Moment and EFG:

When the time average of the spatial distribution of electric charge within a nucleus deviates from perfect spherical symmetry, the nucleus will possess finite electric multipole moments. The
electrostatic field produced at the position of the nucleus by the atomic and molecular configurations generates a non-uniform field.

**Figure 1.10:** System of charges arranged in a particular manner

Considering the system of charges shown in Fig. 1.10, there is no resultant charge and dipole moment. Unlike a dipole, it will experience neither a net force nor a net torque in any external uniform field. It may or may not experience a net force in an external non-uniform field. In case of quadrupole being thought of as two dipoles, each dipole will experience a force proportional to the local field gradient in which it resides. If the field gradients at the location of each dipole are equal, the forces on each dipole will be equal but opposite and there will be no net force on the quadrupole. If, however, the field gradients at the positions of the two dipoles are unequal, the forces on the two dipoles will not be equal and there will be resultant force acting on the quadrupole. Thus there will be a net force if there is a non-zero field gradient. Furthermore, when the system resides in a non-uniform field, it may feel resultant torque acting in a particular direction although there might not be net force unless the field gradient on each pair is unequal. Thus the system possesses a Quadrupole Moment. In comparison with a point charge being a scalar quantity and a dipole moment being a vector quantity, the quadrupole moment is a second order tensor. The quadrupole moment $Q$ has nine components defined by $Q_{xx} = \sum q_l x_l^2$, $Q_{xy} = \sum q_l x_l y_l$ and so on. The matrix representation of this second order tensor is given as follows:
By suitable rotation of axes in the usual way, the matrix can be diagonalized and the diagonal elements are then the Eigen values of the quadrupole moment, and the trace of the matrix is unaltered by the rotation.

In general, quadrupole produces a potential which varies inversely with the cube of distance and its quadrupole moment has the dimensions of (charge) \( \times \) (area).

Multipole moments are also exhibited in the potential due to a single point charge, if that charge is not located at the origin of the coordinate system. In the rectangular coordinates \( x, y, z \) the scalar electrostatic potential \( \varphi \) at the external point \( P (0, 0, d) \) on the \( z \)-axis due to a charge \(+e\) at the point \((x, y, z)\) is:

\[
\varphi = \frac{e}{d_1} = \frac{e}{d} \left( 1 - 2 \frac{r}{d} \cos \theta + \frac{r^2}{d^2} \right)^{-\frac{1}{2}}
\]  

(1.12)

Where \( d_1 = (d^2 - 2rd \cos \varphi + r^2)^{1/2} \) is the distance from the point \( P \) to the charge, \( r = (x^2 + y^2 + z^2)^{1/2} \) is the distance from the origin to the charge and \( \cos \vartheta = r/d \) describes the angle between \( r \) and \( d \). Expanding the eqn. (1.12) and collecting terms in \( \frac{1}{d^n} \), we obtain the general expression:

\[
\varphi = \frac{e}{d} + \frac{er}{d^2} \cos \vartheta + \frac{er^2}{d^3} \left( \frac{3}{2} \cos^2 \vartheta - \frac{1}{2} \right) + \frac{er^3}{d^4} \left( \frac{5}{2} \cos^3 \vartheta - \frac{3}{2} \cos \vartheta \right) + \cdots
\]  

(1.13)

Or, more generally,

\[
\varphi = \sum_{n=0}^{\infty} \frac{er^n}{dn+1} P_n(\cos \vartheta)
\]  

(1.14)

Where \( P_n(\cos \vartheta) \) are Legendre polynomials and \( n \) (or more exactly, \( 2^n \)) is the multipole order.

So, in eqn. (1.13), the coefficient of \( \frac{1}{d} \) is the monopole strength, of \( \frac{1}{d^2} \) is the \( z \)-component of
the dipole moment, of $1/d^3$ is the z-component of the quadrupole moment. Now putting $\cos \theta = z/r$, we obtain the coefficient of $1/d^3$ which is the effective classical quadrupole moment $Q^{(2)}$ in the direction $z$ as exhibited at $P(0, 0, d)$ as:

$$Q^{(2)} = \frac{e}{2} (3z^2 - r^2)$$  \hspace{1cm} (1.15)

For a continuous charge distribution with a mean charge density $\rho$ of nuclear charge in the volume element $d\tau$ at the point $(z, r)$, the nuclear electric quadrupole moment $Q$ is defined as:

$$Q \equiv \frac{1}{e} \int \rho (3z^2 - r^2) d\tau = \frac{1}{e} \int \rho r^2 (3\cos^2 \varphi - 1) d\tau$$  \hspace{1cm} (1.16)

Where $z = r \cos \varphi$

The effective value $Q(m_I)$ in the state $m_I$ is related to its value $Q$ in the state $m_I = l$ by the following two equations:

$$Q(m_I) = \frac{3m_I^2 - l(l+1)}{l(l+1)} Q$$ \hspace{1cm} (1.17)

And $$\cos \varphi = \frac{m_I}{\sqrt{l(l+1)}}$$ \hspace{1cm} (1.18)

Nuclei with $l = 0$ or $l = 1/2$ can show no quadrupole moment. In case of $l = 1/2$, $\cos \varphi = 1/\sqrt{3}$ according to eqn. (1.18) and an average value of $(3\cos^2 \varphi - 1)$ in eqn. (1.16) becomes zero. This does not signify that those nuclei possess a perfect spherical charge distribution, but only the maximum observable component $Q$ is zero. Finite electric quadrupole moments are therefore observed only for those nuclei which have angular momentum $l \geq 1$.

The nuclear quadrupole moment operator $Q_{ij}$ for a discrete system of point charges each with charge $q_l$ and position $\vec{r}_l = (r_{xl}, r_{yl}, r_{zl})$ relative to the coordinate system origin is defined as:

$$Q_{ij} = \sum_l q_l (3\vec{r}_{il} \cdot \vec{r}_{jl} - r_{il}^2 \delta_{ij})$$ \hspace{1cm} (1.19)
The indices $i, j$ run over the Cartesian coordinates $x, y, z$ and $\delta_{ij}$ is the Kronecker delta.

For a continuous system with nuclear charge density $\rho_N(r)$, the components of $Q_{ij}$ are defined by integral over the charge density [102]:

$$Q_{ij} = \int \rho_N(r)(3x_i x_j - r^2 \delta_{ij}) dr$$

(1.20a)

Or can be expressed in terms of nuclear spin operators:

$$Q_{ij} = \frac{e^2 \hbar}{2(2l-1)} \left\{ \frac{3}{2} (I_i I_j + I_j I_i) - \delta_{ij} I(I + 1) \right\}$$

(1.20b)

Nuclear quadrupole moments are generally expressed in the unit of barn (1 barn = $10^{-24}$ cm$^2$) and show a wide range of values for spherical to highly deformed nuclei.

The **quadrupole moment tensor** is a rank-two tensor (3x3 matrix) and is traceless (i.e., $Q_{xx} + Q_{yy} + Q_{zz} = 0$). The quadrupole moment tensor has thus 9 components, but because of the rotational symmetry and zero-trace property, only 5 of these are independent.

The **electric field gradient (EFG)** measures the rate of change of the electric field at an atomic nucleus generated by the electronic charge distribution and the other nuclei. The EFG couples with the nuclear electric quadrupole moment of quadrupolar nuclei (those with spin quantum number greater than one-half) to generate an effect which can be measured using several spectroscopic methods, such as nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR, ESR), nuclear quadrupole resonance (NQR), Mössbauer spectroscopy or perturbed angular correlation (PAC). The EFG is non-zero only if the charges surrounding the nucleus violate cubic symmetry and therefore generate an inhomogeneous electric field at the position of the nucleus. EFGs are highly sensitive to the electronic density in the immediate vicinity of a nucleus.
Figure 1.11: Electric Quadrupole Interaction and splitting of energy levels.

This is because the EFG operator scales as $r^{-3}$, where $r$ is the distance from a nucleus. A given charge distribution of electrons and nuclei, $\rho(r)$, generates an electrostatic potential $V(r)$. The derivative of this potential is the negative of the electric field generated. The first derivatives of the field, or the second derivatives of the potential, are the electric field gradient. The nine components of the EFG are thus defined as the second partial spatial derivatives of a classical electrostatic potential, evaluated at the nuclear site:

$$V_{ij} = \frac{\partial^2 V}{\partial x_i \partial x_j}$$

(1.21)

Where $V_{ij}$ is clearly symmetric. At this point we assume that all the charges producing the electrostatic potential are external to the nucleus. This assumption, which excludes the contribution from s-electrons, is justified by the fact that the s-electrons are spherically symmetrical and thus do not contribute to the field gradient. It is from this assumption that the Laplace’s equation $\nabla^2 V = 0$ is invoked to show that the trace of $V_{ij}$ vanishes. The Hamiltonian
operator describing the nuclear quadrupole interaction with an external electrostatic field is
given by the product of the two rank-two tensors:

\[ H = \frac{1}{2} \sum_{ij} Q_{ij} \mathbf{V}_{ij} \]  

(1.22)

The above eqn. is only valid when the charge producing the external electrostatic field does not
overlap the nuclear charge distribution. Relaxing this assumption, a more general form of the
EFG tensor [103] which retains the symmetry and traceless character is:

\[ \varphi_{ij} = \mathbf{V}_{ij} - \frac{1}{3} \delta_{ij} \nabla^2 \mathbf{V} \]  

(1.23)

where \( \nabla^2 \mathbf{V}(\mathbf{r}) \) is evaluated at a given nucleus.

As \( \mathbf{V} \) (and \( \varphi \)) is symmetric it can be diagonalized. The principal tensor components are usually
denoted \( V_{zz}, V_{yy} \) and \( V_{xx} \). Given the traceless character, only two of the principal components are
independent. Typically these are described by \( V_{zz} \) and the asymmetry parameter, \( \eta \), defined as:

\[ \eta = \left| \frac{V_{xx} - V_{yy}}{V_{zz}} \right| \]  

(1.24)

Where the principle axes are choosen in such a way that \( |V_{zz}| \geq |V_{yy}| \geq |V_{xx}| \). This ensures the
fact that \( 0 \leq \eta \leq 1 \) since \( \nabla^2 \mathbf{V} = 0 \).

1.2.3. Directional Correlation Function:

Any two radiations, emitted in cascade, have definite spatial correlation with respect to their
directions of emission due to the conservation of angular momentum of nuclear levels involved
in the cascade and the multipolarities of the radiations. In other words, there exists a definite
angular distribution of the two radiations emitted in cascade. Under ordinary condition, the
nuclei are randomly oriented in space and emission of the individual radiation is isotropic. An
anisotropic radiation pattern is observed only when the ensemble of nuclei is not randomly
oriented. One way to achieve such an oriented radiation pattern is to place the radioactive source
at a very low temperature in a strong magnetic field or electric field gradient when the nuclei get
aligned and the angular distribution of the emitted radiation is measured with respect to the
direction of the applied field. Other way is to select only those nuclei whose spins are oriented in
a particular direction. In case of nuclei emitting two radiations $R_1$ and $R_2$ successively, the
observation of $R_1$ in a particular direction $k_1$ selects an ensemble of nuclei having a nonisotropic
distribution of spin orientations. Thus, a definite angular correlation with respect to $k_1$ is
observed in case of the succeeding radiation $R_2$. The term angular correlation consists of
directional correlation and polarization correlation. In directional correlation, only the directions
of the two radiations are observed while in polarization correlation, the linear or circular
polarization of one or both of the radiations is observed. In deriving the expression for angular
correlation function for successive emission of two $\gamma$-radiations, we will first consider that there
is no extranuclear field acting on the nucleus. Such measurements of unperturbed directional
correlation function yield the information about the properties of the nuclear levels involved in
the cascade emission of the two $\gamma$-radiations and about the angular momenta carried away by the
$\gamma$-photons. In this present context, it is to be remembered that the $\alpha-\gamma$ or $\gamma-\gamma$ directional
correlation yields the spins of the nuclear levels but not the parities. However the relative parities
can be determined by observing, in addition to the direction, also the polarization of the two $\gamma$-
radiations or by measuring the directional correlation between conversion electrons. After
discussing the unperturbed directional correlation function, we will introduce the influence of
extranuclear fields on the angular correlation function.

Let us consider the following decay scheme:
Figure 1.12: Decay of parent (P) to daughter (D) nuclei and subsequent emission of cascade $\gamma$-rays from the daughter atom.

In case of TDPAC, it requires a $\gamma$-$\gamma$ cascade fed by the decay of a parent isotope. The parent isotope is produced by a nuclear reaction and then decays by particle or $\gamma$-ray emission to produce the daughter isotope. Then the daughter atom, inside the matrix under study, acts as an “wound-up spy” [104] to transfer information of its host matrix while returning to its ground state. The intermediate state of the cascade should have a lifetime in the range of 10-1000 ns. This is a crucial parameter as the intermediate state must have a sufficiently long lifetime to feel the perturbation. Again the extranuclear field must be significant enough to interact with the quadrupole moment of the intermediate state. The interaction of the nuclear electric quadrupole moment with an electric field gradient (EFG) leads to a perturbation or attenuation in the angular correlation pattern. Semiclassically, the interaction produces a precessional motion of the intermediate spin about the symmetry axis defined by the direction of emission of the first $\gamma$-ray. Thus the orientation of the intermediate spin gets altered in the time interval between the emission of $\gamma_1$ and $\gamma_2$ and the angular correlation function is perturbed. Quantum mechanically,
the interaction produces the transition among the non-degenerate m-states leading to the emission of $\gamma_2$ from an m-state with an attenuated population density [105]. The precession of the intermediate spin is characterized by an angular rotation frequency $\omega$. The time change in the correlation function is observed if the rotation is significant in the time scale of the lifetime of intermediate state, i.e., $\omega \tau \geq 0.01$ which assigns the lower limit of the workable lifetime to 10 ps for a typical angular velocity of 1000 Mrad s$^{-1}$. A nucleus that emits $\gamma_2$ immediately after the emission of $\gamma_1$ (prompt coincidence) contributes to an unperturbed correlation because it got no time to precess. In actual experiment, a coincidence histogram is recorded as a function of time elapsed between the emission of $\gamma_1$ and $\gamma_2$ at two different angles, viz., 90º and 180º. The excess (or deficit) of the coincidence count rate at opposite detectors ($\theta=180º$) compared to the isotropic average is called “anisotropy” (positive for excess and negative for deficit). Again when $\gamma_1$ is detected in a particular direction, an aligned ensemble of nuclear spins is selected by virtue of the conservation of angular momentum. However, all the nuclei in that selected ensemble do not emit $\gamma_1$ into the detector with equal probability. Therefore, the emission of a subsequent $\gamma_2$ from the same nucleus which has already emitted $\gamma_1$ will in general depend on the angle between $\gamma_1$ and $\gamma_2$, i.e., the coincidence count rate is anisotropic. For unperturbed system (zero EFG), we would get different count rates for two detectors at 180º and 90º, both decaying exponentially with a lifetime of the intermediate state (in case of lifetime measurement). In presence of the extranuclear field, the coincidence histogram gets modulated over the exponential decay and the modulated exponential decay contains all relevant information on the hyperfine-split intermediate level. It is a common practice to Fourier transform this perturbation function in order to retrieve the energy (or frequency) splitting of the hyperfine split state.
There have been a number of papers [106-114] which describe the general theory of angular
correlation and the effect of extranuclear field on this correlation pattern. In this section, the
discussion will be restricted to only the theory of PAC pertaining to \( \gamma-\gamma \) cascade only.

Let us consider a radionuclide from its first excited state \((I_i, m_i)\) decaying to a final \((I_f, m_f)\) state
by emission of two successive photons \(\gamma_1\) \((L_1, M_1=m_i - m)\) and \(\gamma_2\) \((L_2, M_2 = m - m_i)\) with
propagation vectors \(\vec{k}_1\) and \(\vec{k}_2\) respectively. The excited state is populated from a radionuclide
by \(\alpha\) or \(\beta\) emission, electron capture or an isomeric transition. The intermediate level has a mean
lifetime \(\tau\) and an electric quadrupole moment \(Q\). Let us also choose the \(z\)-axis as the axis of
quantization and \(m_i, m\) and \(m_f\) as quantum numbers for the projection of \((I, I_z, I_{zf})\) of the spin
angular momentum onto this axis. The parities of the three states are denoted by \(\pi_i, \pi\) and \(\pi_f\)
respectively. For the conservation of angular momentum, we have \(I_i = I + L_1\). From Quantum
mechanics, we have the conditional relationship: \(|I_i - I| \leq L_1 \leq |I_i + I|\) and the corresponding
projections of the spin angular momentum as \(m_i = m + M_1\). Similarly, \(|I - I_f| \leq L_2 \leq |I + I_2|\)
and \(m = m_f + M_2\). The emitted \(\gamma\)-ray is then characterised by the multipolarity \(L\), and magnetic
quantum number \(M\), with \(L^2 = L (L+1)\hbar, L_z = M\hbar\). The multipole character of the
electromagnetic radiation field is determined by \(2^L\). For \(L=1\) we have dipole radiation, for \(L=2,
quadrupole radiation and so on.

The emission probability of a photon in the direction \(\vec{k}\) relative to the spin axis \(\vec{I}\) of the nucleus
depends on the angle \((\vec{I}, \vec{k})\). Let us consider \(\vec{k}_1\) be the direction in which the first radiation \(\gamma_1\) is
observed and \(\vec{k}_2\) be that in which the second radiation \(\gamma_2\) is observed. Since the spins of the
nucleus are randomly oriented in space, the emission of radiations \(\gamma_1\) and \(\gamma_2\) is isotropic in nature
when measured independently. To observe the correlation between the directions of the two
successive $\gamma$-rays, it is necessary to select the ensemble of nuclei emitting $\gamma_1$ in a fixed direction $\vec{k}_1$ and to measure the intensity of $\gamma_2$ as a function of the angle $\theta$ with respect to $\vec{k}_1$. Therefore if the detector $D_1$ registers $\gamma_1$, the response of detector $D_2$ at an angle $\theta \equiv (\vec{k}_1, \vec{k}_2)$ is a representation of the directional correlation of the two successive photons. The angular correlation between the two gamma-radiations $\gamma_1$ and $\gamma_2$ holds only if the two gamma quanta originate from the same decaying nucleus. This is possible only if the second $\gamma_2$ quantum is detected in \textit{fast coincidence} with initial gamma. In order to avoid the accidental coincidence, i.e., the second $\gamma_2$ quantum detected from another nucleus, the activity of the source should be sufficiently low. It is assumed that all $m_i$ substates in the initial level are equally populated at the time of emission of $\gamma_1$. The direction of the emission of first $\gamma$ is chosen along the $z$ axis. The relative population $P(m)$ of each $m$ sublevel in the intermediate state is determined by the initial transitions. It is obtained by summing over all $m_i \rightarrow m$ transitions leading to the intermediate $m$ substate

$$P(m) \propto \sum_{m_i} [CG(m_i,m)]^2 F_{L_1}^{M_1}(\tilde{\theta})$$

(1.25)

The term in the square bracket is the Clebsch-Gordan coefficient \[115\] for the $m_i \rightarrow m$ transition. It denotes the transition probability for $m_i \rightarrow m$ transition. $F_{L_1}^{M_1}(\tilde{\theta})$ is the characteristic directional distribution for each $(m_i \rightarrow m)$ transition and $\tilde{\theta}$ is the angle between the emitted $\gamma$ and the $z$-axis. Let $|l_i, m_i\rangle$ be one of an orthonormal set $|l_i', m_i'\rangle$ of eigenfunctions of the operators $l_i^2$ and $(l_i)_z$ with eigenvalues $l_i(l_i + 1)\hbar^2$ and $m_i\hbar$ respectively. Let $|l, m\rangle$ and $|L_1, M_1\rangle$ be similar eigenfunctions for the vector operator $l$ and $L_1$, and $I_i = l + L_1$, $m_i = m + M$. The Clebsch-Gordan coefficient are the coefficients in the expansion of $|l_i, m_i\rangle$ in terms of products $|l, m\rangle |L_1, M_1\rangle$. 

The Clebsch-Gordan coefficients $\langle \ell m_1 | I_i m_i \rangle$ are the elements of a unitary matrix.

$$CG(m_i, m) = \langle \ell m_1 | I_i m_i \rangle$$  \hspace{1cm} (1.27)$$

The phases of the eigen functions are so chosen that the coefficients are real numbers and hence the matrix is orthogonal. We define the relative transition probability to be equal to the square of the Clebsch-Gordan coefficient for the vector addition $I_i = I + L_1$ and $m_i = m + M_1$

$$G(m_i, m) = [CG(m_i, m)]^2 = \langle \ell m_1 | I_i m_i \rangle^2$$  \hspace{1cm} (1.28)$$

The most general derivation of the above equation (1.28) is based on the group theoretical methods [116]. The relative populations $P(m_i)$ depend on the energies of the different $m_i$ states and on the way in which level $i$ was created. If the nuclei are randomly oriented so that all $m_i$ states are equally populated for any choice of the $z$-axis, then $F_L(\theta)$ is independent of $\theta$ and the distribution becomes isotropic.

The choice of $k_1$ as the $z$-axis makes $\bar{\theta} = 0$ and limits the summation to $M_1 = \pm 1$. Hence from eqn. (1.25) and eqn. (1.27), we get:

$$P(m) \propto \sum_{m_i} \langle \ell m_1 \pm 1 | I_i m_i \rangle^2 F_{L_1}^{\pm 1}(0)$$  \hspace{1cm} (1.29)$$

The angular correlation function $W(\theta)$ is the probability of the emission of $\gamma_2$ at angle $\theta$ versus the $z$-axis. It depends on the relative population of the $m$-states, the transition probability $G(m, m_f)$ and the directional distribution $F_{L_2}^{M_2}(\theta)$ for each component. The angular correlation function $W(\theta)$ is then given as:

$$W(\theta) \propto \sum_{m m_f} P(m) [G(m, m_f)]^2 F_{L_2}^{M_2}(\theta)$$  \hspace{1cm} (1.30)$$

Substituting $P(m)$ with $M_1 = m_i - m$ & $M_2 = m - m_f$:

$$W(\theta) \propto \sum_{m_f m m_i} \langle \ell m_1 \pm 1 | l_i m_i \rangle^2 F_{L_1}^{\pm 1}(0) \langle I_f m_f L_2 M_2 | l m \rangle^2 F_{L_2}^{M_2}(\theta)$$  \hspace{1cm} (1.31)$$
The above eqn. (1.31) for directional correlation function involves tedious sums over unobserved magnetic quantum numbers and applies to the directional correlation of two pure $\gamma$-rays emitted by free and unpolarized nuclei. A general expression for the angular correlation function of two successive radiations utilizes the Racah algebra [117-118] and density matrix formalism [119-120]. In the derivation of eqn. (1.31), the quantization axis coincides with the direction of emission of first radiation. This special choice eliminates interference terms and facilitates the description of this radiation. However, the description of the second radiation is not simplified. In the general derivation of the theory [109, 121-123], a separate coordinate system is introduced for each of the two radiations $R_1$ and $R_2$. The $z$-axis of each system coincides with the direction of emission $k_i$ of $R_i$. The two radiations are connected through an arbitrary quantization axis $z$ by using the transformation properties of the eigen functions of $R_1$ and $R_2$. The eigen function of $R$ describes a system with total angular momentum $L$ and thus transforms according to the $(2L+1)$-dimensional irreducible representation $D^L$ of the three dimensional rotation group. Using this fact, the eigen functions of $R_1$ and $R_2$, quantized along the arbitrary $z$-axis, are expressed in terms of the functions quantized along the directions of emission $k_1$ and $k_2$. This approach leads to an expansion of the correlation function $W(k_1,k_2)$ in terms of representations $D^L$ (which reduce to Legendre Polynomials $P_L(cos\theta)$ for directional correlation). The derivation of $W(k_1,k_2)$ is based on first order perturbation theory. A nucleus with spin $l_i$ in its initial level $i$ described by the density matrix $\rho(k_1)$, decays to the intermediate level with spin $l$ when the radiation $R_1$ is emitted in the direction $k_1$. The second step of the cascade $l \rightarrow l_f$ leads to the density matrix $\rho_f(k_1,k_2)$. In presence of the extranuclear field, the density matrix $\rho_a(k_1)$ describing the end product of the first transition is no longer identical with the density matrix $\rho_b(k_1)$ describing the initial state of the second transition. The extranuclear
field induces transitions among different m-states and thus causes a change in the density matrix. The change of $g(k_1)$ can be described by a unitary transformation.

The expression for $W(k_1, k_2)$ is given as follows:

$$W(k_1, k_2) \propto \sum_{m_f m m_i} \langle m_f | H_2 | m \rangle \langle m | H_1 | m_i \rangle \langle m_i | H_1 | m_i \rangle^* \langle m_f | H_2 | m_i \rangle^*$$

(1.32)

Here, the matrix element of the operator $H_1$, describing the interaction between the nucleus and the radiation field of $\gamma_1$, is taken between the initial states $m_i$ and the intermediate state $m$. Similarly, the matrix element of $H_2$, describing the interaction between the nucleus and the radiation field of $\gamma_2$, is taken between $m$ and the final states $m_f$. The complex conjugate matrix elements are also entered in order to obtain an observable probability. Since none of the sublevels $m_i, m$ or $m_f$ is observed separately, we have to sum over all. The angular part of these matrix elements can be factored out using Wigner-Eckart Theorem [115]. From eqn. (1.32), we can arrive at the expression for the correlation function as follows:

$$W(k_1, k_2) \propto \sum_{k_1 k_2 N_1 N_2} A_{k_1}(1) A_{k_2}(2) \frac{1}{\sqrt{(2k_1+1)(2k_2+1)}} Y_{k_1}^{N_1*}(\theta_1, \phi_1) Y_{k_2}^{N_2}(\theta_2, \phi_2)$$

(1.33)

With

$$A_{k_1}(1) = F_k (L_1 L_1 I_1 I) = (-1)^{I+I_1-1} (2L_1 + 1) \sqrt{(2I+1)(2k+1)} \begin{pmatrix} L_1 & L_1 & k \\ 1 & -1 & 0 \\ 1 & I & I_1 \\ L_1 & L_1 & k \end{pmatrix}$$

$$A_{k_2}(2) = F_k (L_2 L_2 I_2 I) = (-1)^{I+I_2-1} (2L_2 + 1) \sqrt{(2I+1)(2k+1)} \begin{pmatrix} L_2 & L_2 & k \\ 1 & -1 & 0 \\ 1 & I & I_2 \\ L_2 & L_2 & k \end{pmatrix}$$

Here, $Y_{k_1}^N(\theta_i, \phi_i)$ is a spherical harmonic with $\theta_i$ and $\phi_i$ representing the polar and azimuthal angles of the vector $k_i$. The symbols in the definition of $A_k$ are vector coupling coefficients, namely Wigner 3j- and 6j-symbols [124]. The $k_1$ and $k_2$ on the right hand side of eqn. (1.33) are summation indices which range from 0 to $k_{\text{max}}$ with even $k$-values as parity is conserved in $\gamma-\gamma$ correlation measurement. Here $k_{\text{max}} = \min (2L_1, 2L_2, 2I)$ with $L_1, L_2$ being the lowest multipolarity of $\gamma_1$ and $\gamma_2$ and $I$ denoting the intermediate state spin. The indices $N_1$ and $N_2$ run
from $-k_1$ to $+k_1$ and $-k_2$ to $+k_2$ respectively in steps of 1. The sum over $N_1$ and $N_2$ in eqn. (1.33) can be carried out using the addition theorem for spherical harmonics:

$$
\sum_N Y_{k_1}^{N_1}(\theta_1, \phi_1) Y_{k_2}^{N_2}(\theta_2, \phi_2) = (2k + 1) P_k \cos \theta
$$

(1.34)

$P_k \cos \theta$ denotes the Legendre polynomial with $\theta$ being the angle between $k_1$ and $k_2$:

$$
\cos \theta = \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos(\phi_1 - \phi_2)
$$

(1.35)

From eqn. (1.35), we finally arrive at the expression for unperturbed angular correlation function:

$$
W(k_1, k_2) = W(\theta) = \sum_k A_k(1) A_k(2) P_k \cos \theta
$$

(1.36)

Considering the lowest order term, we have:

$$
W(\theta) \propto 1 + A_2(1) A_2(2) P_2(\cos \theta) = 1 + A_{22} \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2}\right)
$$

(1.37)

Here, $A_{22}$ (the anisotropy) is abbreviation for $A_2(y_1) A_2(y_2)$.

Considering a finite lifetime of the intermediate level but explicitly excluding any interaction, we would have then a time dependant coincidence count rate:

$$
W(\theta) \propto \exp \left(\frac{-1}{\tau_N}\right) \sum_k A_{kk} P_k(\cos \theta)
$$

(1.38)

Which decays exponentially with lifetime $\tau_N$ but the angular correlation is not perturbed. This situation is used to extract information on nuclear spin and multipolarities of transitions.

### 1.2.4. Perturbed Angular Correlation Function:

If the nucleus in its intermediate excited level interacts with extranuclear perturbing fields, then the intermediate level undergoes splitting as shown in Fig. 1.13:
The possibility of extranuclear perturbations was already mentioned by Hamilton in his pioneer paper [94]. The first detailed study was performed by Goertzel [95] who investigated the hyperfine structure interaction and externally applied magnetic field. The theory was extended by Alder [109] who presented expressions that could be applied to the actual experimental situation. A thorough investigation of magnetic dipole and magnetic quadrupole interaction including time dependant effects has been performed by Abraham and Pound [110]. The non-axial EFG has been demonstrated by Matthias et al. [125]. The angular correlation of a cascade $I_1 \rightarrow I \rightarrow I_f$ will, in general, be altered as soon as the nuclei in their intermediate level $I$ are subject to torque, due to the interaction of either the magnetic dipole moment $\mu$ with an extranuclear magnetic field $B$, or of the electric quadrupole moment $Q$ with electric field gradient $\partial^2 V / \partial x^2$. In semiclassical picture, these interactions produce a precession of the nuclei around the symmetry axis. The changing nuclear orientation results in an altered angular correlation. According to quantum mechanics, if the quantization axis was chosen to coincide with the direction of the first radiation, the interactions cause transitions among the $m$-states. The second radiation is emitted from a level with an altered population distribution and this change is responsible for attenuation of the correlation. The semiclassical picture of precessing nucleus satisfactorily describes the effect of perturbation if the extranuclear field is static. However, the extra nuclear fields might be time-dependent in nature. In time dependent fields e.g viscous liquids, the fluctuating electric
field gradient at the site of the nucleus induce transitions among the m-states. One major
difference between the static and dynamic can be perceived by the following description.
Considering a static interaction in an axially symmetric single crystal, the populations of the m-
states quantized along the symmetry axis remain constant and hence, the correlation is
unperturbed if the symmetry axis points towards the direction of one counter (i.e., coincides with
the direction of emission of one radiation). If it points towards any other direction, then
populations of the m-states quantized along the direction of emission change with time and this
change causes an attenuation of the angular correlation. In a polycrystalline source, this
description applies to each microcrystal and eventually for each nucleus. The angular correlation
in a polycrystalline sample is never completely attenuated because a certain fraction of nuclei
experience the static field in such a direction that their correlation is unperturbed or only slightly
attenuated. Static interactions in polycrystalline samples thus never reduce the correlation below
the ‘hard-core’ value. Time-dependant interactions, can however wipe out the correlation
completely as the direction of the field at each nucleus changes continuously in a random
fashion. The magnitude of the static perturbations is described by the precessional frequency (ω).
In case of magnetic interaction, ω is equal to the Larmor frequency ω_B which is again
proportional to μ and H. In case of electric quadrupole interaction, Quadrupole frequency ω_Q is
proportional to Q and \( \frac{\delta V}{\delta z^2} \). Time-dependant perturbations can be described by an inverse time
constant λ: the m-states approach a uniform population exponentially and λ represents the
corresponding relaxation constant. According to the theory of directional correlation, the angular
correlation equation is given by:

\[
W(k_1, k_2) =
\]
\[ \sum_{m_a^m_b^m_a^m_b^f} \langle m_f | H_2 | m_b \rangle \langle m_a | H_1 | m_l \rangle \delta_{m_a^m_b} \langle m_f | H_2 | m_b' \rangle^* \langle m_a' | H_1 | m_l' \rangle^* \delta_{m_a^m_b} \]  (1.39)

Where \( H_I \) and \( H_2 \) represent the interaction between nucleus and radiation field only. In absence of any external perturbation, the final states \( \langle m_a \rangle \) and \( \langle m_a' \rangle \), after emission of first radiation, are identical with the initial states \( \langle m_b \rangle \) and \( \langle m_b' \rangle \) of the second radiation. Now, we consider an interaction of the nucleus in its intermediate state \( I \) with some extranuclear fields. This interaction, which we describe by the Hamiltonian \( K \), is assumed to act from the time the first radiation is emitted \((t=0)\) until the time \( t \) at which the second radiation is emitted. During this time interval the states \( \langle m_a \rangle \) changes to different states \( \langle m_b \rangle \) under the influence of the extranuclear perturbation. This change can be represented by unitary operator \( \Lambda(t) \) that describes the evolution of the state vectors \( \langle m_b \rangle \) and the perturbed angular correlation can be expressed as,

\[ W(k_1, k_2, t) = \sum_{m_a^m_b^m_a^m_b^f} \langle m_f | H_2 \Lambda(t) | m_a \rangle \langle m_a | H_1 | m_l \rangle \langle m_f | H_2 \Lambda(t) | m_a' \rangle^* \langle m_a' | H_1 | m_l' \rangle^* \]  (1.40)

The states \( |m\rangle \) form a complete set and the state vector \( \Lambda(t) | m_a \rangle \) can be expressed as:

\[ \Lambda(t) | m_a \rangle = \sum_{m_b} | m_b \rangle \langle m_b | \Lambda(t) | m_a \rangle \]  (1.41)

And similar for \( \Lambda(t) | m_{a'} \rangle \). The expansion coefficients are the matrix elements of the time evolution operator \( \Lambda(t) \) in the \( m \)-representation. \( \Lambda(t) \) Operator satisfies the Schrodinger equation,

\[ \frac{\partial}{\partial t} \Lambda(t) = -\frac{i}{\hbar} \hat{K} \Lambda(t) \]  (1.42)

If \( K \) does not depend on the time \( t \) (static interaction), the solution of this equation is:

\[ \Lambda(t) = \exp(-i\hat{K}t/\hbar) \]  (1.43)

For time-dependant interaction, the solution of eqn. (1.42) can be given symbolically as:

\[ \Lambda(t) = \exp\left(-\frac{i}{\hbar} \int_{0}^{t} \hat{K}(t') dt' \right) \]  (1.44)
where the integral must be evaluated according to Feynman’s rules for ordered operators [126].

The perturbed angular correlation can now be written as:

\[ W(k_1, k_2, t) = \sum_{m_i m_a m_b m_a' m_b'} \langle m_f | H_2 | m_b \rangle \langle m_b | \Lambda(t) | m_a \rangle \langle m_a | H_1 | m_i \rangle \langle m_f | H_2 | m_b' \rangle^* \langle m_b' | \Lambda(t) | m_a' \rangle^* \langle m_a' | H_1 | m_i \rangle^* \]  \hspace{1cm} (1.45)

In terms of density matrix operator \( \varrho(k) \), we have the following relationships:

\[ \langle m | \varrho(k_1) | m \rangle = \sum_{m_i} \langle m | H_1 | m_i \rangle \langle m_i | H_1 | m_i \rangle^* \]  \hspace{1cm} (1.46)

\[ \langle m | \varrho(k_2) | m \rangle = \sum_{m_f} \langle m_f | H_2 | m \rangle \langle m_f | H_2 | m \rangle^* \]  \hspace{1cm} (1.47)

The matrix element \( \langle m_a m_a'| G(t) | m_b m_b' \rangle \) describing the influence of an extranuclear perturbation on angular correlation is given by:

\[ \langle m_a m_a' | G(t) | m_b m_b' \rangle = \langle m_b | \Lambda(t) | m_a \rangle \langle m_b' | \Lambda(t) | m_a' \rangle^* \]  \hspace{1cm} (1.48)

Now the correlation function can be written as:

\[ W(k_1, k_2, t) = \sum_{m_a m_b} \langle m_a | \varrho(k_1) | m_a' \rangle \langle m_b | \varrho(k_2) | m_b \rangle \langle m_a m_a' | G(t) | m_b m_b' \rangle \]  \hspace{1cm} (1.49)

The above expression for the correlation function can be simplified as:

\[ W(k_1, k_2, t) = \sum_{k_1 k_2 N_1 N_2} A_{k_1} (1) A_{k_2} (2) G_{k_1 k_2}^{N_1 N_2} (t) \frac{1}{\sqrt{(2k_1 + 1)(2k_2 + 1)}} Y_{k_1}^{N_1} (\theta_1, \phi_1) Y_{k_2}^{N_2} (\theta_2, \phi_2) \]  \hspace{1cm} (1.50)

With the perturbation function:

\[ G_{k_1 k_2}^{N_1 N_2} (t) = \sum_{m_a m_b} (-1)^{2l + m_a + m_b} \sqrt{(2k_1 + 1)(2k_2 + 1)} \langle m_b | \Lambda(t) | m_a \rangle \langle m_b' | \Lambda(t) | m_a' \rangle^* \]  \hspace{1cm} \cdot \begin{pmatrix} I & I & k_1 \\ m_a' & -m_a & N_1 \end{pmatrix} \begin{pmatrix} I & I & k_2 \\ m_b' & -m_b & N_2 \end{pmatrix} \]  \hspace{1cm} (1.51)
The above expression for angular correlation represents the time-differential perturbed angular correlation, i.e., the correlation is measured if the second radiation is observed within the time \( t \) and \( t + dt \) after the emission of the first radiation.

In actual experiment, the probability with which second radiation is registered at a time \( t \) after the emission of the first radiation is given by \( f(t - T) \) where \( T \) is the delay given in that channel of the coincidence analyzer that accepts the first radiation. The measured delayed correlation function is given by the weighted average:

\[
W(k_1, k_2, T) = \frac{\int_0^\infty f(t - T)e^{-t/\tau}W(k_1, k_2, t)dt}{\int_0^\infty f(t - T)e^{-t/\tau}dt} \quad (1.52)
\]

In most of the cases, the time response function of the coincidence system is approximated by a step function:

\[
f(t - T) = \begin{cases} 1 & \text{for } T - \tau_0 \leq t \leq T + \tau_0 \\ 0 & \text{for } T + \tau_0 < t < T - \tau_0 \end{cases}
\]

Where \( \tau_0 \) is the resolving time of the coincidence system. With this approximation, the observed angular correlation function is given by

\[
W(k_1, k_2, T, \tau_0) = \frac{\int_{T-\tau_0}^{T+\tau_0} e^{-t/\tau}W(k_1, k_2, t)dt}{\int_{T-\tau_0}^{T+\tau_0} e^{-t/\tau}dt} \quad (1.53)
\]

The total time-integrated correlation

\[
W(k_1, k_2, \infty) = \frac{1}{\tau} \int_0^\infty e^{-t/\tau}W(k_1, k_2, t)dt \quad (1.54)
\]

is observed if the resolving time \( \tau_0 \) of the coincidence system is much larger than the lifetime of the intermediate level (\( \tau \)): \( \tau_0 \gg \tau \).

Since only the perturbation factors \( G_{k_1k_2}^{N_1N_2}(t) \) depend on the time \( t \), the time-integrated perturbation coefficients can be defined in a similar way:
Now, suppose the evolution operator $\Lambda(t)$ is diagonal and expressed in terms of the eigen values $E_m$ of the perturbing Hamiltonian:

$$\langle m_b | \Lambda(t) | m_a \rangle = \exp \left( \frac{-i}{\hbar} E_mt \right) \delta_{mm_a} \delta_{mm_b} \quad (1.57)$$

Then the perturbation function gets simplified to:

$$G_{k_1k_2}^{NN}(t) = \sum_m (-1)^{2l+m_a+m_b} \sqrt{(2k_1+1)(2k_2+1)} \begin{pmatrix} l & l & k_1 \\ m & -m & N \end{pmatrix} \begin{pmatrix} l & l & k_2 \\ m & -m & N \end{pmatrix} \exp \left[ -\frac{i}{\hbar}(E_m - E_{m'})t \right] \quad (1.58)$$

This is to be noted that here $N_1 = N_2 = N$. This diagonal situation is attained in case of magnetic dipole interaction and axially symmetric electric quadrupole interaction. If the axially symmetric field is parallel to the propagation direction of one of the two radiations, then the angular correlation is not influenced by such a field. It can be understood semiclassically. If we choose $k_I$ as quantization axis and the axially symmetric field is parallel to $k_I$, then the influence of this field can be interpreted as a precession of spin $I$ of the intermediate nuclear level about $k_I$. The projections of $l$ on $k_I$ do not change and the population of $m$-states with respect to $k_I$ remains the same. Thus the angular distribution for the second radiation with respect to $k_I$ is not disturbed.

For non-axially symmetric quadrupole interactions, we need a unitary matrix $U$ which diagonalizes the interaction Hamiltonian $K$: 

$$G_{k_1k_2}^{NN}(T) = \frac{\int_0^\infty f(t-T) e^{-t/\tau} G_{k_1k_2}^{NN}(t)dt}{\int_0^\infty f(t) e^{-t/\tau} dt} \quad (1.55)$$

$$G_{k_1k_2}^{NN}(\infty) = \frac{1}{\tau} \int_0^\infty e^{-t/\tau} G_{k_1k_2}^{NN}(t)dt \quad (1.56)$$
Where $E$ is the diagonal energy matrix with the diagonal elements $E_n$ (energy eigen values). With the expansion of the exponential function, it can be shown that the following relation holds:

$$U e^{-(i\hbar)t} U^{-1} = e^{-(i\hbar)E}$$  \hspace{1cm} (1.60)

Equation (1.43) can now be rewritten as:

$$\Lambda(t) = U e^{-(i\hbar)E} U^{-1}$$  \hspace{1cm} (1.61)

The matrix elements of $\Lambda(t)$ in the $m$-representation are therefore

$$\langle m_b | \Lambda(t) | m_a \rangle = \sum_n \langle n | m_b \rangle^* e^{-(i\hbar)E_n t} \langle n | m_a \rangle$$  \hspace{1cm} (1.62)

Where the $\langle m|n \rangle$ are the matrix elements of the unitary matrix $U$ that is obtained from the solution of the eigen value equation (1.59). The perturbation factor is then

$$G_{k_1 k_2}^{N_1 N_2}(t) = \sum_{m_a m_b n n'} (-1)^{2l + m_a + m_b} \sqrt{(2k_1 + 1)(2k_2 + 1)} \left( \begin{array}{ccc} I & I & k_1 \\ m_a & -m_a & N_1 \\ \end{array} \right) \left( \begin{array}{ccc} I & I & k_2 \\ m_b & -m_b & N_2 \end{array} \right) \langle n | m_b \rangle^* \langle n | m_a \rangle \langle n' | m_b' \rangle \langle n' | m_a' \rangle^* \exp \left[ -(i\hbar) \right] (E_n - E_{n'}) t \right]$$  \hspace{1cm} (1.63)

The sum over $n, n'$ describes the mixing of the sublevels due to the broken axial symmetry. Now, the perturbation function can be further simplified by confining our discussion into the randomly oriented samples (molecules, microcrystals, powders), i.e., we average over the Euler angles describing the quantization axis in each microcrystal with respect to the laboratory coordinate system in which $k_1$ and $k_2$ (directions of emission of the two successive radiations) are defined. This leads to the condition $k_1 = k_2 = k$ and $N_1 = N_2 = N$ (even for non-axial symmetry). The
“powder” perturbation function is defined as a sum over certain “single crystal” perturbation functions:

\[ G_{kk}(t) = \frac{1}{2k+1} \sum_{N=\pm k} G_{N}^{NN}(t) \]  

(1.64)

Since, \( G_{kk}(t) \) is independent of \( N_1 \) and \( N_2 \), the addition theorem of spherical harmonics can be applied to eqn. (1.50) and the “powder” angular correlation is obtained in the form:

\[ W(\theta, t) = \sum_k A_k(1)A_k(2)G_{kk}(t)P_k(\cos \theta) \]  

(1.65)

The effect of the randomly oriented perturbation does not change the form of the angular correlation function. It only leads to an attenuation of the \( P_k(\cos \theta) \). The perturbation factors \( G_{kk}(t) \) for those sources which as a whole do not show any preferential direction are therefore called the attenuation factors.

For axial symmetry, the perturbation function in (1.64) can be rewritten as:

\[ G_{kk}(t) = \frac{1}{2k+1} \sum_n \sum_{n'} \left( \frac{l}{n} - \frac{l}{n'} \right)^2 \cos \left( \frac{(E_n - E_{n'})t}{\hbar} \right) \]  

(1.66)

The total time integrated attenuation factor is:

\[ \overline{G}_k(\infty) = \frac{1}{2k+1} \sum_n \sum_{n'} \left( \frac{l}{n} - \frac{l}{n'} \right)^2 \frac{1}{1 + \left( \frac{(E_n - E_{n'})t}{\hbar} \right)^2} \]  

(1.67)

It is indeed an interesting and important feature of the time integrated attenuation factors for a randomly oriented static interaction is that they have a finite lower limit or “hardcore” value that is independent of interaction. Thus the time-integrated angular correlation is never wiped out completely as long as the interaction is static and random irrespective of the strength of the interacting fields in the microcrystals. For axially symmetric fields, the “hardcore” values are easily obtained from eqn. (1.67):

\[ \overline{G}_k(\infty)_{\text{lim}} = \frac{1}{2k+1} \]  

(1.68)
1.2.5. Static Magnetic and Electric Fields:

The lowest order magnetic interaction is the magnetic dipole interaction. The interaction takes place between the magnetic dipole moment of the probe nuclei and an extranuclear magnetic field. The dipole moment depends proportionally to the total angular moment of the nucleus and is conventionally expressed as dimensionless g-factor. The magnetic field may be either external or internal in case of ferromagnetic- and anti-ferromagnetic materials. Semiclassically, a magnetic field exerts a torque on any nucleus with nonzero magnetic dipole moment resulting in a precession of the moment about the field. The frequency of precession is termed as Larmor frequency $\omega_L$.

For a magnetic field $\mathbf{B}$ in the direction of the positive $z$-axis, the Hamiltonian describing the interaction of a nuclear magnetic dipole moment $\mathbf{\mu}$ with the fixed magnetic field $\mathbf{B}$ is given by:

$$K_B = -\mathbf{\mu} \cdot \mathbf{B} = -\mu_z B$$

where $\mathbf{\mu} = \gamma \mathbf{I}$ is the magnetic dipole moment operator. Since $\mu_z = \gamma I_z$, the interaction matrix is diagonal and the matrix elements are given as

$$E_m = \langle \text{Im} | K_B | \text{Im} \rangle = -B \mu_N m / I$$  \hspace{1cm} (1.70)

The Larmor frequency $\omega_L$ is defined as

$$\omega_L = \frac{E_{m+1} - E_m}{\hbar} = \frac{B \mu_N}{\hbar I} = -g \mu_N B / \hbar$$ \hspace{1cm} (1.71)

where $g$ is the g-factor of the intermediate state and $\mu_N$ is the nuclear magneton. By substituting the value of $\omega_L$ in energy eigen values expression we get

$$E_m = \hbar \omega_L m$$ \hspace{1cm} (1.72)

Quantum mechanically, the magnetic interaction results in a complete lifting of the degeneracy
in the intermediate nuclear spin state of the probe nucleus. The energy difference between successive m-states is \( h\omega_L \) and transitions with frequencies that are integer multiple of \( \omega_L \) take place among different m-states. The perturbation can now be written in the form:

\[
G_{k_1k_2}^{NN}(t) = \sqrt{(2k_1 + 1)(2k_2 + 1)} \exp\left(-iN\omega_L t\right) \sum_m \begin{pmatrix} I & I & k_1 \\ m' & -m & N \end{pmatrix} \begin{pmatrix} I & I & k_2 \\ m' & -m & N \end{pmatrix}
\]

Or, after using the orthogonality rule for 3j-symbols,

\[
G_{k_1k_2}^{NN}(t) = \exp\left(-iN\omega_L t\right)\delta_{k_1,k_2}
\]  

(1.73)

The powder perturbation functions are obtained from eqn. (1.64):

\[
G_{22}(t) = \frac{1}{5} (1 + 2 \cos \omega_L t + 2 \cos 2\omega_L t)
\]  

(1.74)

The higher order perturbation functions are all constructed in the same way.

The interaction Hamiltonian of a fixed electric field gradient (EFG) with the electric quadrupole moment of a nuclear state is given by [127]:

\[
K_q = \frac{4}{5} \pi \sum_q (-1)^q T_q^{(2)} V_q^{(2)}
\]  

(1.75)

Where \( T_q^{(2)} \) is the second rank tensor operator of the nuclear quadrupole moment with the components

\[
T_q^{(2)} = \sum_p e_p r_p^2 Y_2^q (\theta_p, \varphi_p)
\]  

(1.76)

And where \( e_p \) are the (point) charges in the nucleus at the points \((r_p, \theta_p, \varphi_p)\). \( V^{(2)} \) is the tensor operator of the classical external field gradient. If the electrostatic field is produced by point charges \( e_c \) (ions in a crystal lattice) at positions \((r_c, \theta_c, \varphi_c)\) with respect to the nuclear center, the spherical components of the field tensor \( V^{(2)} \) are given by:

\[
V_q^{(2)} = \sum_c \frac{e_c}{r_c^3} Y_2^q (\theta_c, \varphi_c)
\]  

(1.77)
Now choosing a coordinate system \(xyz\) (principal axes system) in such a way that the mixed derivatives of the potential \(V\) disappear, we get:

\[
V_0^{(2)} = \frac{1}{4}\sqrt{\frac{5}{\pi}} V_{zz},
\]

\[
V_{\pm 1}^{(2)} = 0,
\]

\[
V_{\pm 2}^{(2)} = \frac{1}{4}\sqrt{\frac{5}{6\pi}} (V_{xx} - V_{yy}) = \frac{1}{4}\sqrt{\frac{5}{6\pi}} \eta V_{zz}
\]

Where \(\eta\) is the asymmetry parameter as defined by the eqn. (1.24). The EFG tensor is then determined by two parameters \(V_{zz}\) and \(\eta\).

In case of axially symmetric field with respect to \(z\)-axis where \(\eta=0\), the EFG tensor is given by \(V_{zz}\). The interaction Hamiltonian then becomes:

\[
K_Q = \frac{1}{\sqrt{\frac{5}{\pi}}} T_0^{(2)} V_{zz}
\]

(1.79)

The quadrupole interaction matrix elements are obtained by the application of Wigner-Eckart theorem as:

\[
\langle lm|K_Q|lm\rangle = E_m = \frac{3m^2 - l(l+1)}{4l(2l-1)} eQV_{zz}
\]

(1.80)

Here we introduce another parameter Quadrupole Frequency \((\omega_Q)\) defined by the following:

\[
\omega_Q = \frac{eQV_{zz}}{4l(2l-1)\hbar}
\]

(1.81)

The matrix elements for the interaction Hamiltonian in eqn. (1.80) then become:

\[
\langle lm|K_Q|lm\rangle = E_m = \{3m^2 - l(l+1)\}\hbar\omega_Q
\]

(1.82)

The angular frequency \(\omega_0\) equivalent to the smallest non-vanishing energy difference is:

\[
\omega_0 = \begin{cases} 
3\omega_Q & \text{for even } l \\
6\omega_Q & \text{for odd } l 
\end{cases}
\]

(1.83)
The energy splitting due to the static quadrupole interaction is not uniform and the states are twofold degenerate (+m and −m give the same energy). The influence of a quadrupole interaction on an angular correlation can no longer be described semiclassically by a simple precession of the correlation pattern.

The perturbation factor for the static quadrupole interaction is given as:

$$G_{k_1k_2}^{NN}(t) = \sqrt{(2k_1 + 1)(2k_2 + 1)} \sum_{mm'} \begin{pmatrix} I & I & k_1 \\ m & -m & N \end{pmatrix} \begin{pmatrix} I & I & k_2 \\ m' & -m & N \end{pmatrix} \cos(-3i(m^2 - m'^2)\omega_q t)$$

The above perturbation factor can also be written as 128:

$$G_{k_1k_2}^{NN}(t) = \sum_n S_{nN}^{k_1k_2} \cos(n\omega_0 t) \quad (1.85)$$

Where the summation index $n$ can assume all positive integers values (including zero) $|m^2 - m'^2|$ for integer $I$ and 2$|m^2 - m'^2|$ for half-integer $I$. The coefficients $S_{nN}^{k_1k_2}$ are given by:

$$S_{nN}^{k_1k_2} = \sum_{m'm} \begin{pmatrix} I & I & k_1 \\ m' & -m & N \end{pmatrix} \begin{pmatrix} I & I & k_2 \\ m' & -m & N \end{pmatrix} \sqrt{(2k_1 + 1)(2k_2 + 1)} \quad (1.86)$$

Where prime on the summation sign signifies that the summation over $m$ and $m'$ should only include those terms where $m$ and $m'$ satisfy the condition $|m^2 - m'^2| = n$ for integer $I$ and 2$|m^2 - m'^2| = n$ for half-integer $I$. Numerical values of the $S_{nN}^{k_1k_2}$ coefficients are tabulated in ref. [128]. With these, the directional correlation perturbed by an axially symmetric electrostatic gradient in an arbitrary direction can be calculated from eqn. (1.85) and (1.86).

The influence of an axially symmetric quadrupole interaction in a polycrystalline powder source is represented by the attenuation coefficient:

$$G_{kk}(t) = \sum_{mm'} \begin{pmatrix} I & I & k \\ m' & -m & p \end{pmatrix}^2 \exp(-3i(m^2 - m'^2)\omega_q t) \quad (1.87)$$

This expression can also be written in the following form:
\[ G_{kk}(t) = \sum_n S_{kn} \cos(n\omega_0 t) \]  

(1.88)

With

\[ S_{kn} = \sum_{m,m'}^{I,I'} \left( \frac{l}{m} \frac{I}{-m} \frac{k}{-m' + m} \right)^2 \]  

(1.89)

\( S_{kn} \) are the geometric coefficients (square of Clebsch-Gordon coefficients) where again \(|m^2 - m'^2| = n\) for integer \(I\) and \(2|m^2 - m'^2| = n\) for half-integer \(I\) respectively.

Now the theoretical shape of the perturbation function defined by the eqn. (1.88) is greatly affected due to instrumentation, asymmetry of EFG and quality of the sample along with the population mode of the \(\gamma-\gamma\) cascade. First, because of the intrinsic time resolution of the coincidence circuit, an event which is recorded at time \(t\) might actually have occurred at some time prior to or after \(t\). The perturbation measured at time \(t\) is given by:

\[ G_k(t) = \frac{\int G_k(t') P(t' - t) dt}{\int P(t' - t) dt} \]

Where \(P(t')\) is the prompt resolution curve. With the approximation that the resolution function is a Gaussian distribution function of width \(\tau_r\), a correction factor \(\exp\left(-\frac{1}{2} \frac{\omega_n^2 \tau_r^2}{\omega_n^2 \tau_r^2}\right)\) [129] is introduced into the expression of \(G_k(t)\). The multiplication with this correction factor attenuates the amplitude of oscillations and shifts the zero time from its true value. The second effect arises from a situation where the EFG has no axial symmetry or the asymmetry (\(\eta\)) of EFG. The eigenvalues of the \(m\) states are approximated by power series of \(\eta\) [130] and the transition frequencies become \(\eta\)-dependant with the loss of harmonic nature of quadrupole frequency (with exception for \(\eta=1\)). However, the necessary condition \(\omega_1 + \omega_2 = \omega_3\) is still valid.

The effect of asymmetry in EFG is the progressive loss of periodicity and distortion of the perturbation function as shown in Fig. 1.14.
Figure 1.14: Effect of $\eta$ on perturbation function for $I=5/2$ state.

The sensitivity of the perturbation function with asymmetry of EFG is clearly visible from Fig. 1.14. The third effect originates from the inhomogeneity of a polycrystalline solid, defects present in that sample and after-effects of the radioactive decay feeding the $\gamma-\gamma$ cascade.

So far we assumed that the electric field gradients acting on the nuclear quadrupole moments are same at every nuclear site. But in reality there is slight variation of crystalline fields due to lattice imperfections and impurity centres. The defects are introduced during the preparation and labelling of the sample. The radiation damage due to neutron-irradiation of the sample also introduces defects in the matrix. In many cases the radioactive decay process transforms the atom in a lattice into an impurity centre. In addition, the recoil momentum imparted to an atom by a nuclear decay process may displace the atom from its regular lattice position to some less well defined point. This effect may result in situations where the crystalline fields experienced by the nucleus in its intermediate state vary considerably from nucleus to nucleus. This influence of such field variation on angular correlation has been calculated by Matthias et al.[125. The experimental curve cannot be fitted with a single set of three frequencies but rather with a distribution of frequencies. A narrow Lorenzian frequency distribution is generally assumed for a unique type of defect at close distance from the nucleus. More often many defects contribute to the EFG and the distribution is better described by a broad Gaussian distribution:
Where \( \bar{\omega}_n \) is the centroid of the distribution for each of the n-values. The relative width of the distribution is described by the parameter \( \delta = \frac{\sigma}{\bar{\omega}_n} \). The averaged perturbation factor is obtained from the integration over all frequencies:

\[
\overline{G_k}(t) = \frac{\int G_k(t) P(\omega - \bar{\omega}_n) d\omega}{\int P(\omega - \bar{\omega}_n) d\omega}
\]

\[
= S_{k0} + \sum_{n=1}^{3} S_{kn} \exp \left\{ -\frac{1}{2} (\delta_n \bar{\omega}_n t)^2 \right\} \cos \bar{\omega}_n t \quad (1.90)
\]

In practice, it is assumed that \( \delta_1 = \delta_2 = \delta_3 \) and \( \delta_n \) is replaced by a single \( \delta \)-value. After incorporating all the effects into the expression of perturbation function, we get the final form of perturbation function as follows:

\[
G_k(t) = S_{k0} + \sum_{n=1}^{3} S_{kn} \exp \left\{ -\frac{1}{2} (\delta \omega_n t)^2 \right\} \times \exp \left( -\frac{1}{2} \omega_n^2 \tau_r^2 \right) \cos (\omega_n t) \quad (1.91)
\]

Considering the Lorenzian distribution of quadrupole frequency, the above expression is modified and expressed as follows:

\[
G_k(t) = S_{k0} + \sum_{n=1}^{3} S_{kn} \exp (-\delta \omega_n t) \times \exp \left( -\frac{1}{2} \omega_n^2 \tau_r^2 \right) \cos (\omega_n t) \quad (1.92)
\]

The shape of the perturbation function gets modified with the resolution time \( \tau_r \), the frequency distribution \( \delta \) and quadrupole frequency \( \omega_Q \). The effect of the frequency distribution is significant on the shape of the perturbation function and it becomes even more prominent at higher values of quadrupole frequency.

For a static quadrupole perturbation and a polycrystalline sample, the total time-integrated attenuation coefficients are expressed as follows:

\[
\overline{G_k}(\infty) = \frac{1}{\tau} \int_0^\infty e^{-t/\tau} \sum_n S_{kn} \cos \omega_n t dt = S_{k0} + \sum_{n=1}^{3} \frac{S_{kn}}{1+(\omega_n t)^2} \quad (1.93)
\]
In the above expression, the first term $S_{k0}$ is called the “hard core” which is independent of the frequency distribution and varies only with the asymmetry of EFG to a little extent. It implies that the angular correlation can never be attenuated below a limiting value for a polycrystalline sample. Physically it can be perceived in the way that for an ensemble of nuclei, a fraction of nuclei are so oriented that they feel no or negligible perturbation at any time.

Till now either a magnetic dipole or an electric quadrupole interaction on an angular correlation was considered. In this section the combined influence of magnetic and electric interaction will be considered. The Hamiltonian for combined magnetic and electric interaction is represented by the following relation:

$$K_{tot} = K_B + K_Q$$

(1.94)

In the above equation, it has been assumed that the external magnetic field $B$ does not influence the electric crystalline field. The matrix elements (in the $z$-axis system) of the total interaction Hamiltonian describing the combined magnetic and electric interaction can be written in the form:

$$\langle m|K_{tot}|m'\rangle = \langle m|K_B|m'\rangle + \langle m|K_Q|m'\rangle$$

(1.95)

Here the axially symmetric electric field gradient is at an angle $\beta$ with respect to the $z$-axis and $B$ coincides with the $z$-axis. Here the attenuation coefficient is a function of $\tau$, $\gamma$ and $\beta$, where $\gamma = \omega_B/\omega_Q$ is the ratio of the magnetic to the electric interaction frequency. The general theory of combined magnetic and electric interactions and numerical results for the perturbation coefficients have been presented by Adler et al. [128]. The influence of a combined magnetic and nonaxial quadrupole interaction in powder sources on angular correlations has been considered by Matthias et al. [131].
1.2.6. **Time-Dependent Perturbations:**

Due to jump diffusion of vacancies in the solids, the tumbling motion of a molecule in a liquid and atomic collision in the gas phase, the magnetic field or electric field gradient arising due to the movement of electric charges, electric or magnetic moments of ions change in a random fashion. Instantaneously, however, a certain local configuration which is similar to the stationary local configuration in solid [132], can be described by an average value of the local field acting in certain direction $Z'$. Due to random collision there is a continual reorientation of $Z'$ with respect to external co-ordinates. If many such uncorrected directions of $Z'$ occur within the lifetime $\tau$ of the intermediate level of the nucleus in the radiation cascade, there will not be any preferred direction for the nucleus as far as the angular correlation is concerned. However, if the direction of the first radiation is taken as the quantization axis, there will be smearing or damping of the angular correlation of static case. This will depend on the correlation time $\tau$ the time for which the system retains its identity. There are two limiting models for the random reorientation of the magnetic field or the EFG at the nucleus. These are:

1. **Diffusion Model**

2. **Strong Collision Model**

The diffusion model assumes that the reorientation of the molecular axis follows a diffusion equation. In this case, the reorientation takes place through many small angular steps and there exists a strong correlation between the orientation of molecular axis before and after the collision. In the case of strong collision model it is assumed that there is no correlation between the initial and final orientation and all orientation are equally probable. This is also called random phase approximation (RPA).
In case of liquid the reorientation depends on the molecular size and the mass of the probe system compared to that of the solvent. In gas phase this depends on the collision frequency which depends on pressure and temperature. In solids there is jump diffusion of vacancies that lead to reorientation of the field axis through large angles. The perturbation of the angular correlation depends on the relative magnitude of three characteristic times i) correlation time $\tau_c$, ii) inverse of interaction frequency $(\omega^2)^{-1/2}$ and iii) time of observation 't' in the differential and $\tau$ (lifetime of the intermediate level) in the time integral PAC experiment.

**STOCHASTIC THEORY:**

Stochastic theory is used for the calculation of attenuation factor. Blume’s theory [133], in which the perturbing field is assumed to jump between two possible stochastic states, is used to calculate the attenuation factor in solids. On the other hand, in the limit of RPA, Scherrer-Blume model [134-135] is used to calculate the attenuation factor for any $\tau_c$ and it applies to the isotropic hyperfine interaction (magnetic) for free atom in a gas. The atomic angular momentum (J) is assumed to be randomly oriented after each collision with the neighbouring gas atoms. For liquids and gases, a large number of stochastic states are assumed. If one assumes the diffusion model to be valid for reorientation, the perturbation factor can be calculated for fast $(\langle \omega^2 \rangle^{-1/2} \tau_c \ll 1)$ and slow $(\langle \omega^2 \rangle^{-1/2} \tau_c \gg 1)$ relaxation processes using perturbation theory.

**ABRAMAG AND POUND MODEL (FAST RELAXATION):**

For many years, this model [110] remains as the most widely used first order treatment of the perturbation of the angular correlation by random time-dependent interaction for $\tau_c \ll \tau$ and $\tau_c \ll \tau_N$ for time-differential and time-integral measurements respectively. Solving the eqn.
(1.51) for the evolution operator with time-dependent Hamiltonian and using Gaussian correlation function, time-differential perturbation factor is obtained as:

\[ G_k(t) = \exp (-\lambda_k t) \]  

(1.96)

Thus the time-dependent process is described as the relaxation process with a constant:

\[ \lambda_k = \frac{3}{5} \langle \omega_0^2 \rangle \tau (k + 1)[4I(I + 1) - k(k + 1)] \]  

(1.97)

Above expression for the relaxation constant is for randomly fluctuating classical axially symmetric EFG. For magnetic interaction, the expression becomes:

\[ \lambda_k = \frac{1}{3} k(k + 1) \langle \omega_0^2 \rangle \tau_c \]  

(1.98)

The time-integrated perturbation coefficient is expressed as:

\[ \overline{G_k(\infty)} = \frac{1}{\tau} \int_0^\infty e^{t/\tau} dt = \frac{1}{1 + \lambda_k \tau} \]  

(1.99)

For large values of \( \lambda_k \tau \) the attenuation coefficient for a time-dependent perturbation vanishes and observed angular correlation becomes isotropic.

Fast relaxation of EFG takes place in dilute aqueous solutions of radioactive ions. The relaxation constant \( \lambda_k \) is proportional to the correlation time \( \tau_c \) and is small in dilute aqueous solution, \( \tau_c \approx 10^{-11} \) sec. When \( \lambda_k \tau \ll 1 \), the attenuation of the angular correlation is small even for large quadrupole couplings. The undisturbed anisotropies are often observed for free ions in solution. The correlation time increases with the size of the species in solution and with the viscosity of the medium. When \( \tau_c \) is of the order of \( \tau \) or even longer, the relaxation process is better described as the result of the slow rotational diffusion of the ion or molecule to which the probe atom is bound. The tumbling of large molecule produces a more slowly relaxing field than that of small ions solution. The correlation time is approximated by the Debye expression and is given by:
$$\tau_c = \frac{4}{3} \pi a^3 \frac{\eta}{kT} \chi$$

(1.100)

Where $a$ is the radius of the molecule, $\eta$ the viscosity of the solvent at temperature $T$ and $\chi$ is a coefficient between 0 and 1.

**ADIABATIC APPROXIMATION:**

For a slow molecular motion in case of large tumbling molecules in a liquid or small molecule in a viscous medium, Marshall and Meares [136] developed a model in which the quadrupole Hamiltonian acting on the intermediate state has an adiabatic variation with time. So the interaction remains constant with respect to the local frame of reference represented by the molecular axis, however the orientation of this frame within the laboratory co-ordinates changes with the rotational motion of the molecule. The final expression for the perturbation factor is then given by:

$$G_k(t) = G_k(t)_{\text{static}} e^{-\lambda_k t}$$

(1.101)

where the first term of the product is the usual perturbation factor for a static random interaction.

For a spherically symmetric molecule, with a rotational diffusion coefficient $D$:

$$\tau_k = \frac{1}{\lambda_k} = \frac{1}{k(k+1)D}$$

(1.102)

The adiabatic approximation be valid for $\tau_k >> 10^{-7}$ sec. The Marshall-Meares model is only one of the theoretical approaches to the sensitivity of PAC to the molecular dynamics. Slow molecular reorientations by random jumps caused by strong collisions have been considered by Lynden-Bell [137]. The effect of molecular shape and flexibility on $\gamma-\gamma$ angular correlation has been studied by Marshall et al. [138] while Shirley [139] developed extensively the theory of PAC patterns static and rotating labelled macromolecules with different geometrical configurations. These developments have an important impact on the study of biomolecules. The
applications of PAC method to the study of metal-protein have been reviewed by Graf et al. [140].

**DILLENBURG-MARIS THEORY:**

In the treatment of random statistical perturbation by Abragam and Pound theory, it was assumed that a significant change in the spin state of the intermediate level is brought about by many random interactions each of which has a very small effect and hence, the first order perturbation could be used to calculate each independent (small) interaction. However, a time-dependant perturbation can also be caused by a few violent interactions of short durations. This situation can still be described by statistical methods but the effect of a single violent interaction can no longer be estimated by using the square of a first order perturbation matrix element. Dillenburg and Maris constructed a theory [141] of time-dependant perturbation that makes only the assumption of a statistical interaction, random in space, and invariant under the time-reversal and parity-transformation. For small independent magnetic dipole or electric quadrupole perturbation, the results of Dillenburg-Maris theory are reduced to that of Abragam and Pound. This treatment is valid in physical situation where surrounding atoms collide randomly with the atoms containing the probe nuclei in such way that any one collision occurs during a time interval which is short if compared with a typical relaxation time and the lifetime of the intermediate level. For an intermediate state spin \( I=5/2 \) or \( I=2 \) in a parity-conserving cascade, the expressions for second and fourth order perturbation factors are given as:

\[
\begin{align*}
G_2(t) &= (1 - \alpha)e^{-\lambda_2t} + \alpha e^{-\lambda_4t} \\
G_4(t) &= \beta e^{-\lambda_2t} + (1 - \beta)e^{-\lambda_4t}
\end{align*}
\]

(1.103)

\( \alpha, \beta, \lambda_2, \lambda_4 \) are the parameters that are to be determined experimentally. Experimental evidence that \( \alpha \) and \( \beta \) are different from zero would indicate the presence of a statistical perturbation that
that cannot be treated as a first-order coupling to random magnetic dipole or electric quadrupole fields.

1.2.7. Influence of Preceding Decays on Angular Correlations:

The mode of radioactive decay by the parent atom to produce the daughter element is one of the important topics to be discussed in case of PAC study. Apart from Isomeric transition (IT) process, all other decay processes, viz., electron capture (EC), internal conversion (IC), α- and β-decay; convert the parent atom into a different element. So, the effect of this preceding decay on the directional correlation of γ-γ cascade is discussed in this section.

EC AND IC:

EC decay leads to K-capture or K-conversion by creating a hole in the K-shell. After the formation of the K-hole, the excited nucleus tends to reach their ground state by decaying through γ-γ cascade while the excited atomic shell through the emission of Auger electron and X-rays. In case of free atom, the atom remains neutral immediately after the EC-decay. The emission of Auger electrons then makes the atom to become charged [142]. The average charge of an atom after K-capture is quite large. In practice, the probe atom is embedded in a solid or a liquid matrix. So the fate of the atomic shell after the K-capture depends strongly on the surrounding atomic environment. Here, three environments are considered, viz., a metal, an insulator and a liquid. In case of a metal, the atomic shell comes to its ground state after K-capture in a very short time (<10^{-12} sec). Hence the nucleus is not influenced by the field within its atomic shell and the directional correlation remains unperturbed if the atom is embedded in a lattice with zero EFG (cubic symmetry). The radioactive atom embedded in an insulator can act as an impurity center. In general, the impurity centers have long decay times in the outermost shell. The matrix element for the transition of the excited atomic shell to its ground state is small
and the lifetime is large. Thus the directional correlation with the probe embedded in an insulator should be attenuated. In a liquid, the effect should not differ to any significant extent from that in the corresponding solid. In a molten metal, the excited atomic shell relaxes very fast to its ground state and hence K-capture has no effect on the directional correlation. In a liquid insulator, the influence of the K-capture depends on the correlation time and the molecular interaction in the liquid. If the molecule containing the decaying nucleus rotates very fast in the liquid, the correlation will be unperturbed even if the atomic shell is not in the ground state due to the very small correlation time. However, if the correlation time can be increased so that $\tau_c \gg \tau$, the attenuation effect of K-capture in liquid can be perceived. Otherwise, it is hard to decide whether the K-capture exerts any influence or not.

**$\beta$ - EMISSION:**

The escape of a $\beta$-particle from an atom takes place in a time scale that is short compared to the orbital period of the shell electrons. The abrupt change in the nuclear charge from $Z$ to $Z \pm 1$ introduces a perturbation into the electrostatic potential in which the shell electrons move. This sudden perturbation may result in the excitation and ionization of the electron shell. In case of $\beta^-$ emission it has been observed [143] that ~80% of the daughter atoms have a single positive charge after the loss of a $\beta^-$-particle. The remaining 20% of the atoms have a positive charge of two or more units indication an additional shake-off of electrons from the shell. Thus the probability of the daughter atom to be in a highly ionized and excited state is much smaller for $\beta$-emission than for EC or IC. The recovery of the excited ionized or excited atoms follows the similar mechanism as that in case of EC.
ALPHA DECAY:

In a typical α-decay with decay energy of 5MeV and a mass number of 200, the emitted α-particle imparts recoil energy of 100 keV to the daughter nucleus. This recoil effect has to be taken care of in case of α-γ correlation experiments.

1.2.8. Methodology and PAC Isotopes:

The methodology in PAC experiments implies the whether the method is time differential or time integral. This is decided by three characteristic times, viz., the resolving time of the coincidence setup, interaction time and the lifetime of the intermediate state of the probe nucleus. Since the interaction time is not known beforehand, the methodology is decided by the other two characteristic times. When the resolving time is shorter than the lifetime, one goes for time differential measurements. This reveals the details of the mechanism of interaction between the nucleus and the extranuclear surrounding. On the other hand, if the resolving time is large compared to the other characteristic times one has to go for time integral measurements in which only the gross or an average picture is obtained. The ultimate goal of a Time Differential PAC experiment is to extract the perturbation factor which contains all the information regarding the interaction of the probe atom with its surrounding. Experimentally the attenuation or perturbation factor is obtained by measuring the coincidence counts at least at two different angles, viz., 90° and 180°. The perturbed angular correlation function, following the eqn. (1.65), can be rewritten as:

\[ W(\theta, t) = \sum_{k=even} A_k G_k(t) P_k(\cos \theta) \]

In general, the term with \( k = 2 \) is the most significant in the above summation series. Neglecting the higher order terms, the second order perturbation factor is expressed as:
As discussed earlier, theoretical shape of the perturbation function gets affected by three different factors, viz., resolving time of the coincidence setup, asymmetry of EFG and statistical distribution of frequency. The final theoretical function of $G_2(t)$, as expressed in eqn. (1.91) or (1.92), is least-square fitted with the experimental $G_2(t)$ values as obtained from the coincidence measurements to extract the perturbation factor.

PERTURBED ANGULAR DISTRIBUTION (PAD):

In PAC the nuclear orientation is achieved by taking the direction of the first gamma radiation as the reference and then the angular distribution of the second gamma is observed in a cascade. In PAD this reference direction is obtained by particle beam which is used to produce the intermediate level of the probe nucleus. Although the basic principle is same for PAC and PAD, they differ by some essential features. In PAC the gamma-gamma cascade is populated by the preceding decay, usually the beta-decay from the parent isotope. The number of atoms required in this case is determined by its half-life activity. Considering the half-life ranging from few hours to days, the number of atoms required for PAC experiment is of the order of $10^{12}$ atoms.

In PAD, the probe atoms are produced in a nuclear reaction. The beam serves as start input to TAC. Various pulsed heavy ion beams are used to produce the isomeric states. In this case, only one gamma is counted in the direction with respect to the beam direction. So counting statistics does not pose any problem in PAD experiment. PAD is an online experiment and the probe nucleus is either produced in the matrix to be studied or it can be implanted to other matrices. This implantation is possible due to its large recoil energy. So only problem arises about the uncertainty in the position of the probe nucleus in the lattice during implantation.
The kind of information PAD can generate is similar to those obtained by PAC. Both these techniques can give hyperfine parameters like other nuclear techniques such as NMR, ESR and MB spectroscopy. The lacking information on the isomer shift in comparison with the MB is balanced by details in the magnetic contributions resolved in PAD and not easily detectable with the present Mossbauer cases. Also the experiments dealing with the temperature variation study or the study of lattice dynamics etc are amenable to PAD. Some important studies [144] such as local moments determination, magnetic characterisation of defects, Knight shift in nonmagnetic metals, study of high Tc superconductors are worth mentioning.

IN-BEAM PAC:

It is another PAC technique used in case of those probe nuclei with the initial level of half-lives below several minutes. The half-life of the probe atom is of prime consideration in order to apply the PAC technique for any application. Nuclei having half-lives below minute order cannot be used in TDPAC or IPAC studies. Again the number of PAC probes with suitable half-life is not large. In the In-Beam technique [145], probe nuclei can be periodically produced in a nuclear reaction. In the beam-on condition, the gamma-gamma cascade is populated and then in the beam off condition, the coincidence is measured. This procedure is repeated as long as the desirable statistics is achieved. This In-Beam PAC technique can be used in the field of nuclear physics to obtain nuclear moments, spins and multipolarities. It can also be used in solid state physics as well. By the use of the probes with life times in μs to ms range, the In-Beam PAC method can offer valuable additional information about the fast annealing processes.

CHOICE OF TDPAC ISOTOPE:

The suitability of TDPAC probe is based on the following criteria: Long lifetime of the parent isotope (or the isomeric state), large anisotropy of the cascade, suitably long lifetime and large
quadrupole moment of the intermediate level, not too low \(\gamma\)-energy to avoid any absorption, suitable difference between two cascade \(\gamma\)-lines so that they can be separated. All the PAC probe-isotopes are either commercially available or produced by nuclear reactions such as thermal neutron capture, cyclotron irradiations or fission followed by radiochemical separation. The probe is then incorporated by a variety of methods: during synthesis of the matrix under study via coprecipitation, by implantation including recoil-implantation technique, irradiation of the sample etc. The following situations in choosing a PAC probe may arise:

a. In the ideal case, the probe atom has a long-lived isomeric state and is a natural constituent of the sample. Here the interpretation of the PAC results is quite straightforward.

b. The parent isotope is a constituent of the sample but its daughter is not. In this case, the sample preparation has no difficulty, but the daughter atom, on which the NQI is determined, becomes foreign atom to the matrix under study. Here, electronic (if the electronic rearrangement is too slow compared to the lifetime of the start level) or chemical after-effects (including breaking of weak bonds) may arise and the data-interpretation is not straightforward.

c. The daughter atom is a constituent of the sample but parent is not. There can be impurity-specific problem during sample-preparation. However, usually the electronic and lattice rearrangement is fast enough to neglect the after-effects. There is no such problem in data-interpretation.

d. Neither the parent nor the daughter isotope is a constituent of the sample. In this case, all possible above-mentioned complications are expected.
In most of the applications, the atom on which the NQI is studied is preferred to be the constituent of the sample. However, there are a large number of applications where a foreign atom at “infinite dilution” is used for the NQI study. In these cases, the study of impurity-defect or impurity-impurity interactions is also performed purposefully.

The list of isotopes for TDPAC study is given in Table 1.2. The relevant properties of the probe atoms have been mentioned in the table. In case of doping the probe atom inside the matrix under study, the doping condition has to be optimized in such a way that the probe atom occupies the definite lattice site inside the matrix. In practice, the probe atom is added in such a high dilution into the matrix (<0.01 atom %) that it hardly affects the crystal structure of the matrix even if the probe atom is foreign to that matrix and the same probe can be used for the study of different matrices. Now, the effect of preceding decay on the angular correlation pattern has already been discussed. Apart from the decay via isomeric transition (IT), the nuclear probe becomes chemically different from the parent atom. A prerequisite for the probe atom in case of PAC applications is the minimization of all the after-effects at the time of emission of first photon of the cascade and attainment of chemically stable configuration by the daughter atom in the host matrix.

In the present thesis, two probes, viz., $^{181}$Hf/$^{181}$Ta and $^{111}$In/$^{111}$Cd have been used to study different matrices. In case of the first probe, $^{181}$Hf undergoes $\beta$ decay to produce $^{181}$Ta which has 133-482 keV cascade being utilized for the PAC measurements. The emission of 0.4 MeV $\beta$-particle by the parent nuclei imparts a maximum recoil energy of 1.6 eV to a free daughter atom. This exerts hardly any mechanical effect on the daughter atom. However, most of the Ta-atoms have one unit of positive charge more than the parent Hf-atom as a result of the $\beta^+$ decay and the neutralization of the excess charge of Ta depends on the availability of electrons in the
surroundings. The outermost electronic configurations of Hf and Ta atoms are $5d^26s^2$ and $5d^36s^2$. So Hf exists in $+4$ oxidation state with the $5d^0$ configuration while Ta exists in $+5$ state. Had Ta been existed in $+4$ state with $5d^1$ configuration, it would have exhibited a strong magnetic perturbation of the angular correlation which has never been observed. Again, the mean lifetime of the initial level of the $\gamma-\gamma$ cascade is sufficiently long (24$\mu$s) to allow the complete relaxation of the atomic and molecular rearrangement processes. Hence it is assumed that $^{181}$Ta can attain its chemically stable form in the Hf-compounds and remains at the place of the parent Hf-atoms at the time of first $\gamma$-emission. In case of $^{111}$Cd $\gamma-\gamma$ cascade, the nature of decay feeding the cascade has a consequence on the directional correlation. There is no after-effect associated with the IT decay of $^{111m}$Cd or $\beta^-$ decay of $^{111}$Ag. However, the situation is quite different in case of $^{111}$In EC decay. The EC decay, as discussed earlier, is followed by intense Auger emission resulting in atomic and molecular disruptions. The daughter atom is left with a variety of charge states and the local defects introduced by the Auger electrons affect the correlation pattern.

The decay schemes of the two probes used in the present thesis have been presented in Fig. 1.15.

![Decay schemes](image.png)

**Figure 1.15:** Decay schemes of $^{181}$Hf/$^{181}$Ta (left) and $^{111}$In/$^{111}$Cd probes
<table>
<thead>
<tr>
<th>Parent Nuclide</th>
<th>Half-life</th>
<th>Intermediate Level lifetime (ns)</th>
<th>$E_1$ (keV)</th>
<th>$I_1$ (%)</th>
<th>$E_2$ (keV)</th>
<th>$I_2$ (%)</th>
<th>Intermediate Level Spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{48}$Ti</td>
<td>48y</td>
<td>153</td>
<td>78</td>
<td>100</td>
<td>68</td>
<td>100</td>
<td>2</td>
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<tr>
<td>$^{99}$Rh</td>
<td>16d</td>
<td>21</td>
<td>354</td>
<td>20</td>
<td>90</td>
<td>80</td>
<td>3/2</td>
</tr>
<tr>
<td>$^{100}$Pd</td>
<td>3.7d</td>
<td>214</td>
<td>84</td>
<td>70</td>
<td>75</td>
<td>70</td>
<td>2</td>
</tr>
<tr>
<td>$^{111}$Ag</td>
<td>7.5d</td>
<td>84</td>
<td>95</td>
<td>0.5</td>
<td>247</td>
<td>1</td>
<td>5/2</td>
</tr>
<tr>
<td>$^{111m}$Cd</td>
<td>49m</td>
<td>84</td>
<td>150</td>
<td>100</td>
<td>247</td>
<td>100</td>
<td>5/2</td>
</tr>
<tr>
<td>$^{111}$In</td>
<td>2.7d</td>
<td>84</td>
<td>173</td>
<td>100</td>
<td>247</td>
<td>100</td>
<td>5/2</td>
</tr>
<tr>
<td>$^{117}$Cd</td>
<td>2.4h</td>
<td>60</td>
<td>89</td>
<td>7</td>
<td>345</td>
<td>16</td>
<td>3/2</td>
</tr>
<tr>
<td>$^{131m}$Te</td>
<td>30h</td>
<td>5.9</td>
<td>102</td>
<td>5</td>
<td>200</td>
<td>10</td>
<td>9/2</td>
</tr>
<tr>
<td>$^{181}$Hf</td>
<td>42d</td>
<td>10.8</td>
<td>133</td>
<td>93</td>
<td>482</td>
<td>85</td>
<td>5/2</td>
</tr>
<tr>
<td>$^{187}$W</td>
<td>24h</td>
<td>560</td>
<td>480</td>
<td>30</td>
<td>72</td>
<td>15</td>
<td>9/2</td>
</tr>
<tr>
<td>$^{199m}$Hg</td>
<td>43m</td>
<td>2.3</td>
<td>375</td>
<td>100</td>
<td>158</td>
<td>100</td>
<td>5/2</td>
</tr>
<tr>
<td>$^{204m}$Pb</td>
<td>67m</td>
<td>260</td>
<td>912</td>
<td>98</td>
<td>375</td>
<td>99</td>
<td>4</td>
</tr>
<tr>
<td>$^{204}$Bi</td>
<td>11h</td>
<td>260</td>
<td>984</td>
<td>20</td>
<td>375</td>
<td>90</td>
<td>4</td>
</tr>
<tr>
<td>$^{172}$Lu</td>
<td>6.7d</td>
<td>7.8</td>
<td>91</td>
<td>4.54</td>
<td>1094</td>
<td>62.5</td>
<td>3</td>
</tr>
<tr>
<td>$^{140}$La</td>
<td>40.3h</td>
<td>3.5</td>
<td>329</td>
<td>20.3</td>
<td>487</td>
<td>45.5</td>
<td>4</td>
</tr>
</tbody>
</table>

1.2.9. Application of TDPAC Technique:

This hyperfine technique has a variety of applications in the interface of Physics, Chemistry and Biology. A brief overview of these applications will be presented in this section.

**SOLID STATE PHYSICS AND CHEMISTRY:**
The determination of NQI in solids yields valuable information and a distribution of $V_{zz}$ characterizes the short-range order [146]. The great advantage of TDPAC technique is that the formation of molecule or compound along with the recrystallization process can be observed at an extremely early stage. The TDPAC spectroscopic technique is highly sensitive to the variations in charge-distribution around the neighborhood of the probe atoms. In case of surface study, the NQI parameters identify the atomic configuration around the probe nucleus in case of perfect surfaces. The surface reactions can also be monitored via the identification of different species formed by their previously known respective hyperfine parameters. Such studies are of great importance in case of technical surfaces used for different practical applications [147-149]. The probe-defect interaction is also studied by this hyperfine technique. Defects are created by irradiating the matrix at a low temperature (e.g. 4.2K) with high-energy particles, viz., proton, alpha, neutrons etc., via radiation damage. The defects are annealed by isochronous annealing where the sample is first kept for a fixed duration at consecutively increasing temperatures and then cooled down to the same measuring temperature. The defects, mainly interstitial atoms and vacancies, get trapped by the probe atoms forming probe atom-defect complexes during annealing. Otherwise, they cannot be detected due to their very low concentration. The potential of PAC is realized in the case of two or more coexisting complexes. The distinctively different PAC parameters for the different complexes along with the information regarding the variation of individual fraction with annealing temperature provide the insight about the formation and dissociation enthalpies of the coexisting complexes along with their fate with annealing [150-155]. The metal-metal interaction can be studied by the TDPAC technique where noble metals are used as the reaction media for investigating attractive interactions between probe atoms and impurity atoms added in a high dilution [156-157]. There occurs a formation of probe atom-
impurity atom pair which gradually vanishes with increasing temperature due to the pair-
dissociation. From the temperature dependence of this pair-component, the formation enthalpy
can also be derived. The structural phase transitions, involving the change in lattice position and
electron density distribution, are studied via the variation in NQI parameters. In spite of the
superiority of diffraction techniques to hyperfine techniques for the study of structural phase
transition, there are cases where the structural changes are minute. Then PAC spectroscopy can
determine the number and population of inequivalent sites in contrast to diffraction techniques.
The information about the other dynamic processes, viz., fluctuations, rotations and diffusion
processes, can also be extracted from the hyperfine technique. In magnetically ordered materials
EFG measured by PAC has been used to study the phase transition in ferroelectric and
antiferroelectric perovskites. Temperature dependence of EFG at $^{181}$Hf in BaTiO$_3$ [158] obtained
from PAC measurements in the temperature range from -200°C to 100°C shows a phase
transition of lattice from rhombohedral to tetragonal through monoclinic structure. Phase
transitions in metal-hydrogen systems as well as hydrogen diffusion processes have been
investigated in the metals Pd, Hf, Ta and Nb with different probes, viz., $^{99}$Rh/$^{99}$Ru, $^{100}$Pd/$^{100}$Rh,$^{181}$Hf/$^{181}$Ta and are described in a review article by Weidinger [159]. The creation and
destruction of recoil phonon influences angular correlation [160]. This method of PAC technique
has been used to detect sound generated by electromagnetic field in liquid metals [161].
Attempts have been made to reveal the mechanism of superconductivity in high $T_c$
superconductors by employing the PAC technique. Transient magnetic field (TMF) and transient
EFG are expected to act at the nucleus of highly charged ions penetrating a ferromagnetic or a
nonmagnetic material respectively. These are very intense in nature and so there is unique
possibility to measure, by using these fields, the magnetic dipole and the electric quadrupole
moments of the nuclear states in the lifetime range of picoseconds. Magnetic field is considered to be experience at low ion velocities. Research in this field [162] has created interests experimentally as well as theoretically. PAC technique has proved to be very important in this connection. The TDPAC technique is also utilized in the investigation of solid state reactions where the different phases are quantitatively characterized by their known hyperfine parameters. An essential advantage of TDPAC technique over other spectroscopic techniques is that the sensitivity of detection is largely sample-independent, i.e., the relative fractions of the observed spectral components are identical with the mole fractions of the individual phases. The temporal evolution of the different components can also be monitored provided that the data-acquisition is minimized by the multi-detector system with high efficiency. In the field of solid state reaction, the dehydration/rehydration reaction of HfF₄·3H₂O [163], the thermal decomposition of (NH₄)₂ZrF₆ [164], the formation of CuIn₂ at the interfaces [165], the oxidation of Hf metal and internal oxidation processes of gas-phase transport reactions in situ [166] have been investigated by TDPAC technique. There are several studies on Hf(IV) complexes [167] with different legends. TDPAC of Hf(IV) complexes with the ligands. PAC studies on tropolone, cupferon and N-benzoyl n-phenyl hydroxylamine (NBPHA) show that the quadrupole coupling parameters are sensitive to the nature of covalent legends. The quadrupole interaction frequency increases from NBPHA to cupferon to tropolone, which indicates the increase in the electronic delocalisation on the chelate ring in the above order. From PAC pattern the tropolonate complex shows considerable relaxation behaviour at room temperature and 77K. For the other complexes, however, this is not observed because of rapid inter-conversion of cis-trans isomers. Apart from what has been mentioned above, a large number of studies by PAC technique in solid state chemistry can be obtained elsewhere [105, 113-114].
SOLID STATE PHYSICS AND BIOLOGY:

Due to the limited number of TPPAC isotopes having physiological function in biomolecules, the application of this hyperfine method in biology is also restricted. Still there are enough scope for mentioning the versatile application of TDPAC in the interface of solid state physics and biology. In general, two methods are adopted for labelling the biomolecule with the PAC probe. First method involves the unspecific labelling of biomolecules where the dissolved probe is added to the biomolecule in solution and the binding is recorded quantitatively by comparing the spectra of the dissolved probe with that of the bound probe. The second method involves the specific labelling of the biomolecule and the metal substitution in metalloenzymes. The “label” can be offered as free ions or “packed”, as, e.g., in EDTA or serum albumin. The area of application of TDPAC in biology can be classified in two categories: a. Coordination studies where non-uniform sites are identified and characterized according to their NQI parameters and b. Molecular dynamics where the tumbling motion of the biomolecules in solution is studied. The systematic investigation on Coordination studies was carried out by Bauer et al. [168] with $^{111m}$Cd probe ($\tau_{1/2}$=48min) for Zn-containing enzymes in highly viscous medium. Bauer tried to correlate absolute values of NQI parameters with different coordination and different ligands. For the investigation of the tumbling motion of biomolecules in solution [169-170], $^{111}$In/$^{111}$Cd probe was bound unspecifically to the biomolecule. Due to this unspecific binding, the spectra of immobilized molecules are also very featureless and the information about the reorientational correlation is difficult to extract. However, the specifically bound $^{111}$In/$^{111}$Cd in serum albumin 169 also yields featureless spectra for immobilized states indicating a more fundamental problem, e.g., chemical aftereffects. It is important, in labelling cellular component of blood, to know the relative stability of a chelate of a metal ion with respect to other possible complexes
with macromolecules e.g. transferrin, albumin, haemoglobin etc with which the chelate comes into contact. PAC application in this connection has been made [171] in the case of the dissociation of In-chelate with ligands e.g. tropolone, acetylactetone, oxine and oxine sulphate in presence of transferrin and haemoglobin. In presence of a potransferrin at certain mole ratio, it has been found that all these four chelates dissociate completely, releasing $^{111}$In for incorporation into the specific binding sites of transferrin. However for the iron free haemoglobin, the tropolonate chelate did not dissociate completely. Instead, In was bound to protein together with a single ligand molecule. TDPAC technique studies can give the dynamic aspects of binding of In-DNA as well [172]. $^{181}$Hf has been also been used for biological study. TDPAC technique has been employed [173] for finding the binding parameters of Hf after in vivo uptake of $^{181}$Hf in rat plasma. Same authors [174] also investigated this at different temperatures to see the dynamical aspects of the binding. They also studied [175] the difference of binding configuration for Hf with human and rat serum.

**SOLUTION CHEMISTRY:**

In solution, the Hamiltonian between the intermediate state and the surrounding field becomes time dependent. In addition to this, there may be relaxation due to rotational diffusion of the species to which the probe atom is attached. So determination of the attenuation factor which is related to the correlation time, can be used to study the complexation in term of its nature and stability constant, polymerisation, binding sites of the probe nucleus etc. The changes in the correlation time with the size of the species containing the PAC probe (e.g., in polymerisation reaction) can also modify the PAC parameters significantly. The application of TDPAC to the macromolecules in solution, biomolecules and their rotational correlation times, determination of conformational changes of the macromolecules, binding constants, metal-protein interaction etc.
is still left almost unturned. The potentiality of the PAC technique in the field of complexation has been demonstrated [176]. It has been found that as the fluoride to hafnium ratio is increased the attenuation factor increases and reaches the unperturbed value as the ration reaches 6:1. The symmetric arrangement of six fluoride ions around hafnium nucleus reduces the EFG and thus resulting in the unperturbed value of the attenuation factor.

Influence of the complexation on the relaxation in aqueous solution has been demonstrated [177] for hydration of In$^{3+}$ ion. Very weak perturbation at very high acidic or alkaline medium has been explained by formation of the symmetric complexes, [In(H$_2$O)$_6$]$^{3+}$ and [In(OH)$_6$]$^{3-}$ respectively. Stronger perturbation in the range of intermediate acidity is due to the formation of a less symmetric complex such as [In(H$_2$O)$_{6-x}$(OH)$_x$]$^{3-x}$. An interesting study has been carried out [178] in case of Cd(CH$_3$)$_2$ in polycrystalline form as well as in frozen solution. Quadrupole coupling constants in both the cases were found to be same. So it was concluded that the origin of the EFG was molecular in nature and the correlation time obtained in this case was unambiguous.

SUPER-VISCOUS MEDIUM:

Super-viscous system is a class of liquids which have properties different than the normal liquids in view of their transport properties e.g. viscosity and diffusion constant and their variation with temperature. Examples of such systems are molten glass, lubricating oil, glycerol, metallurgical slags etc. The study of such systems has practical as well as theoretical implications. The measurement of this kind is very rare. One such investigation [179] has been carried out in case of H$_3$PO$_4$·H$_2$O system at different temperatures. Stochastic models have been used to obtain the relaxation constants. Theses when plotted in log scale against temperature show an Arhenius
type of relation below 217K which is indication of super-viscous phase and above this temperature the transition takes place to normal liquid.

Further experiment in the other systems will be worthwhile to understand the basic nature of molecular motion in the super-viscous phase.

**HOT ATOM CHEMISTRY:**

The effect of the preceding decay feeding the $\gamma$-$\gamma$ cascade on the directional correlation pattern has already been discussed. In all the preceding decays except isomeric transition, apart from the obvious changes in the nuclear charge, the after effects involve kinetic recoil, shake off excitation, secondary ionisation, Auger charging processes etc. So if the “hot” daughter atom does not attain the stable configuration, then PAC cannot be used for the insitu study of the above mentioned after effects. On the other hand, if the nucleus attains a stable configuration, then there exists a unique relationship between the chemical states of the daughter and so the PAC study pertaining to the daughter atom will help in understanding the insitu properties of the recoil atom which is the main feature of the hot atom chemistry.

Different probes such as $^{181}$Ta and $^{111}$Cd have been used to study several aspects of the hot atom chemistry. This includes the charge neutralisation process of the daughter nucleus after beta decay of the parent and its relation to the host matrix [113] depending on whether it is a metal or an insulator. In another study [176] it has been found that the after effects which are produced by the beta decay of the parent $^{181}$Hf do not exist during the first gamma emission of the cascade due to the long span of 24 $\mu$s which is the lifetime of the initial level of the cascade. This has been carried out by observing the anisotropy in IPAC of $^{181}$Hf fluoride in aqueous solution as a function of time delay after the beta emission by $^{181}$Hf. It was found that the anisotropy remains constant as a function of delay time. This investigation of hafnium recoil chemistry has been
applied in case of Hf-EDTA and Hf-CDTA chelates. A recent study [180] has demonstrated the after effects of the beta decay of $^{181}$Hf which has been doped in monoclinic ZrO$_2$ and TDPAC of $^{181}$Ta has been observed over a temperature range of 10K to 1300K. For high purity samples, the effective anisotropy has been found to be equal to the expected value above 200°C but decreased abruptly approximately by a factor of two at lower temperature. This unusual behavior has been explained in terms of the after effects of the beta decay that populates with approximately 50% probability an electron trap located about 1 eV below the conduction band. At low temperature this trapped electron causes Ta nucleus to relax rapidly and contributes to $G_2(t)$ only near $t=0$. At high temperature or in doped samples the electron escapes quickly enough to have negligible effects on $G_2(t)$. The $\gamma-\gamma$ cascade of $^{111}$Cd has also been used to study the after effects. $^{111}$Cd obtained from IT of $^{111m}$Cd have little after effects. However the EC decay of $^{111}$In will have large after effects on atomic and molecular disruption following the Auger processes. This effect has been shown up in the smearing of the oscillation pattern in $A_2G_2(t)$ for InPO$_4$ [113]. So $^{111}$In can be used, as probe to study the after effects but not as a probe to study the matrix where well defined EFG is required to interpret the host matrix properties.

**RADIATION DAMAGE STUDY:**

In the context of hot atom chemistry, the use of PAC as a microscopic tool for the study of radiation damage in solids must be mentioned. The probe can be implanted into the matrix by ion-beam or by nuclear reactions. The local radiation damage surrounding the probe atom can be revealed by this technique. If the interstitials and vacancies can be frozen by performing the implantation at low temperatures, the probe-defect interaction can also be studied. In fact, $^{111}$In/$^{111}$Cd has been used as a probe in this connection. Several studies in this regard can be found in few articles [181-182]. A similar study on the different nuclear materials, viz., cladding
materials, fuel matrices etc., can be performed with this hyperfine tool TDPAC under simulated reactor condition.

1.3. Other Techniques:

Apart from TDPAC, few other techniques were also used in order to either compliment the TDPAC data or to characterize the samples. The techniques include X-ray Diffraction (XRD), Transmission Electron Microscope (TEM), Scanning Electron Microscope (SEM), Atomic Force Microscope (AFM), UV-Vis Spectrophotometry and Rutherford Back-Scattering (RBS). Here, a brief account of all these techniques will be furnished.

1.3.1. XRD Measurement:

X-rays are short wavelength electromagnetic radiation produced by the deceleration of high energy electrons in the inner orbitals of atoms. The wavelength range of X-rays is from $\sim 10^{-5}$ Å to 100 Å. X-rays have three major applications: X-ray radiography, X-ray Crystallography and X-ray fluorescence. Here, only the use of X-rays in X-ray Crystallography will be discussed.

XRD is used to characterize the long-range ordering in a crystal lattice and it can supplement the PAC spectroscopy very well as the PAC describes the short range ordering. X-ray crystallography is a method used for determining the atomic and molecular structure of a crystal, in which the crystalline atoms cause a beam of X-rays to diffract into many specific directions. By measuring the angles and intensities of these diffracted beams, a crystallographer can produce a three-dimensional picture of the density of electrons within the crystal. From this electron density, the mean positions of the atoms in the crystal can be determined, as well as their chemical bonds, their disorder and various other information. Crystals are regular arrays of atoms, and X-rays can be considered waves of electromagnetic radiation. Atoms scatter X-ray waves, primarily through the atoms' electrons. In common with the other types of
electromagnetic radiation, the interaction between the electric vector of X-radiation and the electron of the atoms in the crystal through which it passes results in scattering. When X-rays are scattered by the ordered environment in a crystal, interference (both constructive and destructive) takes place among the scattered rays because the distance the scattered centers are of the same order of magnitude as the wavelength of radiation. Diffraction is the result. The requirements for X-ray diffraction are: (i) the spacing between the layers of atoms must be roughly the same as the wavelength of the radiation and (ii) the scattering centers must be spatially distributed in a highly regular way. The requirement for constructive interference is that the optical path difference between the two waves be equal to an integral multiple of wavelengths. The Bragg’s law is as follows:

\[ n\lambda = 2dsin\theta \]  

(1.106)

The spectrum contains the diffraction intensity versus the diffraction angle. Then the computer software compares the results to the analytical standards to determine the composition of the sample. The intensity of the diffracted peaks is related to the long range ordering of the sample. The sharper and more intense the peaks are, more will be the uniformity of the crystal lattice. Again the FWHM of the peak at a particular diffraction angle can be related to the particle size of the sample by Debye-Scherrer formula. The Scherrer equation [183-184] in X-ray diffraction and crystallography, is a formula that relates the size of sub-micrometre particles, or crystallites, in a solid to the broadening of a peak in a diffraction pattern.

The Scherrer equation can be written as:

\[ \tau = \frac{K\lambda}{\beta \cos \theta} \]  

(1.107)

\( \tau \) is the mean size of the crystallite, \( K \) is a dimensionless shape factor, with a value close to unity. The shape factor has a typical value of about 0.9, but varies with the actual shape of the
crystallite, \( \lambda \) is the X-ray wavelength, \( \beta \) is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians and \( \theta \) is the Bragg angle.

In the present thesis, XRD measurements have been performed in bulk as well as nano samples in order to study the long-range ordering. In some cases, the particle size has also been determined using the Debye-Scherrer formula.

1.3.2. Transmission Electron Microscopy (TEM):

Transmission electron microscopy (TEM) is a microscopy technique where a beam of electrons is transmitted through an ultra-thin specimen, gets scattered as they pass through it, is focussed by an objective lens, gets amplified by a magnifying lens and finally produces the desired image. Electrons interact much more strongly with matter than do X-rays or neutrons with comparable energies or wavelengths. For ordinary elastic scattering of 100 keV electrons, the average distance traversed by the electrons between scattering events (mean free path) varies from ten to hundreds of nanometers for heavy elements. The best results are obtained in electron microscopy by using film thicknesses that are comparable with the mean free path. In the present thesis, TEM has been used to characterize the core-shell nanoparticles which were prepared along with the PAC probe and studied with TDPAC method.

1.3.3. Scanning Electron Microscope (SEM):

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern (rectangular pattern of image capture), and the beam's position is combined with the
detected signal to produce an image. SEM can achieve resolution better than 1 nanometer. It is one type of scanning microscopy to obtain surface information of a specimen. Here, the electrons are deflected magnetically through magnetic fields generated by electric currents flowing through coils. The strength of the magnetic field produced by a coil is proportional to the voltage applied to the coil. The magnetic field produced by the coils exerts a force that deflects the electron beam from left to right along the direction of the line drawn at the bottom of the sample. Thus the electron beam scans repeatedly from left to right across the sample in a raster pattern that eventually covers the entire frame area on the sample.

The spatial resolution of the SEM depends on the size of the electron spot, which in turn depends on both the wavelength of the electrons and the electron-optical system that produces the scanning beam. The resolution is also limited by the size of the interaction volume, or the extent to which the material interacts with the electron beam. The spot size and the interaction volume are both large compared to the distances between atoms, so the resolution of the SEM is not high enough to image individual atoms, as is possible in the shorter wavelength (i.e. higher energy) transmission electron microscope (TEM). The SEM has compensating advantages, though, including the ability to image a comparatively large area of the specimen; the ability to image bulk materials (not just thin films or foils); and the variety of analytical modes available for measuring the composition and properties of the specimen. Depending on the instrument, the resolution can fall somewhere between less than 1 nm and 20 nm.

1.3.4. Atomic Force Microscope (AFM):

The technique in wide use for nanostructured surface studies is AFM which is also a scanning microscopy technique. AFM monitors the force exerted between the surface and the probe tip. It has resolution on the order of fractions of a nanometer. The AFM has two modes of operation. In
close-contact mode, the core-to-core repulsive forces with the surface dominate and in a greater separation non-contact mode, the relevant force is the gradient of the Van der Waals potential.

The AFM is one of the foremost tools for imaging, measuring, and manipulating matter at the nanoscale. The information is gathered by "feeling" the surface with a mechanical probe. Piezoelectric elements (piezoelectricity means electricity resulting from pressure) that facilitate tiny but accurate and precise movements on (electronic) command enable the very precise scanning. The AFM consists of a cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. The cantilever is typically silicon or silicon nitride with a tip radius of curvature on the order of nanometers. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke's law. Typically, the deflection is measured using a laser spot reflected from the top surface of the cantilever into an array of photodiodes. If the tip was scanned at a constant height, a risk would exist that the tip collides with the surface, causing damage. Hence, in most cases a feedback mechanism is employed to adjust the tip-to-sample distance to maintain a constant force between the tip and the sample. Traditionally, the sample is mounted on a piezoelectric tube that can move the sample in the $z$ direction for maintaining a constant force, and the $x$ and $y$ directions for scanning the sample.

AFM has several advantages over the scanning electron microscope (SEM). Unlike the electron microscope which provides a two-dimensional projection or a two-dimensional image of a sample, the AFM provides a three-dimensional surface profile. Additionally, samples viewed by AFM do not require any special treatments (such as metal/carbon coatings) that would irreversibly change or damage the sample. While an electron microscope needs an expensive vacuum environment for proper operation, most AFM modes can work perfectly well
in ambient air or even a liquid environment. This makes it possible to study biological macromolecules and even living organisms. In principle, AFM can provide higher resolution than SEM. A disadvantage of AFM compared with the scanning electron microscope (SEM) is the single scan image size. In one pass, the SEM can image an area on the order of square millimeters with a depth of field on the order of millimeters, whereas the AFM can only image a maximum height on the order of 10-20 micrometers and a maximum scanning area of about 150×150 micrometers. One method of improving the scanned area size for AFM is by using parallel probes. The scanning speed of an AFM is also a limitation. Traditionally, an AFM cannot scan images as fast as a SEM, requiring several minutes for a typical scan, while a SEM is capable of scanning at near real-time, although at relatively low quality. The relatively slow rate of scanning during AFM imaging often leads to thermal drift in the image making the AFM less suited for measuring accurate distances between topographical features on the image. AFM images can also be affected by nonlinearity, hysteresis and creep of the piezoelectric material and cross-talk between the x, y, z axes that may require software enhancement and filtering. In the present thesis, AFM has been utilized in order to study the surface morphology of thin film.

1.3.5. UV-Vis Spectrophotometry:

Molecular absorption spectroscopy is based on the measurement of the transmittance $T$ or the absorbance $A$ of solutions contained in transparent cell having a pathlength of $b$ cm. Ordinarily, the concentration $c$ of an absorbing analyte is linearly related to absorbance as represented by the equation

$$A = -\log T = \log \frac{P_0}{P} = \varepsilon bc$$

(1.108)
The power of the beam transmitted by the analyte solution \((P_0)\) is usually compared with the power of the beam transmitted by an identical cell containing only solvent \((P)\). The present spectroscopic technique has been used to characterize the pure and core-shell nanoparticles.

1.3.6. RBS Spectroscopy:

Rutherford Backscattering Spectrometry (RBS) is a widely used nuclear technique for the surface layer analysis of solids. A target is bombarded with ions at energy typically in the range of 0.5–4 MeV and the energy of the backscattered projectiles is recorded with an energy sensitive detector, typically a solid state detector kept at an angle of 150-170°. RBS allows the quantitative determination of the composition of a material and measurement of depth profiling of individual elements. RBS is quantitative without the need for reference samples and non-destructive. It has a good depth resolution of the order of several nm and a very good sensitivity for heavy elements of the order of parts-per-million (ppm). The drawback of RBS is the low sensitivity for light elements. This technique has been used to measure the thickness of a thin film sample in the present thesis.

1.4. Motivation and Scope of the Thesis:

The physico-chemical study in the atomic level has importance in order to investigate the microstructural aspects of the system under study. The information on the short-range interaction is also important in order to explain the different modifications of the macroscopic properties of the chemical systems required for different applications. To study such microscopic properties, the technique is expected to have a resolution in the range of atomic scale. TDPAC is a nuclear probe technique based on hyperfine interaction with atomic scale resolution. The short-range information is obtained with high sensitivity. In case of multiple species containing the probe atom inside the matrix under study, all the species can be identified along with their individual
populations. The analysis of the PAC spectrum provides the information about the strength of EFG, its asymmetry and the crystalline purity of the sample under study.

The technique TDPAC is a nuclear technique where a suitable radionuclide is doped inside the chemical matrix under study as a probe atom and its nuclear property under the chemical environment is exploited to acquire the microstructural information about the host matrix. To carry out TDPAC spectroscopy, it is required to develop the electronics coupled with a suitable data-acquisition system. For a fast-timing measurement, it is a prerequisite to have a fast detector. In addition, the best-possible energy resolution for the detectors is also desirable in order to separate the close-lying energy peaks. So the latest available LaBr$_3$(Ce) detectors have been chosen for the present TDPAC spectrometer. A fast-slow coincidence circuit has been developed coupled to a CAMAC-based data-acquisition system. The advantage of this coincidence circuit lies in the fact that the data are collected in LIST mode and gates are given in the post-acquisition period. The energy resolution of the LaBr$_3$(Ce) detectors is so good ($\leq$3% at 662 keV $\gamma$-energy) that it could separate the closely spaced $\gamma$-cascades. In order to optimize the operational condition for the spectrometer without hampering the time resolution of the coincidence circuit, a characteristics study on the LaBr$_3$(Ce) detectors has also been carried out.

The study has been carried out with the group-IVB metal oxides, viz., TiO$_2$, ZrO$_2$ and HfO$_2$, based on their versatile applications both in pure and in doped forms. Again the method of sample preparation has also been a mild process following the coprecipitation technique. At first, the known TDPAC parameters for rutile system have been established with the above spectrometer and then the parameters for anatase system have been measured. The other two oxides in pure form have also been studied with this technique and their structural similarity has been established. The method has been uniquely applied in case of doped rutile systems, thin
films and nanoparticles including core-shell type. The minute changes under different chemical conditions have been perceived by this hyperfine tool and furnished in the thesis. The new observations in case of doped and core-shell nanosystems have been explained in the present work. The sensitivity and versatility of TDPAC technique in different types of chemical phenomena have also been presented in the present thesis.