Chapter 1

Introduction to Solid State NMR and Methods for the Determination of
Chemical Shielding and Electric Field Gradient Tensors
1.1 Introduction

Nuclear Magnetic Resonance (NMR) is a versatile and ubiquitous branch of radio frequency spectroscopy and has made great strides in Physics, Chemistry, Biology and Medicine. The success of NMR spectroscopy as a primary spectroscopic tool is due to our ability to obtain highly resolved spectra in which chemically distinct sites can be identified and well distinguished. NMR phenomenon originates from gyromagnetic property of atomic nuclei immersed in an externally applied magnetic field and subjected to a resonant RF irradiation in a perpendicular direction. NMR was originally discovered as a continuous-wave (cw) absorption and induction techniques in 1946. The introduction of pulse Fourier-Transform techniques in 1972 and the subsequent developments in methodology and practice have brought modern NMR spectroscopic practices in the realm of multi-nuclear multi-dimensional NMR. NMR spectroscopy is widely practiced in the liquid state and the vast majority of NMR applications lie in molecular structure elucidation of a wide range of soluble organic, inorganic and biological substances. At the cutting edge, modern NMR spectroscopy vies with X-ray crystallography in the determination of the three-dimensional architecture of protein molecules. Herein, modern NMR practices are continuously refined and adapted for the automated generation of protein structures, relevant to the proteomics area.

While the superior spectral resolution is inherent to the liquid state, owing to the total averaging of all the orientation dependent spin interactions, NMR spectra of solid samples suffer from excessive line broadenings due to the lack of Brownian motions. However, ingenious coherent averaging methods have been developed during the last three decades for obtaining high resolution spectra in the solid state. Experimental techniques based on "coordinate" and "spin space" averaging have led to many significant methodological developments and advancements and these, in turn, have fuelled numerous applications in various areas of Materials and Biological Sciences. Solid state NMR not only equips us to achieve high spectral resolution, but also provides us with novel experimental approaches and tools for the selective averaging and portrayal of spin interactions in their full tensorial form. Presently, solid state NMR is extensively sought in biomolecular structure determinations, such as peptides, amyloid fibrils and
membrane proteins. Bio-molecular solid state NMR is also emerging as a discipline of its own with new methodological developments and advancements which continue to offer new structure elucidation tools.

The major objective of the research work carried out and reported in this thesis is the determination of spatially dependent interaction tensors from solid-state NMR experiments as well as advanced quantum chemical calculations. The computational methods, in particular, exploit the recent advancements in quantum chemical approaches for the determination of interaction tensors with increased numerical accuracy. It is therefore, pertinent to provide a brief introduction to solid state NMR and the quantum chemical methods used so that necessary framework is laid out before the research work carried out by the author is presented and discussed.

1.2 Spin Interactions in Solid State NMR

The hallmark of NMR spectroscopy is that rich structural information is provided by the manifestation of various spin interactions in the NMR spectra. These interactions originate in the molecule and affect the spectral response in different ways. For a theoretical description of solid state NMR spectroscopy, we start by writing the total Hamiltonian as

\[ H_{\text{tot}} = H_Z + H_{\text{RF}} + H_C + H_D + H_J + H_Q \]  

where \( H_Z \) is the Zeeman Hamiltonian, by far the strongest one, and \( H_{\text{RF}} \) is the Hamiltonian governing the irradiation of the spin system by the radio-frequency field at the Larmor frequency \( \omega_0 \) in a direction perpendicular to the main magnetic field. The Zeeman Hamiltonian is,

\[ H_Z = -\gamma \vec{B} \cdot \vec{I} \]  

where \( \vec{B} \) is the static magnetic field vector and \( \vec{I} \) is the nuclear spin vector. With the magnetic field applied along the laboratory \( z \)-axis, this becomes

\[ H_Z = -\gamma B_0 I_z \]
The term $\gamma B_0 (= \omega_0)$ gives the Larmor frequency of the nucleus. When the nucleus spins are irradiated with a linearly polarized RF-field of strength $2B_I$ and frequency $\omega_0$ along the $x$- axis in the laboratory frame,

$$H_{RF} = 2\alpha \cos(\omega_0 t + \phi) \hat{I}_x$$

(4)

It is customary to transform to a frame rotating at the Larmor frequency. Eq. (4) becomes,

$$H_{RF} = \omega_1 (\cos \phi \hat{I}_x + \sin \phi \hat{I}_y)$$

(5)

All the other Hamiltonians in Eq. (1) are due to internal interactions. The four main interactions of interest in diamagnetic solids are: chemical shielding, dipolar coupling (homonuclear and heteronuclear), indirect spin-spin coupling and quadrupolar interactions. Of these, the chemical shielding and quadrupolar interactions and their exploitation in experimental measurements and theoretical calculations for structural elucidation are of special interest in the present work. These interactions, which are molecule fixed, are described as tensors of rank two. They act as a perturbation on the Zeeman interaction and cause line broadening in the solid state NMR spectra of powder samples. Although single crystal rotation studies enable the determination of the interaction tensors, it is desirable to employ powder samples. In static samples, the line broadening and spectral overlap complicate the spectral analysis and the determination of anisotropic parameters. Modern solid state NMR spectroscopy is devoted towards retrieving these tensors through experimental strategies that are performed in the high-resolution regime. The spin interactions are cleverly manipulated in experimental schemes under coordinate space and spin space averaging, allowing the anisotropic parameters to be determined under high-resolution conditions. Besides, advances in quantum chemical methods and the increased computing power available at the desk top allow the interaction tensors to be determined by theoretical means with increased efficiency and numerical accuracy.

Solid state NMR spectra result from a perturbation of the Zeeman Hamiltonian by one or more of the above interaction Hamiltonians. Spectral response is essentially determined by the allowed transitions within the perturbed energy levels of the spin system under consideration. We will now discuss each of the interaction Hamiltonians, using the spherical tensor formalism.
1.2.1 Spherical Tensor Formalism

The various spin interactions can be written in a general and compact form using the spherical tensor formalism. The common NMR interactions may all be represented by second-rank Cartesian tensors $R$ which are familiar. In the irreducible tensor representation of spin interactions we express the interactions by spherical rather than Cartesian tensors. Any second-rank Cartesian tensor may be readily decomposed in spherical tensor operators, namely, a scalar $R^{(0)}$ (one term), first rank antisymmetric tensor operator $R^{(1)}$ (3 terms) and a symmetric second-rank spherical tensor operator $R^{(2)}$ (5 terms). The relevance of this decomposition is the particular transformation properties they possess under rotation from one Cartesian frame to the other using Wigner rotation matrices. The components of $R^{(0)}$, $R^{(1)}$ and $R^{(2)}$ transform in the same way as the spherical harmonics of order zero, one and two, respectively. Denoting the irreducible spherical tensor components for the spin and spatial parts by $T_{lm}$ and $R_{lm}$, the interaction Hamiltonian can be represented as

$$H = C^4 \sum_{l=0}^{l} \sum_{m=-l}^{l} (-1)^m R_{lm}^4 T_{lm}^4$$

The irreducible tensor components $T_{lm}$ are related to the various spin operators and the $R_{lm}$ to the Cartesian tensor components. $C^4$ denotes a constant involved in the interaction being considered.

1.2.2 Euler Angles and Coordinate Transformation

All the internal interactions, due to their molecular origin, are initially defined in the Principal Axis System (PAS) and the matrix is diagonal. Since the energy eigen values must be determined in the Zeeman frame or the Zeeman Axis System (ZAS), one must transform the interaction Hamiltonian from the PAS to ZAS. When employing sample rotation, one must additionally transform the Hamiltonian through the rotor frame. The transformation from one frame to another is carried out using Euler rotations. This is shown in Figure 1. Following the Rose convention, transformation from a coordinate system $(X,Y,Z)$ to another $(x,y,z)$ is carried out as follows: 1) rotation of
X, Y, Z by angle $\alpha$ about the z(1) axis to generate x(2), y(2), z(2); 2) rotation of x(2), y(2), z(2) by angle $\beta$ about y(2) axis to generate x(3), y(3), z(3) and finally 3) rotation of x(3), y(3), z(3) by angle $\gamma$ about z(3) to arrive at the final frame x, y, z. Thus the coordinate transformation is governed by the three independent Euler angles $\alpha$ (0 to $2\pi$), $\beta$ (0 to $\pi$) and $\gamma$ (0 to $2\pi$).

The rotation matrix for each of the three rotations is

$$R_x(\alpha) = \begin{pmatrix} \cos \alpha & \sin \alpha & 0 \\ -\sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$R_y(\beta) = \begin{pmatrix} \cos \beta & 0 & -\sin \beta \\ 0 & 1 & 0 \\ \sin \beta & 0 & \cos \beta \end{pmatrix}$$

$$R_z(\gamma) = \begin{pmatrix} \cos \gamma & \sin \gamma & 0 \\ -\sin \gamma & \cos \gamma & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

The overall coordinate transformation in the matrix form is

$$R = R_z(\gamma) R_y(\beta) R_x(\alpha) = \begin{pmatrix} \cos \alpha \cos \beta \cos \gamma - \sin \alpha \sin \gamma & \sin \alpha \cos \beta \cos \gamma + \cos \alpha \sin \gamma & -\sin \beta \cos \gamma \\ -\sin \alpha \cos \beta \cos \gamma - \cos \alpha \sin \gamma & \cos \beta \sin \gamma + \cos \alpha \cos \gamma & \sin \beta \sin \gamma \\ \cos \alpha \sin \beta & \sin \alpha \sin \beta & \cos \beta \end{pmatrix}$$

Since $R_{00}$ is rotationally invariant, the spatial tensor components of $R_{2m}$ in the rotated frame are related to the components in the initial frame $\rho_{2m'}$ by

$$R_{2m} = \sum_{m'=-2}^{2} D_{m'm}^{(2)}(\alpha, \beta, \gamma) \rho_{2m'}$$

where the $D_{m'm}^{(2)}$ are the second-order Wigner rotation matrix elements

$$D_{m'm}^{(2)}(\alpha, \beta, \gamma) = \exp(-im'\alpha) D_{m'm}^{(2)}(\beta) \exp(-im\gamma)$$
The second-order reduced matrix elements $d_{m^2}^{(2)} (\beta)$ are given in Table 1. The angles $\alpha$, $\beta$ and $\gamma$ are the same Euler angles through which the original system must be rotated to

| $m$ | $|m|$ | $d_{m^2}^{(2)} (\beta)$ |
|-----|------|--------------------------|
| -2  | 2    | $\frac{1}{4}$            |
| -1  | 1    | $\frac{1}{2}$ $\cos^2 \beta$ |
| 0   | 0    | $\frac{1}{4}$ $\sin^2 \beta$ |
| 1   | 1    | $\frac{1}{2}$ $\cos\alpha \cos\beta$ |
| 2   | 2    | $\frac{1}{4}$ $\cos 2\alpha \cos 2\beta$ |

Table 1: Wigner Rotation Matrix $D_{3/1} (\alpha,\beta,\gamma)$.
bring the axes in line with the new axis system. Whenever multiple rotations are involved, such as in experiments where sample is mechanically rotated, the transformation of the coordinate system from PAS to the laboratory frame involves a two-step transformation with the Euler angles defined for each step. The transformation of the spatial tensor $R_{2m}$ from its PAS to the rotor frame and subsequently to the laboratory frame takes the form

$$R_{2m} = \sum_{m=-2}^{2} D^{[2]}_{m\ell} (0, \theta, \omega_I) \sum_{m'=-2}^{2} D^{[2]}_{m'm} (\alpha, \beta, \gamma) \rho_{2m'}$$

(11)

In Eq. (11), the transformation from PAS to rotor frame involves Euler angles $(\alpha, \beta, \gamma)$ and from rotor frame to laboratory frame, $(0, \theta, \omega_I)$. These kinds of transformations will be required especially in dealing with the Hamiltonians under Magic Angle Spinning.

1.2.3 Chemical Shielding Interaction

The chemical shielding interaction is due to the interaction of a nuclear spin $I$ with the induced local magnetic field generated by the electrons that surround the nucleus. The applied external magnetic field causes a slight change in the orbital motion of the electrons surrounding the nucleus. This induces a small additional magnetic field at the nucleus, proportional to the applied field strength. This, in diamagnetic solids, opposes the main field and the decrease of the field strength sensed by the nucleus results in a shift of the resonance position compared to the Larmor frequency of a bare nucleus. The chemical shielding is very sensitive to the chemical environment of the nucleus and is described by the Hamiltonian

$$H_{CS} = \gamma I \bar{\sigma} \bar{B}$$

(12)

The chemical shielding is an anisotropic interaction represented by the tensor $\bar{\sigma}$ and in the principal axis frame (PAS) the matrix is diagonal, having principal elements $\sigma_{11}$, $\sigma_{22}$ and $\sigma_{33}$ ($\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}$). It is also useful to describe the chemical shielding tensor in terms of the following three parameters derived from $\sigma_{ii}$.

1. Isotropic chemical shift: $\sigma_{iso} = \frac{1}{3} Tr(\sigma) = \frac{\sigma_{11} + \sigma_{22} + \sigma_{33}}{3}$

(13)

This is the average value of the tensor which is orientationally independent.
2. Chemical Shift Anisotropy: \[ \Delta \sigma = \sigma_{33} - \sigma_{11}, \quad \Delta \sigma \geq 0 \] (14)
This is a measure of the span or the maximum width of the powder pattern.

3. Skew or Asymmetry Parameter: \[ \eta = \frac{3(\sigma_{11} - \sigma_{22})}{\Delta \sigma}, \quad -1 \leq \eta \leq 1 \] (15)
If \( \eta = \pm 1 \), the shielding tensor is axially symmetric. Often, \( \eta \) provides a visualization of the symmetry of the local electronic environment due to bonding arrangement and serves as a structural aid along with \( \sigma_{11} \) and \( \Delta \sigma \). We have used the Herzfeld-Berger\(^{12}\) convention in Eq. (14) and (15), which can be readily converted to the standard and Haeberlen conventions.\(^{13}\) It may be noted that we have used the representation \( \sigma \), against \( \delta \) used to denote the chemical shifts in liquid state NMR. The \( \sigma \) scale is appropriate in the solid-state context, since positive values of \( \sigma \), with respect to a reference compound, denote shielding and negative values denote deshielding.

In the spherical tensor notation, we can write for the chemical shielding Hamiltonian
\[
H_{CS} = \sum_{l=0,2,4} \sum_{m=-l}^{l} (-1)^{l} T^{CS}_{lm} R^{CS}_{l-m}
\] (16)
The components of \( T^{CS} \) involve the spin and are defined in the laboratory frame, so it is necessary to express \( R^{CS} \) in this frame as well. The components of \( T^{CS} \) are given by
\[
T^{CS}_{00} = B_0 \hat{I}_z, \quad T^{CS}_{20} = \sqrt{2} B_0 \hat{I}_z, \quad T^{CS}_{22} = \frac{1}{\sqrt{2}} B_0 \hat{I}_z, \quad T^{CS}_{22} = 0
\] (17)
The spatial tensor \( R^{CS} \) is related to the spatial tensor \( \rho^{CS} \) in the PAS as
\[
R^{CS}_{2m} = \sum_{n=0}^{l} D^{(3)}_{m,n} (\alpha, \beta, \gamma) \rho^{CS}_{2m'}
\] (18)
where the components of tensor \( \rho^{CS} \) are
\[
\rho^{CS}_{20} = -\frac{2}{\sqrt{3}} \Delta \sigma, \quad \rho^{CS}_{22} = 0, \quad \rho^{CS}_{222} = \frac{1}{2} \left( \sigma_{yy}^{CS} - \sigma_{xx}^{CS} \right)
\] (19)
At high magnetic fields, we have \( H_z \gg |H_{CS}| \) and \( H_{CS} \) can be considered as a perturbation on \( H_z \) to first order. We retain only the secular part of the Hamiltonian and hence discard terms with \( m > 0 \). The shielding Hamiltonian becomes
\[ H_{CS} = C[R_{00}T_{00} + R_{22}T_{22}] \] (20)

In order to determine the orientation dependent single quantum transition frequencies in a powder sample, we transform from PAS to the Zeeman frame (ZAS), using Euler angles \((\theta, \phi, 0)\).

\[ \text{PAS} \xrightarrow{\theta, \phi, 0} \text{ZAS} \] (21)

In Eq. (20), \(R_{00}\) is rotationally invariant and only \(R_{22}\) is to be transformed from PAS to ZAS.

\[ H_{CS} = \lambda \left[ R_{00}T_{00} + T_{30} \sum_{m'} D_{m'0}(\theta, \phi, 0) \rho_{2m'} \right] \] (22)

Substituting for the Wigner matrix element \(D_{m'0}\) from Table 1, we finally arrive at

\[ H_{CS} = \omega_{\text{iso}} \hat{I} \left[ \sigma_{iso} + \frac{\delta}{2} \left\{ (3\cos^{2}\theta - 1) + \eta\sin^{2}\theta\cos2\phi \right\} \right] \] (23)

The chemical shielding Hamiltonian thus contains an orientationally independent term, which is the isotropic chemical shift \((\sigma_{iso})\) and an orientation dependent term that gives rise to the anisotropy in a powder sample. In a polycrystalline sample, the random orientations of various crystallites lead to a distribution of \((\theta, \phi)\) values giving rise to an anisotropic line shape for the chemical shielding interaction. Figure 2 shows a typical static powder pattern depicting the anisotropy and asymmetry of chemical shielding.

**Figure 2:** The chemical shielding powder pattern from a nucleus with anisotropic chemical shielding, defined with the parameters \(\sigma_{iso} = 0\) ppm, \(\Delta\sigma = 200.0\) ppm and \(\eta_{\sigma} = 0.0\). The singularities in the powder pattern correspond to \(B_{0} \parallel \sigma_{11}, B_{0} \parallel \sigma_{22}\) and \(B_{0} \parallel \sigma_{33}\) as shown.
For the experimental determination of chemical shielding tensors from powder samples, the powder patterns as shown in Fig. 2 can be analyzed and the principal elements \( \sigma_0 \) determined. However, when more than one chemical environment is present, the powder patterns overlap and the exercise becomes difficult, if not impossible. Therefore one has to resort to high-resolution conditions under which the shielding tensors can be determined. Fortunately, this is feasible under Magic Angle Spinning (MAS) by a mechanical rotation of the sample. MAS is introduced and discussed below.

1.2.4 Magic Angle Sample Spinning

The situation in solids contrasts sharply with that of a liquid, where the Brownian tumbling motion of the molecules is isotropic and the motional correlation frequency \( (1/\tau_c) \) is many orders of magnitude larger than the strength of any of the NMR interactions. This results in a total averaging of the various spatially dependent interactions so that the anisotropic interactions are now replaced by their isotropic values. The dipolar and quadrupolar interactions, being traceless, vanish while the CSA and J-coupling interactions average to their respective scalar values \( \sigma_{iso} \) and \( J_{iso} \), respectively.

The orientation dependent chemical shielding interaction [Eq. (23)] can however be rendered time dependent by a bodily motion of the sample and the time average over the bodily motion of the sample can be made to mimic, in some sense, the Brownian motion in liquids. Andrew\textsuperscript{14,15} and Lowe\textsuperscript{16} realized that although the interaction vectors for the different crystallites make different angles \( (\theta) \) with respect to the magnetic field \( B_0 \), a periodic mechanical rotation of the sample at a speed \( \omega \) about a fixed axis projects the time average over one rotation for all the interaction vectors along this fixed rotational axis. The orientation dependence with respect to the magnetic field \( B_0 \) [Eq. (23)], i.e., \( (3\cos^2 \theta - 1)/2 = P_2(\cos \theta) \), is now transformed into an orientation dependence with respect to the spinning axis i.e., \( (3\cos^2 \beta' - 1)/2 = P_2(\cos \beta') \), which varies from crystallite to crystallite, multiplied by the orientation of the spinning axis with respect to \( B_0 \) i.e., \( (3\cos^2 \beta - 1)/2 = P_2(\cos \beta) \), which is same for all crystallites.

\[
P_2(\cos \theta) = P_2(\cos \beta) \cdot P_2(\cos \beta')
\] (24)
When $\beta$ is chosen to be $\cos^{-1}(1/\sqrt{3})$, or $\beta = 54.736^\circ = \text{"magic angle"}$, the anisotropic interaction is averaged to its isotropic value. We will now proceed to discuss the effect of sample rotation on the chemical shielding interaction with an aim to retrieve the interaction tensor components.

We start with the secular Hamiltonian given in Eq. (20). Since $R_{00}$ is invariant to rotation, only the orientation dependent term $R_{20}$ is of interest, and the same has to be transformed from the PAS to the laboratory frame (ZAS) via the spinner frame (RAS) using two sets of Euler angles as indicated in Eq. (25) and shown in Figure 3.

$$\text{PAS} \rightarrow RAS \rightarrow \text{LAS}$$

![Figure 3: Sample rotation at an angular frequency $\omega_s$, with the spinner axis inclined at the angle $\beta$ with respect to $B_0$. The Euler angles for the transformation from PAS to the spinner frame and from spinner frame to the laboratory frame correspond to $(\theta, \phi, \psi)$ and $(0, \beta, \omega_s)$, respectively.](image)

The spatial tensor in the laboratory frame is

$$R_{20}^{CS} = \sum_m D^{(2)}_{m,0}(0, \beta, \omega_s) \sum_n D^{(2)}_{m,-n}(\theta, \phi, \psi) \rho_{2n}. \tag{26}$$

Putting in the values from Wigner’s rotation matrix (Table 1), we have

$$R_{20}^{CS} = \xi(t) = \frac{1}{2} \left[ \frac{3 \cos^2 \beta - 1}{2} \right] \left[ \frac{3 \cos^2 \theta - 1}{2} \right] \sqrt{2} \delta + \frac{3}{2} \eta \delta \sin^2 \theta \cos 2\psi$$

$$+ c_1 \cos \omega_s t + s_1 \sin \omega_s t + c_2 \cos 2\omega_s t + s_2 \sin 2\omega_s t. \tag{27}$$

$$c_1 = \frac{\sqrt{3}}{2\sqrt{2}} \delta \sin 2\beta \sin \theta \{\cos \theta \cos \phi (\eta \cos 2\psi - 3) - \eta \sin \phi \sin 2\psi\} \tag{28}$$

$$s_1 = \frac{\sqrt{3}}{2\sqrt{2}} \delta \sin 2\beta \sin \theta \{\cos \theta \cos \phi (3 - \eta \cos 2\psi) - \eta \sin \phi \sin 2\psi\} \tag{29}$$

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It may be noted that in the above equations the chemical shielding parameters are defined\(^{17}\) as: \(\delta = \sigma_{33} - \sigma_{\text{iso}}\) and \(\eta = (\sigma_{11} - \sigma_{22}) / \delta\). Eq. (27) contains both time-independent and time-dependent terms that can be considered separately. The time independent part in Eq. (25) vanishes when \(\beta = \cos^{-1}(1/\sqrt{3})\), the 'magic angle'. Eq. (27) also shows that line broadening occurs away from the ‘magic angle’, and in the extreme cases \(\beta = 0^\circ\) and \(\beta = 90^\circ\), the chemical shielding anisotropy is fully retained and halved, respectively, in the observed NMR spectrum. Thus, under MAS, the Hamiltonian is

\[
H^\text{CS} = \omega_0 \hat{I} : \left[ \sigma_{\text{iso}} + \delta \hat{\xi}(t) \right]
\]  

(32)

The time dependent part of Eqs. (27, 32) also brings out the spinning-induced periodicity of the spin Hamiltonian. The periodic rotation of the sample at the frequency \(\omega_r\) causes the modulation terms to appear at integer multiples of \(\omega_r\) and \(2\omega_r\). These lead to the generation of spinning side bands in MAS spectra, whose intensities are determined by \(\delta\) and \(\eta\) through the modulation coefficients \(c_1, c_2, s_1\) and \(s_2\). An analysis of spinning side band intensities therefore enables the determination of chemical shielding parameters under high-resolution conditions. Slow MAS experiments are especially suited for the determination of chemical shielding parameters since they entail the generation of many side bands in the spectrum. The side band analysis in slow MAS is facilitated by the time domain approach due to Maricq and Waugh.\(^{17}\) In this approach, we seek to observe the time domain response of the spinning sample whose frequency spectrum obtained from Eq. (32) is,

\[
\omega_{n_0}(t) = \omega_0 \sigma_{n_0} + \omega_0 \delta_0 \xi_{n_0}(t)
\]  

(33)

In a sample containing \(n\) chemically distinct species, with their crystallite orientations denoted by \(k\), the phase accumulated by the precessing magnetization following an RF pulse is given by

\[
\phi_{n_0}(t) = \int_0^t \omega_{n_0}(t') \, dt' = \omega_0 \sigma_{n_0} t + \omega_0 \delta_0 \int_0^t \xi_{n_0}(t') \, dt'
\]  

(34)
Each spin packet, having its magnetization initially along the x-axis of the rotating frame, precesses in time to the azimuth whose factor is independent of k. The x and y components of magnetization are proportional to $\cos \phi_k$ and $\sin \phi_k$ and appear in the real and imaginary parts of the normalized free induction decay

$$g(t) = \sum_n \sum_k p_n \exp[i \phi_k(t)]$$

Combining Eqs. (34) and (35)

$$g(t) = \sum_n p_n \exp(i \omega_0 \sigma_{n;iso} t) \sum_k \exp(i \omega_0 \delta_k \int_0^t \xi_{isn}(t') dt')$$

where, the isotropic chemical shift, anisotropy, asymmetry parameter and the site population for the $n^{th}$ species are denoted by $\sigma_{n;iso}$, $\delta_n$, $\eta_n$ and $p_n$, respectively. In Eq. (35), the summation index $k$ extends over all crystallites and denotes the powder average. Because $\xi_{isn}$ are all purely oscillatory, the integral vanishes for $t = p(2\pi/\omega_0)$, $p$ any integer. The sum on $k$ then represents a train of so-called ‘rotational echoes’, all of which have the same shape. The Fourier-transform of these echoes gives rise to the isotropic signal and its associated side bands, as shown in Figure 4. We have employed this approach in determining $^{29}$Si shielding tensors from slow MAS experiments.

Figure 4: The effect of Magic Angle Spinning on anisotropic chemical shielding (axially symmetric tensor). Static spectrum (a) and MAS spectra at 3405 Hz (b) and 3010 Hz (c).
1.2.5 Dipolar Interaction

Dipolar coupling is a through-space magnetic dipole-dipole interaction between two like or unlike nuclei. It has a classical analogy in the interaction of two magnetic dipoles located a distance $r$ away from each other. Since the strength of the dipolar coupling is inversely proportional to the cube of the internuclear distance $r$, its determination is of special interest in solid state NMR. The through-space, or direct, dipolar coupling Hamiltonian can be obtained by applying the correspondence principle to the expression defining the energy for the interaction between two magnetic dipoles,

$$
E = \frac{\hbar}{r_{ij}^3} [3(\vec{\mu}_i \cdot \vec{r}_{ij})(\vec{\mu}_j \cdot \vec{r}_{ij}) - (\vec{\mu}_i \cdot \vec{\mu}_j)]
$$

where $r_{ij}$ is the distance between the dipoles and $\vec{r}_{ij}$ is a unitary vector in the direction of the vector joining the nuclei $i$ and $j$. The interaction Hamiltonian is

$$
H_{ij}^D = \vec{I}_i \cdot \vec{D}_{ij} \vec{I}_j
$$

In the principal frame (PAS), the dipolar tensor has the unique axis lying along the internuclear vector and hence has cylindrical symmetry about this axis. Dipolar tensor is therefore axially symmetric and, besides, it is traceless. The dipolar tensor in PAS is

$$
\mathbf{D}_{PAS} = \begin{pmatrix}
-D_z & 0 & 0 \\
0 & -D_z & 0 \\
0 & 0 & D_z
\end{pmatrix} = \frac{1}{r^3} \begin{pmatrix}
-1/2 & 0 & 0 \\
0 & -1/2 & 0 \\
0 & 0 & 1
\end{pmatrix}
$$

In a more explicit form, after the secular truncation, the dipolar Hamiltonian is

$$
H_{ij}^D = \frac{\gamma_i \gamma_j \hbar}{r_{ij}^3} \frac{(3 \cos^2 \theta_{ij} - 1)}{2} (3 I_z I_{zj} - I_i I_j)
$$

$$
= b_{ij} d_{00}^2 (\theta_{ij}) (3 I_z I_{zj} - I_i I_j)
$$

$$
= d_{ij} T_{ij}^D
$$

where

$$
b_{ij} = \gamma^2 \hbar / r_{ij}^3
$$

is the dipolar coupling constant, expressed in frequency units, and $\theta_{ij}$ accounts for the orientation of the dipolar vector with respect to the external magnetic field. The dipolar
tensor has a vanishing zeroth rank component and so does not have any direct effect on isotropic-phase spectra (neglecting relaxation) and only the rank-two component is important for spectra in anisotropic phases. This interaction is of great importance for many purposes and the geometrical information content is evident. For the heteronuclear case, the dipolar Hamiltonian is further simplified

$$H_{D,hetero}^{ij} = 2d_{ij}T_{ij}^{0}$$

(44)

$$H_{D,hetero}^{ij} = 2d_{ij}I_z^{i}S_z^{j}$$

(45)

by removing the flip-flop term from the homonuclear Hamiltonian.

The spectral response to the dipolar interaction is determined by treating \( H_D \) as a perturbation on \( H_Z \). This gives rise to the dipolar frequency

$$\omega^*(\theta) = d_{ij}(3\cos^2\theta - 1)$$

(46)

The orientation dependence in a powder sample gives rise to the classic 'Pake Pattern'. Since the orientation dependence for dipolar broadening goes as \( P_2(\cos\theta) \) [Eq.(46)], dipolar broadening can be removed by sample rotation at the magic angle. Although dipolar coupling is altogether removed by magic angle spinning, it can be reintroduced in MAS experiments using pulse schemes such as REDOR. We have so far considered only an isolated two-spin system, but most often the dipolar interaction extends over many coupled spins in a strongly laid network. This causes homogeneous broadening in NMR spectra of solid samples. Heteronuclear dipolar broadening is easily removed by RF decoupling.

### 1.2.6 J-coupling Interaction

The J-coupling interaction, also known as spin-spin or scalar coupling, between two like or unlike nuclei, occurs through bonding electrons. Its properties and magnitude are therefore strongly dependent upon the nature of the chemical bond and on the orbitals involved in such interaction. Like any other interaction, J-coupling interaction is described as a tensor of rank two. The Hamiltonian for a J-coupling between spins \( i \) and \( j \) can be expressed in the form

$$H_{J}^{ij} = \tilde{I}_i . J . \tilde{I}_j$$

(47)
where $\overline{J}$ is the scalar coupling tensor and $I_i$ and $I_j$ are the spin operators associated with the interacting nuclei. In PAS the $J$ tensor is,

$$J_{PAS} = J_{iso} + \Delta J = \begin{pmatrix} -1/2 & 0 & 0 \\ 0 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

(48)

Similar to the chemical shift, the $J$ tensor is also described by the parameters $J_{iso}$ and $\Delta J$, given by

$$J_{iso} = \frac{J_{11} + J_{22} + J_{33}}{3}$$

(49)

$$\Delta J = \frac{3}{2}(J_{33} - J_{iso})$$

(50)

After decomposition into spherical tensors, the rank 0 interaction is

$$H_{J}^{ij,J_{iso}} = J_{iso} \tilde{I}_i \tilde{I}_j$$

(51)

$$= J_{iso} (I_{iz} I_{iz} + \frac{I_{ix} I_{ix} + I_{iy} I_{iy}}{2})$$

(52)

This contribution, even though still present in solid state spectra, is often hidden within wide lines. The rank 1 tensor is usually neglected since it is purely non-secular. Both dipolar and $J$ coupling interactions are bilinear in spin variables and have the same orientation dependence, thus making them inseparable from each other in the NMR spectra of solid samples. The $J$-anisotropy, even though present, has the same transformation properties of the through-space dipolar coupling (Sect. 2.11) and it is therefore difficult to distinguish from it. In tensor form, the $J$-coupling can be expressed as

$$H_{J,aniso}^j = J_{ij} T^j_{00} + T^j_{20}$$

(53)

In practice, for light nuclei the $J$-anisotropy is much smaller than the through space coupling. For cases in which the coupled spins have very different isotropic chemical shifts, or in the case of heteronuclear $J$-couplings, the Hamiltonian is further simplified. The second term in Eq. (52), known as flip-flop operator, can be removed according to the same ideas behind the secular truncation.
### 1.2.7 Quadrupolar Interaction

Nuclei with spin quantum number greater than ½ belong to the class of quadrupolar nuclei. Nearly two-thirds of NMR-active nuclei in the periodic table are quadrupolar, most of which belong to the half-integer family ($S = 3/2, 5/2, 7/2$ and $9/2$). The non-spherical nature of the charge distribution gives rise to electric quadrupole moment ($\mathbf{Q}$), where $\mathbf{Q}$ denotes the quadrupole moment tensor. Further, this quadrupole moment interacts with the electric field gradient (EFG), thus giving rise to the quadrupolar interaction. The strength of the quadrupolar interaction depends on the size of the nuclear quadrupole moment and the extent of departure of the field gradients from cubic symmetry. Additionally, quadrupolar nuclei also experience anisotropic chemical shielding interaction. Due to the additional coupling of the electric quadrupole moment of the nucleus to local variations in electric field, quadrupole nuclei offer a large dynamic range in magnetic resonance measurements for probing local environments. Although quadrupolar nuclei were initially sought as probes in pure quadrupole resonance (NQR), their exploitation in solid state NMR has been propelled in recent times by the development of new techniques for both spin 1 and half-integer quadrupolar nuclei.

The classical interaction energy between the nuclear charge distribution density $\rho(r)$ with an electric field potential $V(r)$ caused by external sources is

$$E = \int \rho(r)V(r)d^3r$$

The nucleus is not being viewed simply as a point charge since the potential could still vary appreciably over the nuclear volume. The electric field potential $V(r)$ depends upon the spatial orientation of all the electric charges that originate from the nuclei and electrons of the system of interest. The potential is varied as a Taylor series about the center of mass of the nucleus, that is,

$$V(r) = V(0) + \sum_{\alpha=1}^{3} \left( \frac{\partial V}{\partial x_\alpha} \right)_{r=0} + \frac{1}{2} \sum_{\alpha=1}^{3} \sum_{\beta=1}^{3} x_\alpha x_\beta \left( \frac{\partial^2 V}{\partial x_\alpha \partial x_\beta} \right)_{r=0} + \cdots$$
where the variables \( x_a \) and \( x_p \) are the Cartesian coordinates: \( x_1 = x \), \( x_2 = y \) and \( x_3 = z \). The subscript \( r = 0 \) means that the derivatives of the potential are evaluated at the origin which is defined as the center of mass of the nucleus.

A direct relation to physical properties of the classical charged body is retained if the following substitutions are made:

The total charge of the nucleus:

\[
\int_\nu \rho (r) d^3r = Ze
\]

(56)

The \( \alpha \) component of the electric dipole moment \( P \) (a vector)

\[
\int x_\alpha \rho (r) d^3r = P_\alpha
\]

(57)

And the \( \alpha \beta \) component of the electric quadrupole moment \( Q' \) (a second rank tensor)

\[
\int x_\alpha x_\beta \rho (r) d^3r = Q'_{\alpha \beta}
\]

(58)

The electrostatic energy is hence,

\[
E = ZeV(0) + \sum_{\alpha=1}^{3} P_\alpha \left( \frac{\partial V}{\partial x_\alpha} \right)_{r=0} + \frac{1}{2} \sum_{\alpha=1}^{3} \sum_{\beta=1}^{3} x_\alpha x_\beta Q'_{\alpha \beta} \left( \frac{\partial^2 V}{\partial x_\alpha \partial x_\beta} \right)_{r=0}
\]

(59)

The first term in Eq. (59) is the classical interaction of a charged nucleus with a constant potential at the origin and is independent of nuclear orientation and hence, does not affect the magnetic resonance spectrum and drops out of consideration. The second term, classical electric dipole interaction, vanishes since the center of charge and the center of mass of the nucleus are assumed to coincide. The third term is the nuclear electric quadrupole interaction. Higher-order terms are assumed to be insignificant.

In the electric quadrupole interaction, the charge distribution external to the nucleus enters into the calculation as second derivatives of the potential. The tensor constructed from these second derivatives is called the electric field gradient (EFG) tensor designated the symbol \( V_{\alpha \beta} \),

\[
V_{\alpha \beta} = \left( \frac{\partial^2 V}{\partial x_\alpha \partial x_\beta} \right)_{r=0}
\]

(60)

\( V_{\alpha \beta} \) is a symmetric second-rank tensor which is traceless and hence, has five independent components. On transforming the tensor to PAS, the EFG tensor is
The components of EFG in the PAS are used to define two parameters, namely, 

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

Here, \( \eta \) is the asymmetry parameter that lies between 0 and 1 \((0 \leq \eta \leq 1)\), with \( \eta = 0 \) denoting axial symmetry. If the gradient is spherically symmetric, or has cubic or higher symmetry, then each component of the tensor is identically zero and the quadrupole interaction vanishes completely.

### 1.2.7.1 Quadrupole Hamiltonian

The operator form of the quadrupolar Hamiltonian is

\[ H_{Q} = \frac{e^{2}qQ}{4I(2I-1)} \left[ 3I_{z}^{2} - I^{2} + \eta \left( I_{z}^{2} - I_{x}^{2} \right) \right] \]  

where \( I \) is the spin quantum number, \( eQ \) is the quadrupole moment, now a scalar, its product with the magnitude of the field gradient, \( e^{2}qQ/\hbar \), is the quadrupole coupling constant in Hertz and \( \eta \) is the asymmetry parameter already introduced. It may be noted that Eq. (64) is expressed in the PAS in which the field gradient tensor is diagonal. This is the Hamiltonian that will be used for further derivations. We can write the above Hamiltonian in the spherical tensor form as

\[ H_{Q} = \sum_{m=-2}^{2} T_{2m}^{Q} R_{2m}^{Q} \]  

where the components of \( T_{2m}^{Q} \) can now be expressed as

\[ T_{20}^{Q} = \frac{1}{\sqrt{6}} \left( 3I_{z}^{2} - I^{2} \right), \quad T_{21}^{Q} = \frac{1}{\sqrt{2}} (I_{z}I_{21} + I_{21}I_{z}), \quad T_{22}^{Q} = I_{z}^{2} \]  

The spatial tensor components \( R_{2m}^{Q} \) are evaluated as
where $\rho_{2m}^0$ are the components of the EFG in the PAS.

$$R_{2m}^0 = \sum_{m=-2}^{2} D_{m m}^{(2)}(\alpha, \beta, \gamma) \rho_{2m}^0$$  \hspace{1cm} (67)$$

The angles $(\alpha, \beta, \gamma)$ are the Euler angles that define the orientation of the PAS with respect to the laboratory frame.

In the NMR studies dealing with quadrupolar nuclei, we invariably have $H_Z \gg H_Q$ so that the quadrupolar Hamiltonian is treated as a perturbation on the Zeeman Hamiltonian. It turns out that quadrupolar interaction affects spin 1 and half-integer quadrupolar nuclei differently.

1.2.7.2 Spin 1

We consider the behavior of spin 1, such as $^{14}\text{N}$ that is of special interest in this thesis, subjected to Zeeman and quadrupolar interaction. The Hamiltonian is

$$H_{\text{tot}} = H_Z + H_Q$$  \hspace{1cm} (69)$$

Since the quadrupole couplings of $^{14}\text{N}$ are in the range of 1-4 MHz, at moderate $B_0$ fields, $H_Z \gg H_Q$ holds, allowing us to treat $H_Q$ as a perturbation on the Zeeman interaction. Treating $H_Q$ to first order, we have

$$H_Q = C_Q \sum_{m=-2}^{2} (-1)^m T_{2m} V_{2-m}$$  \hspace{1cm} (70)$$

where $C_Q = e^2 qQ/4I(2I-1)$ and the spin and spatial tensors are denoted by $T$ and $V$, respectively. For the static case, we transform only the $V_{20}$ term from the PAS to the laboratory frame as

$$PAS \xrightarrow{(\phi, \theta, \phi)} ZAS$$  \hspace{1cm} (71)$$

Taking the values of $V_{2,0}^{(PAS)}$ from Table 1, we get

$$V_{2,0} = \frac{1}{2} V_x \left\{ (3\cos^2 \theta - 1) + \eta \sin^2 \theta \cos 2\phi \right\}$$  \hspace{1cm} (73)$$
We get for the orientation dependent frequencies,

$$\Delta \omega(\phi, \theta) = \frac{3}{2} \left( \frac{e^2 q Q}{h} \right) \left( \frac{3 \cos^2 \theta - 1}{2} + \frac{\eta}{2} \sin^2 \theta \cos 2\phi \right)$$  \hspace{1cm} (74)$$

This simplifies for an axially symmetric tensor to,

$$\Delta \omega(\theta) = \frac{3}{2} \left( \frac{e^2 q Q}{h} \right) \left( \frac{3 \cos^2 \theta - 1}{2} \right)$$  \hspace{1cm} (75)$$

The orientation dependence is governed by the angular terms in Eq. (74) and leads to characteristic powder patterns to be observed in polycrystalline samples.

Under sample spinning, $H_Q$ becomes time dependent. The transformation of $V_{20}$ from the PAS to the laboratory frame (ZAS) through the spinner frame (RAS) with the Euler angles $(\theta, \phi, \psi)$ and $(\theta, \beta, \alpha t)$ yields,

$$V_{20}(t) = (3 \cos^2 \beta - 1) \left( \frac{3 \cos^2 \beta - 1}{2} \right) \left[ \frac{3}{2} C_Q + \frac{5}{8} \eta C_Q \sin^2 \theta \cos 2\psi \right]$$

$$+ c_1 \cos \omega t + s_1 \sin \omega t + c_2 \cos 2\omega t + s_2 \sin 2\omega t$$  \hspace{1cm} (76)$$

The modulation terms, which the author has derived are,

$$c_1 = \sqrt{\frac{3}{2}} C_Q \sin 2\beta \sin \theta \left\{ \cos \theta \cos \phi (\eta \cos 2\psi - 3) - \eta \sin \phi \sin 2\psi \right\}$$  \hspace{1cm} (77)$$

$$s_1 = \sqrt{\frac{3}{2}} C_Q \sin 2\beta \sin \theta \left\{ \cos \theta \cos \phi (3 - \eta \cos 2\psi) - \eta \sin \phi \sin 2\psi \right\}$$  \hspace{1cm} (78)$$

$$c_2 = \sqrt{\frac{3}{2}} C_Q \sin^2 \beta \left[ \cos 2\phi \left( \frac{3}{2} \sin^2 \theta + \frac{\eta}{2} \cos 2\psi \left( 1 + \cos^2 \theta \right) \right) - \eta \cos \theta \sin 2\phi \sin 2\psi \right]$$  \hspace{1cm} (79)$$

$$s_2 = \sqrt{\frac{3}{2}} C_Q \sin^2 \beta \left[ -\sin 2\phi \left( \frac{3}{2} \sin^2 \theta + \frac{\eta}{2} \cos 2\psi \left( 1 + \cos^2 \theta \right) \right) - \eta \cos \theta \sin 2\phi \sin 2\psi \right]$$  \hspace{1cm} (80)$$

The first term in Eq. (76) vanishes at the magic angle $\beta = \cos^{-1}(1/\sqrt{3})$. Under MAS, sidebands are generated at integer multiples of the rotation frequency. As is with the case of chemical shielding interaction, the spinning side band spectrum, or equivalently the time domain rotational spin echoes, can be analyzed to determine the quadrupole interaction parameters, $C_Q (= e^2 q Q/h)$ and $\eta$. The removal of first-order broadening by MAS in the case of $^{14}$N is shown in Figure 5.
From Eq. (76), it may be recognized that magic angle setting becomes very critical when \( C_Q \) becomes large. When the angle is very precisely set, \(^{14}\text{N} \) spectra for systems with moderate to large \( C_Q \) values (1-4 MHz) can be recorded and analyzed. Recent work has demonstrated the new opportunities offered in \(^{14}\text{N} \) MAS NMR.\(^{24}\) The removal of first-order broadening by MAS further leads to the revelation of second-order effects in spin 1 \(^{14}\text{N} \) nuclei, which can be exploited in 2D correlation experiments.\(^{25}\)

### 1.2.7.3 Half-integer (n/2) Quadrupolar Nuclei

About two-thirds of the nuclei in the periodic table belong to the half-integer spin family and serve as useful probe nuclei in many materials studies. The NMR behavior of quadrupolar nuclei belonging to the half-integer spin family is different from their spin 1 counterparts because of the ‘central transition’ (CT) (+1/2 ↔ -1/2), present only in the case of half-integer spins, which can be excited and detected in NMR experiments. The present section is mainly devoted to a discussion of the spin behavior of CT under sample spinning conditions. We now write the Hamiltonian for a half-integer quadrupolar nucleus, experiencing Zeeman and quadrupolar interaction, to second-order, as,

\[
H_{\text{tot}} = H_Z + H_Q^{(1)} + H_Q^{(2)}
\]  

(81)
$H_Z$ is the Zeeman Hamiltonian as before and $H_Q$ is treated as a perturbation to the first and second-order. Figure 6 shows the energy level diagram in the case of spin 3/2 experiencing quadrupolar interaction to first- and second-order.

\begin{align*}
\text{Figure 6: (a) Energy level diagram showing the quadrupolar perturbation to first and second order on the Zeeman interaction. CT: 'central transition', ST: 'satellite transition'. (b) Static (top) and MAS (bottom) CT spectra ($\eta_Q = 0$) [$A = (I(I+1)-3/4)\nu_0^2/\nu_b$].}
\end{align*}

The dominant Zeeman Hamiltonian contributes the zeroth-order term and the first-order correction is found by keeping the secular terms of the Hamiltonian, that is, terms that commute with $H_Z$. Using, $[I_z, T_{2m}] = mT_{2m}$, we find that terms for which $m\neq 0$ vanishes that the total Hamiltonian is simplified to first-order as

$$H = -\omega_l + cR_2T_{20}$$

(82)

For the static case, transformation of $R_{20}$ from PAS to laboratory frame (ZAS) yields for the single quantum transition frequency between states $(m+1)$ and $m$, namely

$$\omega^{(j)}_{m+1,m} = \left( m + \frac{1}{2} \right) \frac{\omega_Q}{2} \left[ (3\cos^2 \beta - 1) + \eta \sin^2 \beta \cos 2\alpha \right]$$

(83)

where $\omega_Q$, the quadrupolar frequency, is $\omega_Q = 3e^2Q/2I(2I-1)\hbar$ and the angular dependence is governed by the trigonometric parts of Eq. (83). In the case of half-integer quadrupolar nuclei, Eq. (83) shows that first-order effects dominate for the ‘satellite’ transitions (e.g., $\pm 3/2 \leftrightarrow \pm 1/2$). Eq. (83) more importantly shows that for CT, the frequency is unchanged from the Larmor frequency irrespective of the crystallite
orientation. Hence half-integer quadrupolar nuclei do not suffer any broadening due to first-order effects. This necessitates extending the quadrupolar perturbation to second-order to compute the orientation-dependent frequencies.

Thus, while first-order effects strongly influence spin 1 nuclei, only second-order effects become important in the case of half-integer quadrupolar nuclei. Here, we are mainly concerned with the central (+1/2 ↔ -1/2) spin transition, since as noted earlier, there is no quadrupolar broadening to first-order. We therefore seek to determine the quadrupole-perturbed energies to second-order, namely,

\[ E_n^{(2)} = \sum_{n' \neq n} \frac{\langle n | H_0 | n' \rangle \langle n' | H_0 | n \rangle}{E_n^{(0)} - E_{n'}^{(0)}} \]  

Using first-order coherent averaging theory, the secular second-order quadrupolar Hamiltonian can be written in the spherical tensor notation as,

\[ H_Q^{(2)} = \frac{C^2}{\alpha b} \left( R_{21} R_{21} [T_{21}, T_{21}] + \frac{1}{2} R_{22} R_{22} [T_{22}, T_{22}] \right) \]  

The reduction of the product \( R_{2,m} R_{2m} \) leads to

\[ H_Q^{(2)} = \frac{C^2}{\alpha b} \left[ \xi_0 R_{00} + \xi_2 R_{02} + \xi_4 R_{04} \right] \]  

where \( R_{i0} \) are the new irreducible spherical tensors of spatial operators, and \( \xi_i \) include all the terms in Eq. (85) resulting from the expansion of the commutators \([T_{2,m}, T_{2m}]\). Under sample rotation, with the spinning axis inclined at angle \( \chi \) with respect to \( B_0 \), the second-order quadrupolar Hamiltonian can be written after transforming from the PAS to the laboratory frame (ZAS) through the rotor frame (RAS) with the Euler angles \((\alpha, \beta, 0)\) and \((\chi, 0, 0)\), respectively, as

\[ H_Q^{(2)} = \frac{C^2}{\alpha b} \left\{ d_{00}^{(0)}(\chi) \left( \xi_0 D_{00}^{(0)}(\alpha, \beta, 0) \overline{\rho_{00}} \right) + d_{02}^{(0)}(\chi) \left( \xi_2 \sum_{m=-2}^{2} D_{m0}^{(2)}(\alpha, \beta, 0) \overline{\rho_{2m}} \right) + d_{04}^{(0)}(\chi) \left( \xi_4 \sum_{m=-4}^{4} D_{m0}^{(4)}(\alpha, \beta, 0) \overline{\rho_{4m}} \right) \right\} \]  

In Eq. (87), we have considered only the time-independent terms and neglected the time-dependent terms which lead to sidebands in CT MAS spectra. The orientation dependent CT eigen frequencies are obtained from matrix elements of second-order
Hamiltonian in the Zeeman basis according to Eq. (83). This leads to the second-order quadrupolar frequency,

$$\omega_{\text{aniso}} = \omega_{\text{iso}}^{2Q} + \omega_{\text{aniso}}^{2Q}(\alpha, \beta, P_2(\cos \chi), P_4(\cos \chi)) \quad (88)$$

An important interpretation of Eqs. (86) and (87) is that these involve a sum of rank-0, rank-2 and rank-4 terms. Clearly, the first term is rotationally invariant. It may be noted that the rank-0 term also leads to a frequency shift for the central line, the shift being proportional to $C_0^2/\omega_b$ and is referred to as the quadrupole-induced shift (QIS).

$$\omega_{\text{iso}}^{2Q} = -\frac{3}{10} \left( \frac{e^2 qQ}{4I(2I-1)h} \right)^2 \frac{4I(1+I)-3}{a_o} \left( I + \frac{\eta^2}{3} \right) \quad (89)$$

The second rank-2 term has the familiar $d_{00}^2(\chi)$ dependence and averages to zero under MAS. It is the emergence of the rank-4 $d_{00}^4(\chi)$ term that is unique in the case of half-integer quadrupolar nuclei. The angular dependence of $d_{00}^2(\chi)$ and $d_{00}^4(\chi)$ which vary as Legendre polynomials of the second and fourth degree, namely, $P_2(\cos \chi)$ and $P_4(\cos \chi)$, respectively is plotted in Figure 7.

$$P_2(\cos \chi) = (3\cos^2 - 1)/2$$
$$P_4(\cos \chi) = (35\cos^4 \chi - 30\cos^2 \chi + 3)/8$$

Figure 7: Angular dependence of $P_2(\cos \chi)$ and $P_4(\cos \chi)$ functions present the second-order quadrupolar Hamiltonian $H_{Q}^{(2)}$. The nulls of the two functions correspond to the angles indicated.
Since $P_4(\cos \chi)$ is not nulled at the magic angle, the value of the function reduces to a value of 0.3889 at the magic angle. This implies that, under MAS, a reduction in line broadening by approximately a factor of three can be achieved. $P_4(\cos \chi)$ is nulled at angles 30.56° and 70.12°, but broadening due to $P_2(\cos \chi)$ term emerges at these angles, however. Second-order quadrupolar broadening can therefore be minimized at the angles, although it can not be completely eliminated. This is demonstrated in Figure 8.

**Figure 8:** The effect of magic-angle spinning on the Central Transition (CT) lineshape under static (left) and MAS (right) for different values of asymmetry parameter ($\eta$). $[\eta = (I(I+1)-3/4)I^2/\hbar^2]$.

Removal of second-order broadening by Variable Angle Sample Spinning experiments in systems with negligible chemical shielding anisotropy and more generally by Double Rotation (DOR) and Dynamic Angle Spinning (DAS) have led to further developments in the case half-integer Quadrupolar nuclei. The emergence of Multiple Quantum Magic Angle Spinning (MQMAS) has allayed some of the technical limitations of DOR and DAS and is now extensively sought in various applications. MQMAS is introduced and discussed below.
1.3 Experimental Techniques Used

We have used the following techniques for the experimental determination of chemical shielding and EFG tensors and these have been compared with those determined from theoretical calculations. In each case, the choice of the technique was dictated by the nuclei inspected and the kind of chemical systems investigated and was also guided by the kind of NMR facilities that were available at the time of carrying out the research. The experimental techniques used by the author are presented below and discussed at some length.

1.3.1 Cross-Polarization Magic Angle Spinning (CP-MAS)

In the study of \(^{31}\text{P}\) and the rare spin \(^{29}\text{Si}\), which are of interest in this thesis, we seek to enhance the sensitivity while acquiring 1D and 2D spectra. This is best achieved by Cross Polarization (CP). CP serves to enhance the signal of rare spins (\(^{13}\text{C}, \, ^{15}\text{N}, \, ^{29}\text{Si}\)) by a polarization transfer from the abundant spins (\(^{1}\text{H}\)). The polarization transfer is accomplished by a Hartmann–Hahn matching, namely,

\[ \gamma_H B_H = \gamma_S B_S \]

\( \gamma_H \) and \( \gamma_S \) are the gyromagnetic ratios of \(^{1}\text{H}\) and \(^{31}\text{P}/^{29}\text{Si}\), respectively and \( B_H \) and \( B_S \) are their corresponding RF magnetic field strengths. In the case of \(^{29}\text{Si}\), the protons of the template molecules are used to transfer polarization to the nearby silicons. In our \(^{31}\text{P}\) studies, CP experiments provide more sensitivity since proton relaxation tends to be short compared to the prohibitively long \(^{31}\text{P}\) spin-lattice relaxation time, allowing a faster data acquisition. The optimum condition required to achieve the maximum sensitivity is determined by the proper choice of the mixing period \( \tau_{\text{CP}} \), which depends on the strength of the \(^{1}\text{H} – X \) (\( X = ^{31}\text{P}, ^{29}\text{Si} \)) dipolar coupling, amidst the leakage effects due spin-lattice relaxation in the rotating frame. Since quantitative estimates of signal enhancement were not warranted in our studies, the CP could be set up with the optimal value of \( \tau_{\text{CP}} \).
In addition to the sensitivity enhancement by CP, hetero-nuclear dipolar broadening was removed $^1$H decoupling. Since the abundant spins ($^1$H) are strongly dipolar coupled by mutual spin-spin interactions, the conditions required for efficient decoupling are rather demanding and requires strong RF-fields to be employed (> 80 kHz). Efficient decoupling schemes, such as TPPM,\cite{24} spinal-64,\cite{25} XiX,\cite{36} swept TPPM\cite{37} have been developed and so far TPPM has been widely used. In addition to the removal of heteronuclear dipolar broadening by TPPM decoupling, MAS has been employed to remove the broadening due to anisotropic chemical shielding.\cite{38} While employing MAS, due considerations must be given to the interference between the sample rotation and the RF irradiation since both serve to attenuate heteronuclear dipolar couplings. The effects are in fact well separated if one works on one of the two regimes, namely the very fast or the slow sample spinning. The removal of hetero-nuclear dipolar coupling is mainly due to sample spinning or due to RF decoupling, as the case may be. However, in the intermediate regime unwanted interference effects occur under MAS if the decoupling precession frequency $\gamma B_1$ is equal to the rotation frequency $\omega$. In consideration of this, the CP-MAS experiments in our studies were conducted with decoupling field strengths of $\gamma B_1/2\pi \approx 100$ kHz, which was well above the maximum spinning speed employed (13.5 kHz). The standard CP pulse sequence employed by the author is shown in Figure 9.
1.3.2 Two Dimensional Magic Angle Turning

One of the main objectives of the present work is the experimental determination of chemical shielding tensors. Single crystal rotation studies afford the determination of both the eigen values and the corresponding eigen vectors and hence is the most desirable. Since polycrystalline samples are invariably used, as we have done, the experimental determination of chemical shielding tensors can be made under high resolution conditions using magic angle spinning. The determination of chemical shielding tensors from slow-MAS experiments has already been discussed in Section 2.2.2. The author has employed slow-MAS experiments in cases where the center band signals and their associated side bands could be identified in the MAS/CP-MAS spectra. However, in samples which contain many isotropic resonances, such as Disodium 5'-ATP.3H2O discussed in Chapter 4, the side band interference was severe and hence slow-MAS could not be employed. Similarly, in systems which have very small chemical shielding anisotropy, such as the siliceous zeolites we have studied, slow-MAS is of no avail since large number of side bands can not be generated even at very slow speeds.

Two-dimensional isotropic-anisotropic chemical shielding correlation techniques that enable us to inspect the isotropic and anisotropic behavior along two orthogonal axes can alleviate the above problem. Such experiments essentially fall under two different classes: One, in which the anisotropy is reintroduced during spinning by tailored pulse schemes and two, in which the anisotropy is retained by coordinate space manipulation. The second class of experiments is attractive because no scaling of the chemical shielding interaction is involved. One of the first such experiments was the magic-angle hopping experiment of Maciel et al., which was later extended to the magic angle turning experiment (MAT) introduced by Gan. In the MAT experiment, the evolution time over a rotor period (or integer multiples of the rotor period), is divided into three equal periods, and at the end of each period, the crystallite orientation being sampled is essentially the same as in the hopping experiment. Thus, during $t_1$, an isotropic evolution ensues for the chemical shielding tensor. Since in the MAT experiment the sample is spinning ever so slowly (10-30 Hz), the acquisition dimension ($t_2$) retains the full anisotropy in the form of static line shapes. 2D MAT has enabled us to determine the
principal values of $^{31}\text{P}$ and $^{29}\text{Si}$ shielding tensors in samples containing multiple sites. In our studies, we have employed the PHORMAT sequence developed by Prof. Grant’s group. PHORMAT is a phase-corrected MAT sequence which overcomes some of the limitations of MAT and enables delayed acquisition to overcome probe ring down problems. Further, absorption mode 2D spectra can be obtained without any data shearing. The CP-PHORMAT sequence employed by the author in $^{31}\text{P}$ shielding tensor determinations is shown in Figure 10.

Figure 10: Pulse sequence of PHORMAT experiment. $90^\circ$ pulses are represented by narrow rectangles; two adjacent rectangles denote a $180^\circ$ pulse. The cross-polarization pulses are shaded and have fixed phases. Projection pulses $p_1$ and $p_2$ have downward-sloping crosshatching. Readout pulses have upward-sloping crosshatching and fixed phases. The time $T$ is an integral number of rotor periods (excluding a multiple of three rotor periods).

1.3.3 3Q-MAS: Three-pulse z-filter Sequence

Multiple Quantum Magic Angle Spinning (MQMAS), introduced by Frydman and Harwood, is a very efficient MAS-only technique to remove second-order quadrupolar broadening of half-integer quadrupolar nuclei. As we have seen in the previous section, the second-order quadrupolar frequency has the form

$$\omega_{\text{aniso}} = \omega_{\text{iso}}^{2Q} + A_2(I, p)\omega_{\text{aniso}}^{2Q}\left[(\alpha, \beta, P_z(cos \chi))\right] + A_4(I, p)\omega_{\text{aniso}}^{2Q}\left[\alpha, \beta, P_z(cos \chi)\right]$$

(90)
The above equation has spin variables contained in $A_2$ and $A_4$, the angular factors contained in $B_2$ and $B_4$ and also has the $P_2\cos(\chi)$ and $P_4\cos(\chi)$ terms to sample spinning. Under MAS, we consider only the last term in Eq. (90) and notice that there is a definite relationship between $A_4(I,p)$, where $p$ is the order of the coherence, and $A_4(I, p = -1)$, namely, $[A_4(I,p)/A_4(I,-1) = R]$ (e.g., $R = 9/7$ for $p=3$ and $I = 3/2$ in the case of $^{23}\text{Na}$). Thus, by a manipulation of the multiple quantum and the single quantum CT frequencies during evolution and detection periods, respectively, in a two dimensional experiment, the anisotropic frequencies are refocused and isotropic spectra devoid of second-order quadrupolar broadening can be obtained after a shearing transformation.

For the determination of EFG tensors, we have employed the robust and widely used three-pulse sequence incorporating a $z$-filter. The $z$-filter experiment is a modification of the first two-pulse sequence. The pulse sequence is shown in Figure 11. The first pulse is a non-selective hard pulse, which is first optimized for maximum MQ creation. The second pulse transfers the coherence level $\pm p$ to the level $p = 0$ so that the jump involved is equal to $|\Delta p| = 3$. The delay after this pulse helps to symmetrize the echo and anti-echo pathways after the conversion step. The last central transition selective $90^\circ$ pulse generates single quantum coherence and is readily observed. The advantage of the $z$-filter method is that the equal contribution of the echo and anti-echo pathways ($0 \rightarrow \pm p \rightarrow 0 \rightarrow -1$) is achieved regardless of the spin number and the order of the selected coherences. The MQ-MAS spectra presented in this thesis were recorded exclusively using the $z$-filter sequence incorporating a TPPM decoupling scheme as shown in Figure 11.

![Figure 11](image-url)

**Figure 11:** Three-pulse sequence incorporating $z$-filter used for $^{23}\text{Na}$ triple quantum magic angle spinning (3QMAS) experiments.
The experimentally optimized TPPM decoupling was used in the \(^1\text{H}\) channel mainly to remove hetero-nuclear dipolar broadening and improve the signal resolution of the quadrupolar nuclei in the isotropic dimension. The following phase cycling was employed: \(\phi_1 = 0; \phi_2 = 0, 60, 120, 180, 240, 300; \phi_3 = 0, 90, 180, 270; \phi_{hec} = 0, 240, 120, 0, 240, 120, 90, 330, 210, 90, 330, 210, 180, 60, 300, 180, 60, 300, 270, 150, 30, 270, 150, 30\). For the hypercomplex 2D experiment, the first pulse was shifted by 30° between successive experiments.

### 1.3.3.1 Determination of Chemical Shielding and EFG Parameters

In MQMAS experiments, the refocusing occurs along a slope \(R\) given by the relation \(R = \frac{A_d(I,p)}{A_d(I,-1)}\), where \(A_d\) is the coefficient due to second-order terms and \(I\) and \(p\) denote the spin number and the order of multiple quantum coherence, respectively. Since the echo signal moves along the slope \(R\), the 2D spectra obtained after FT operations would also yield isotropic resonances when a skew projection is taken along a line of slope \(R\). However, it is often convenient to perform a shearing operation during or after the FT operations so that the isotropic spectra are aligned parallel to the \(\omega_1\) axis to get the isotropic spectrum, while a projection parallel to \(\omega_2\) would yield the MAS spectrum. In the 3Q-MAS spectrum, obtained after a shearing transformation, the \(F_1\) and \(F_2\) axes are denoted as \(\delta_{so}\) and \(\delta\) respectively. After shearing, the MQ dimension is scaled by an effective Larmor frequency so that the chemical shift (CS) and Quadrupole Induced Shift (QIS) can be subsequently defined. Denoting \(\delta_{QIS}\) and \(\delta_{QIS}^{so}\) as the Quadrupolar Induced Shifts on the \(\delta\) and \(\delta_{so}\) axes respectively, we have

\[
\delta_{QIS}^{so}(I,C_0,\eta) = -\frac{10}{17} \delta_{QIS}(I,C_0,\eta)
\]

Therefore, the QIS axis can be drawn with a slope of -10/17 that correlates the Quadrupolar Induced Shift in both the dimensions. The scaling of the data by an effective Larmor frequency leads to a slope of -10/17 for the QIS axis and this is independent of the spin number \(I\) as well as the coherence order \(p\). This allows us to use a single definition of the QIS axis for different MQMAS experiments.\(^{45}\) Thus, a quantification of...
Figure 12: Graphical representation of MQ-MAS spectrum showing the CS axis at a slope of unity and the QIS axis at a slope of \(-10/17\).

Various isotropic resonances resolved by the MQ-MAS method can be carried out by a graphical analysis\(^\text{46}\) of the 2D contour plot. When the 2D spectrum is plotted with "normalized" $\delta$ and $\delta_{30}$ ppm scales,\(^\text{46}\) the chemical shift (CS) axis ($\delta_{CS}$) lies along a slope of unity, whereas the quadrupole induced shift (QIS) direction has a slope of $-10/17$. This is illustrated in Figure 12. For each species, resolved by MQ-MAS, the projection of the center of gravity of the corresponding contours onto the CS and QIS axes yields the values for the isotropic chemical shift ($\delta_{CS}$) and quadrupole induced shift ($\delta_{QIS}$). From the latter, the second-order quadrupole parameter is calculated, as $P_2 = C_Q (1 + \eta^2/3)^{1/2}$, which for $^{23}$Na is $(\nu_0/300)(15\delta_{QIS})^{1/2}$, where $\nu_0$ is the Larmor frequency. It must be noted that MQ-MAS graphical analysis does not lead to the determination of both $C_Q$ and $\eta_0$. One must therefore additionally employ simulation of 1D MAS spectra for their determination. Quantification of MQ-MAS data can also be carried out by iterative simulation and fitting of 2D MQ-MAS spectra using the program DMFIT developed by Massiot.\(^\text{47}\)
1.4 Quantum Chemical Calculations of NMR Interaction Tensors

We have discussed the four main NMR tensorial interactions and how they affect the NMR spectra of solid samples. We have also outlined experimental strategies for the determination of chemical shielding and quadrupolar interaction tensors which are of special interest in this thesis. Akin to the experimental determinations of the above interaction tensors, their theoretical determination by advanced quantum chemical methods has also been of special interest since they offer new opportunities in signal assignments and in the development of new structure refinement tools. Importantly, challenges are offered in the theoretical determination of the NMR interaction tensors since the ultimate aim is to bring the experimental and calculated results to an undisputable agreement. Several informative articles dealing with the calculation of nuclear magnetic shielding and other NMR properties have been published recently.

Advances in quantum chemical theory coupled with better algorithms to solve many-parameter equations have offered new opportunities for the theoretical determination of many state properties, such as, energy, molecular electrostatic potential, dipole moment, electron density, etc, including NMR interaction tensors. Traditional quantum chemical approaches which were extensively used in NMR calculations were semi-empirical methods. By and large such calculations were invariably restricted to crude estimates and small molecules. However, with the advent of new methods, such as GIAO and LAPW and the use of Density Functional Theory with new functionals, new access has been gained to larger molecular systems which have till now eluded theoretical inspection for the end NMR properties. We have chosen to employ, in our work, two different approaches, the choice of which was guided by the efficiency of the calculation and the accuracy of the result for the particular interaction investigated (chemical shielding or EFG). The two approaches that we have used for the calculation of chemical shielding and electric field gradient tensors are the atomic orbital method and the augmented plane wave method, respectively.
The atomic orbital approach essentially involves modeling an infinite periodic solid with a finite sized cluster in such a way that the nucleus of interest is at the center and its interactions within the first few coordination spheres are preserved. This is an excellent model for the chemical shielding since the local electronic environment largely determines the shielding tensor. The cluster based atomic orbital approach is however restrictive in the case of EFG determinations since EFG is a long range interaction, requiring very large clusters to be employed for each site of interest. Even though periodic boundary conditions are brought in to relax the above requirement by exploiting translational symmetry, one is unable to handle molecular systems of moderate size (more than 15 atoms). A periodic approach based on plane waves provides a simple and attractive mathematical alternative by computations in inverse space, although the same iterative methods are used to solve the many body Schrodinger equation.

In the following, we provide a background of the general *ab initio* theory, followed by the treatment of the theory of nuclear shielding and electric field gradients. We also lay out the framework of the atomic orbital and plane wave approaches that we have employed for the chemical shielding and EFG determinations, respectively.

### 1.4.1 Overview of *ab initio* Theory

In the calculation of molecular properties, the main computational effort is to solve the many body problem, for which one needs a quantum mechanical solution to the following Hamiltonian:

\[
H_{\text{tot}} = \frac{\hbar^2}{2} \sum_i \frac{\nabla^2_{R_i}}{M_i} - \frac{\hbar^2}{2} \sum_i \frac{\nabla^2_{r_i}}{m_e} - \frac{1}{4\pi\varepsilon_0} \sum_{i,j} \frac{e^2 Z_i}{|\vec{R}_i - \vec{r}_j|} + \frac{1}{8\pi\varepsilon_0} \sum_{i<j} \frac{e^2 Z_i Z_j}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{8\pi\varepsilon_0} \sum_{i<j} \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{R}_j|}
\]

(92)

In Eq. (92), N positively charged nuclei and negatively charged electrons interact electromagnetically. The mass of the nucleus at $\vec{R}_i$ is $M_i$, the electrons have mass $m_e$ and are at $\vec{r}_i$. The first term is the kinetic energy operator for the nuclei; the second is the kinetic energy term for the electrons. The last three terms describe the Coulomb
interaction between electrons and nuclei, between electrons and other electrons, and
between nuclei and other nuclei. It is not possible to solve this problem exactly because
of the variables involved and the level of complexity. Hence to get acceptable
approximate solutions, the first assumption made is the Born-Oppenheimer
approximation,\(^5\) which states that the nuclei being much heavier and slower than the
electrons and are regarded as fixed. They then become an "external" potential to the
electron cloud, a collection of NZ interacting negative particles. The first term vanishes
and the last term reduces to a constant. The Hamiltonian reduces to

\[ H = T + V + V_{\text{ext}} \] (93)

This quantum many-body problem is simpler than the one we first started with but still
too difficult to solve. We then use the Hartree Fock or Density Functional Theory (DFT)
approach approximations. A brief outline of the Hartree-Fock and DFT methods is given
below.

1.4.1.1 The Hartree-Fock Method

The HF method\(^5\) assumes each electron to move independently in the mean field
generated by the other electrons. Effects arising from deviations from the mean field
approximation, are completely neglected (electron exchange, however, is fully accounted
for). Each energy eigenfunction is assumed to be describable by a single Slater
determinant,\(^5\) an anti-symmetrized product of one-electron wavefunctions. Relativistic
effects are completely neglected and the final variational solution is assumed to be a
linear combination of a finite number of basis functions. The finite basis set is assumed to
be approximately complete. Another approximation is brought about by the use of the
variational theorem.

The variational theorem states that for a time-independent Hamiltonian operator,
any trial wavefunction will have an energy expectation value that is greater than or equal
to the true ground state wavefunction corresponding to the given Hamiltonian which
implies that the Hartree-Fock energy is an upper bound to the true ground state energy of
a given molecule. In the Hartree-Fock method, first, we optimize the set of approximate
one-electron wavefunctions variationally for an atomic calculation. For a molecular or
crystalline calculation, as used in this thesis, the initial approximate one-electron wavefunctions are usually a linear combination of atomic orbitals (LCAO) (usually, the atomic orbitals are themselves linear combinations of Gaussian functions.) The orbitals are then optimized by requiring them to be the eigenfunctions of a new one-electron operator, the Fock operator. The Fock operator is an effective one-electron Hamiltonian operator being the sum of kinetic energy operators for each electron, the internuclear repulsion energy, and nuclear-electronic coulombic attraction terms and, Coulombic repulsion terms between electrons in a mean field theory; a net repulsion energy for each electron in the system, which is calculated by treating all of the other electrons within the molecule as a smooth distribution of negative charge.

As the electron-electron repulsion term of the electronic molecular Hamiltonian involves the coordinates of two different electrons, it is necessary to reformulate it in an approximate way. Under this approximation, all of the terms of the exact Hamiltonian except the nuclear-nuclear repulsion term are re-expressed as the sum of one-electron operators.

\[ \hat{F} = \hat{H}^{\text{core}} + \sum_{j \neq i} \{2\hat{J}_j - \hat{K}_j\} \]  

(94)

Where \( \hat{F} \) is the one-electron Fock operator

\[ \hat{H}^{\text{core}} = -\frac{1}{2} \nabla_i^2 - \sum_{a} \frac{Z_a}{r_{ia}} \]  

(95)

is the one-electron core Hamiltonian, \( \hat{J}_j \) is the Coulomb operator, defining the electron-electron repulsion energy due to the \( j \)-th electron, \( \hat{K}_j \) is the exchange operator, defining the electron exchange energy. Finding the Hartree-Fock one-electron wavefunction is then equivalent to solving the eigenfunction equation,

\[ \hat{F}\phi_i = \epsilon_i \phi_i \]  

(96)

where \( \phi_i \) are a set of one-electron wavefunctions, called the Hartree-Fock Molecular Orbitals. In fact, we seek a solution to these one-electron wavefunctions as a prelude to calculating various molecular properties. We will discuss this after introducing the DFT approach.
1.4.1.2 Density Functional Theory

In DFT, the energy is considered to be a functional of the total charge density, thereby reducing significantly the dimensionality of the problem. As it incorporates more electron correlation than HF and is equally efficient for solids, the DFT approach is considered to be better for systems containing lighter atoms. Established by the theorems of Hohenberg and Kohn, it states that there is a one-to-one correspondence between the ground state density of a many electron system and the external potential. The consequence of this is that any state variable is a unique functional of the exact ground-state electron density.

\[ \langle \psi | \hat{O} | \psi \rangle = O[\rho] \quad (97) \]

And when \( \hat{O} \) is the Hamiltonian, the ground state total energy functional

\[ H[\rho] = E_{\text{ex}}[\rho] \quad (98) \]

is of the form

\[ E_{\text{ex}}[\rho] = \langle \psi | T + V | \psi \rangle + \langle \psi | V_{\text{ex}} | \psi \rangle \quad (99) \]

\[ = F_{\text{H-K}}[\rho] + \int \rho(r) V_{\text{ex}}(r) d^3r \quad (100) \]

where the Hohenberg-Kohn density functional \( F_{\text{H-K}}[\rho] \) is universal for any many-electron system. \( E_{\text{ex}}[\rho] \) reaches its minimal value (equal to the ground state total energy) for the ground-state density corresponding to \( V_{\text{ex}} \). This, in effect, means that the electron density contains as much information as the wavefunction can provide us. Hence all observable quantities can be written as functionals of the density.

The Kohn-Sham equations made Density Functional Theory based calculations quite feasible and brought them to the realm of the computational chemist by suggesting a practical method to determine the ground state density. The correlation energy \( V_c \) is the part of total energy found in the exact solution but absent in the Hartree-Fock solution. The total energy functionals \( E_c[\rho] \) and \( E_{\text{HF}}[\rho] \) found in the exact solution and in the Hartree-Fock solution, respectively are
\[ E_x = T + (V_H + V_s) \quad \text{and} \quad E_{\text{HF}}[\rho] = T_0 + (V_H + V_s) \] (101)

with the value in brackets representing \( V \). \( T \) and \( V \) are the exact kinetic and electron-electron potential energy functionals, \( T_0 \) is the functional for the kinetic energy of a non-interacting electron gas, \( V_H \) stands for the Hartree contribution and \( V_s \) for the exchange contribution. The functional for the correlation contribution appears to be:

\[ V_c = T - T_0 \] (102)

with the Hartree functional given by, \( E_H = T_0 + V_H \) (103)

the exchange contribution can be given by, \( V_x = V - V_H \) (104)

Hence we can rewrite the Hohenberg-Kohn functional as

\[ F_{\text{HK}} = T_0 + V_H + (V_x + V_c) \] (105)

This functional \( F_{\text{HK}} \) can be called the energy functional of a non-interacting classical electron gas, subject to the external potentials of, one, the nuclei and, two, exchange and correlation effects. The corresponding Hamiltonian – called the Kohn-Sham Hamiltonian – is

\[ H_{\text{KS}} = T_0 + V_H + V_{\text{xc}} + V_{\text{ext}} \]

\[ = -\frac{\hbar^2}{2m_e} \nabla^2 + \frac{e^2}{4\pi \epsilon_0} \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + V_{\text{xc}} + V_{\text{ext}} \] (106)

where the exchange-correlation potential is given by the functional derivative \( V_{\text{xc}} = \frac{\partial V_{\text{xc}}[\rho]}{\partial \rho} \). Now the Kohn-Sham theorem may be written as:

\[ H_{\text{KS}} \phi_i = \epsilon_i \phi_i \] (107)

\( \phi_i \) does not have physical meaning and the single particle energies \( \epsilon_i \) are not single-electron energies but we get a familiar Schrödinger-like equation of non-interacting single-particles which are solvable by the self-consistent field iterative procedure.

### 1.4.1.3 Self-consistent Field Method

Both the Hartree operator \( V_H \) and the exchange-correlation operator \( V_{\text{xc}} \) [Eq. (106)] depend on the density \( \rho \), which in turn depends on the \( \phi \) which are being
searched. This is a self-consistency problem where the solutions \((\phi)\) determine the
original equation \((V_k\) and \(V_{xc}\) in \(H_k\)), and the equation cannot be written down and solved
before its solution is known. Hence, an iterative procedure is used to escape from this
paradox by guessing some starting density and solving the equation repeatedly using the
solutions as the new guesses till a convergence in values is reached. This is the consistent
solution for the Hamiltonian \(H_k\), which is elaborated below.

The solution of the Fock operator for Hartree-Fock method is also arrived at by
this iterative procedure

We have to formulate a set of infinite equations of the type 52

\[
\left( -\frac{\hbar^2}{2m_r} \nabla^2_m + \frac{e^2}{4\pi\varepsilon_0} \int \frac{\rho(\vec{r})}{|\vec{r} - \vec{r}'|} d\vec{r}' + V_a + V_{xc} \right) \phi_m(\vec{r}) = \varepsilon_m \phi_m(\vec{r})
\]

(108)

\[
\widehat{H}_\text{sp} \phi_m(\vec{r}) = \varepsilon_m \phi_m(\vec{r})
\]

(109)

where \(\widehat{H}_\text{sp}\) is the single particle Hamiltonian. For HF, \(V_a\) [Eq. (104)] is the exchange
operator. The \(\phi_m\) are true one-electron (or single particle) orbitals for HF. Exchange is
treated exactly, but correlation effects are not included at all. For DFT, \(V_a\) is the
exchange-correlation operator. Exchange and correlation are both treated, but both
approximately. The \(\phi_m\) are mathematical single-particle orbitals.

The similarity between the Hartree-Fock and Kohn-Sham equations means that
the same mathematical techniques can be used to solve them. “Solving” in most methods
means that we want to find the coefficients \(c_p^m\) needed to express \(\phi_m\) in a given basis set
\(\phi_p^m\).

\[
\phi_m = \sum_{p=1}^{P} c_p^m \phi_p^m
\]

(110)

The wave functions \(\phi_m\) belong to a function space which has an infinite dimension, \(P\) is
therefore in principle infinite. In practice one works with a limited set of basis functions.
Having chosen a basis (and hence a finite value for \( P \)), we can tackle the equations (111) as an eigenvalue problem. For a given \( m \), we get

\[
\begin{pmatrix}
\vdots & \vdots & \vdots \\
\langle \phi_i^m | \hat{H}_0 | \phi_j^m \rangle - \epsilon \langle \phi_i^m | \phi_j^m \rangle & \vdots \\
\vdots & \vdots & \vdots \\
\langle \phi_i^m | \phi_j^m \rangle & \vdots & \vdots \\
\end{pmatrix}
\begin{pmatrix}
c_1^m \\
\vdots \\
c_P^m \\
\end{pmatrix}
= \begin{pmatrix}
0 \\
\vdots \\
0 \\
\end{pmatrix}
\tag{111}
\]

We recognize here the matrix elements of the single-particle Hamiltonian in the basis states and the overlap matrix \( S_{ij} \). Diagonalization of the Hamiltonian matrix will lead to \( P \) eigenvalues and \( P \) sets of coefficients that express each of the \( P \) eigenfunctions in the given basis. \( P \) is large for a heavy basis. Hence, we need to generalize the solution describing the eigenfunctions and limit \( P \). This leads to approximate eigenfunctions that may be unacceptable and force the solution to the problem in a built-in direction and such basis sets are hence called biased. The art of this solution lies in finding a basis set that is simultaneously efficient and unbiased. We have used two kinds of basis sets – atomic orbitals and plane waves – in this thesis and this is discussed below.

### 1.4.2 Basis Sets

A Basis set is a group of numerical constants used in wavefunctions. It is a complete set of basis functions that is used to represent the molecular orbitals. A general expression for a basis function is given as:

\[
Ne^{-\zeta r}
\tag{112}
\]

where \( N \) is the normalization constant, \( \zeta \) controls width of the orbital and \( r \) is the radius in Angstrom. This is an example of a Slater Type Orbital (STO). Although the STO equation is a very good approximation for the molecular orbitals, it requires enormous time and computational power for calculating the integrals using them. Hence, we approximate the basis set by simpler functions.

#### 1.4.2.1 Gaussian-type Orbitals

Basis sets that are specific to an atom are called Atomic Orbital type basis sets. Here the STO equation is approximated by a combination of Gaussian Type Orbitals\(^{63,64}\). The following is the Gaussian Type Orbital (GTO) equation,
The main difference in the ‘r’, STO uses ‘r’ and GTO uses ‘r’. GTOs are easier and faster to calculate, but they are not as accurate as STOs. To circumvent this problem a combination of many Gaussians are used. Most of the present day cluster calculations are done using Gaussian Type Orbitals (GTOs). Three important terms have to be mentioned here to describe the basis sets used commonly in current quantum chemical calculations.

- **Split-valence basis set** –
  Since inner-electron shells are not as vital as the valence-electron shells for calculations, they are described by a single basis function, whereas a larger basis is used for valence atomic orbitals. This method is called split-valence basis set.

- **Polarization functions** –
  Although treating each orbital as a sole entity like ‘s’, ‘p’, ‘d’, ‘f’, etc. is a good representation for an isolated atom, the picture changes when atoms come together, that is, when there is bonding. When atoms come close the charge distribution causes polarization effect which distorts the shape of the atomic orbitals. For example, ‘s’ orbital can have a tinge of ‘p’ and ‘p’ can have a tinge of ‘d’ and so on. Hence this polarization should be taken into account by a good basis set.

- **Diffuse functions** –
  When an electron is held far away from the nucleus like for an anion or in an excited state or for loosely bonded electrons, it needs to be described more accurately by the basis set.

An example of a split valence Pople’s basis set is represented as –

- 6-31G\(^{65,66}\) - This means the core or the inner-shell GTO is represented by 6 Gaussians and the valence is described by two GTOs, one made of 3 Gaussians and the other with 1 Gaussian.
- 6-31G\(^*\) or 6-31G(d,p)\(^{67}\) - This is same as a 6-31G basis set with the addition of polarization functions. The first ‘*’ means that a ‘d’ polarization function is added for
non-hydrogen atoms and the second ‘*’ means that a ‘p’ polarization function is added for hydrogen atoms.

- 6-31++G** or 6-31++G(d,p) – This is same as 6-31G** with the addition of diffuse functions. First ‘+’ represents an addition of diffuse function for non-hydrogen atoms and the second ‘+’ for hydrogen atoms.

### 1.4.2.2 Plane Waves and Methods

In addition to being unbiased and efficient, for computational efficiency, we would like the basis set to be mathematically simple functions. A plane wave is of the form $e^{i\mathbf{r} \cdot \mathbf{k}}$. Any eigenfunction $\psi^n_k$ of a periodic Hamiltonian can be expressed exactly in this basis set by means of an infinite set of coefficients $c^n_\mathbf{k}$.

$$\psi^n_k(\mathbf{r}) = \sum_\mathbf{k} c^n_\mathbf{k} \exp\{i(\mathbf{k} + \mathbf{K}) \cdot \mathbf{r}\}$$  \hspace{1cm} (114)

One basis function for $\psi^n_k(\mathbf{r})$ is therefore

$$\phi^n_k(\mathbf{r}) = |\mathbf{K}\rangle = \exp\{i(\mathbf{k} + \mathbf{K}) \cdot \mathbf{r}\}$$  \hspace{1cm} (115)

all eigenstates $\psi^n_k$ that have the same $\mathbf{k}$ but a different $n$ will be expressed in the basis set with this particular value of $\mathbf{k}$. In practice, we limit the size of the basis set and for plane waves, this is done by limiting the set to all $\mathbf{K}$ with $K \leq K_{\text{max}}$. This corresponds to a sphere with radius $K_{\text{max}}$ centered at the origin of reciprocal space. All reciprocal lattice vectors that are inside this sphere are taken into the basis set. Instead of $K_{\text{max}}$, we can also take the free electron energy corresponding to $K_{\text{max}}$, called the cut-off energy $E_{\text{cut}} = \frac{\hbar^2 K_{\text{max}}^2}{2m_r}$.

Plane waves are orthogonal hence the overlap matrix $S$ is a unit matrix. The matrix elements of the effective single-particle Hamiltonian (Kohn-Sham Hamiltonian) are calculated in the plane wave basis, and the resulting matrix diagonalized. To each eigenvalue $\varepsilon^n_\mathbf{k}$ and eigenvector $[c^n_\mathbf{k}]$ of $P$ values for $c^n_\mathbf{k}$ corresponds. Hence we have found $P$ eigenvalues, each with their own set of coefficients with same $\mathbf{k}$ but
different band index $n$. This process is repeated for as many $\bar{k}$-points as needed to densely sample the first Brillouin zone.

- **Pseudopotential Method**

  The number of plane waves is determined by the smallest length scales that are to be described in real space. In order to describe, for example, the steep behavior of a 3s wave function in Ca near the nucleus we would need about $10^8$ plane waves. This would require diagonalization of (many) $(10^8 \times 10^8)$ matrices which is beyond the capability of even supercomputers.

  However, we notice that the most oscillating part of the wave functions are the tails that reach out into the region close to the nucleus. This region of the solid is quite well shielded from the more outer regions of the atoms where chemistry happens, and the electrons will not behave very differently from free atom electrons there. One can therefore replace the potential in these inner regions by an augmented region which describes this region with a mathematically different function.

  In the pseudopotential method, the region near the nucleus is described by a pseudopotential that is designed to yield very smooth tails of wavefunctions inside the atom (and hence need only a few plane waves to describe them). In the outer regions of the atoms, the pseudopotential continuously evolves into the true potential, such that this region of the crystal is unaffected by the substitution. In this way, it is possible to use an (ultrasoft) plane wave basis set for realistic cases with low cut-off energies. The pseudopotential method is implemented in the program PARATEC (PARAllel Total Energy Code) developed at the University of California at Berkeley.

- **Augmented Plane Wave Method**

  The augmented plane wave basis set came about due a need to improve on the pseudopotential method to describe more general situations like hyperfine fields or core-level excitations and also for more efficient functions. It is necessary to understand the APW method before going on to its successors, Linearized Augmented Plane Wave and
Augmented Plane Wave plus Local Orbitals methods\textsuperscript{53} implemented in contemporary quantum-chemical packages like WIEN which we have used.

Similar to the pseudopotential method, the augmented plane wave method is based on the idea that close to the nuclei, the electrons behave quite as they are in a free atom, and they can be described more efficiently by atomic like functions. Space is therefore divided now into two regions: around each atom a sphere with a radius $R_\alpha$ (called $S_\alpha$). Such a sphere is called a muffin tin sphere, and the part of space occupied by the spheres is called the muffin tin region. The remaining space outside the spheres is called the interstitial region (I). This is shown in Figure 13.

One augmented plane wave (APW) used in the expansion of $\psi^\alpha_k$ and is defined as

$$\phi^\alpha_k(\mathbf{r},E) = \frac{1}{\sqrt{V}} \exp\{i(\mathbf{k} + \mathbf{K})\mathbf{r}\} \quad \text{for } \mathbf{r} \in I \tag{116}$$

and

$$\phi^\alpha_k(\mathbf{r},E) = \sum_{\ell,m} A^{\alpha,\ell+K}_{\ell m} u^\ell_\ell(r') Y^\ell_{\ell m}(\hat{\mathbf{r}}') \quad \text{for } \mathbf{r} \in S_\alpha \tag{117}$$

where $V$ is the volume of the unit cell. This basis set is also $\mathbf{k}$-dependent as the plane wave basis was. The position inside the spheres is given with respect to the center of each sphere by $r' = \mathbf{r} - \mathbf{r}_\alpha$. $Y^\ell_{\ell m}$ are spherical harmonics. The $A^{\alpha,\ell+K}_{\ell m}$ are yet to be determined.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure13.png}
\caption{(a) The shaded spheres represent the augmented region while in the interstities, the energy contours of plane waves are shown. (b) Corresponding to the lower edge of (a), the behaviour of the molecular wavefunction, clearly showing it to be continuous at the boundary of the augmented region. Red: Mapping of interstities with plane wave, Blue: mapping of nuclear region with spherical wave function.}
\end{figure}
and $u_{l}^{E}$ are solutions to the radial part of the Schrödinger equation for a free atom at the energy $E$.

We do have to insure that the eigenfunction is continuous so that its kinetic energy is well-defined. This requires that the plane wave outside the sphere matches the function inside the sphere over the complete surface of the sphere (in value, not in slope). Hence, expanding the plane wave in spherical harmonics,

$$\frac{1}{\sqrt{V}} \exp \left\{ i(\vec{k} + \vec{K}) \cdot \vec{r} \right\} = \frac{4\pi}{\sqrt{V}} \exp \left\{ i(\vec{k} + \vec{K}) \cdot \vec{r} \right\} \sum_{l,m} i^{l} j_{l} \left( \left| \vec{k} + \vec{K} \right| \right) Y_{lm}^{*} \left( \vec{k} + \vec{K} \right) Y_{lm} \left( \vec{r} \right)$$

(118)

$j(x)$ is the Bessel function of order $l$. Requiring this at the sphere boundary (where $r = R_{a}$, which defines $\overrightarrow{R}_{a}$) to be equal to the Im-part in $\phi_{l}^{*} \left( \vec{r}, E \right)$ defines

$$A_{l_{m}}^{a, \vec{i} + \vec{K}} = \frac{4\pi i^{l} \exp \left\{ i(\vec{k} + \vec{K}) \cdot \vec{R}_{a} \right\}}{\sqrt{V} u_{l}^{a} \left( \vec{R}_{a}, E \right)} j_{l} \left( \left| \vec{k} + \vec{K} \right| R_{a} \right) Y_{lm}^{*} \left( \vec{k} + \vec{K} \right)$$

(119)

This uniquely defines $A_{l_{m}}^{a, \vec{i} + \vec{K}}$ and we now only have to determine $E$. In principle, there are infinite terms in Eq. (114), which would mean an infinite number of $A_{l_{m}}^{a, \vec{i} + \vec{K}}$. In practice, we truncate at some value of $l_{\text{max}}$. The cut-off for the plane waves ($K_{\text{max}}$) and for the angular functions ($l_{\text{max}}$) is of comparable quality if the number of nodes per unit length is identical. This gives the condition $R_{a} K_{\text{max}} = l_{\text{max}}$.

Now we proceed in a similar manner to the plane wave to find the coefficients of $c_{l_{m}}^{a, \vec{i} \cdot \vec{K}}$ in the expansion of the searched eigenfunction except that we do not know $E$ hence we make an initial guess and find $E$ in an iterative procedure similar to that of the Fock operator. This process is repeated for $n=1,2,3,\ldots$ etc.

With a plane wave basis, $P$ eigenvalues are found simultaneously, but with APW one diagonalization is needed for each eigenvalue. This makes the APW method much slower than the pseudopotential method and gives way to the Linearized APW and LAPW + LO methods.
Linear Augmented Plane Wave Method

The problem with the APW method that the \( u_i^a(r', E) \) have to be constructed from the unknown eigenenergy \( E = \varepsilon_i^a \) of the searched eigenstates. This is overcome when we recover \( u_i^a(r', \varepsilon_i^a) \) from known quantities in the Linearized Augmented Plane Wave method. When we know \( u_i^a \) at some energy \( E_0 \), we can make a Taylor expansion to find the energies nearby

\[
u_i^a(r', \varepsilon_i^a) = u_i^a(r', E_0) + \frac{\partial u_i^a(r', E)}{\partial E} \left[ E_0 - \varepsilon_i^a \right] + \mathcal{O}\left( E_0 - \varepsilon_i^a \right)^2 \tag{120}\]

Substituting the first two terms of the expansion in the APW for a fixed \( E_0 \) gives the definition of an LAPW. However, since the energy difference \( \left( E_0 - \varepsilon_i^a \right) \) is unknown, we introduce an unknown \( B_{\alpha m}^{\vec{k} + \vec{K}} \)

\[
\phi_k^i(r, E) = \frac{1}{\sqrt{V}} \exp\left\{ i(\vec{k} + \vec{K}) \cdot \vec{r} \right\} \quad \text{for} \quad \vec{r} \in I \tag{121}
\]

And

\[
\phi_k^i(r, E) = \sum_{l,m} \left\{ A_{\alpha m}^{\vec{k} + \vec{K}} u_l^a(r', E_0) + B_{\alpha m}^{\vec{k} + \vec{K}} \tilde{u}_l^a(r', E_0) \right\} Y_m^i\left( r \right) \quad \text{for} \quad \vec{r} \in S_{\alpha} \tag{122}
\]

More ever, often we would like to describe an eigenstate \( \psi_r^a \) that has a predominantly \(^s\), \(^p\), \(^d\) or \(^f\) character. Here the \( A_{\alpha m}^{\vec{k} + \vec{K}} u_l^a \) are large. Therefore it is advantageous to choose \( E_0 \) near the centre of the dominant band. In this way, the \( \mathcal{O}\left( E_0 - \varepsilon_i^a \right)^2 \) remain small, and cutting after the linear term is allowed. Hence we do not choose a universal \( E_0 \) but a set of well-chosen \( E_{ij}^a \) up to \( l = 3 \) and the final definition of LAPW is

\[
\phi_k^i(r, E) = \frac{1}{\sqrt{V}} \exp\left\{ i(\vec{k} + \vec{K}) \cdot \vec{r} \right\} \quad \text{for} \quad \vec{r} \in I \tag{123}
\]

And

\[
\phi_k^i(r, E) = \sum_{l,m} \left\{ A_{\alpha m}^{\vec{k} + \vec{K}} u_l^a(r', E_{ij}^a) + B_{\alpha m}^{\vec{k} + \vec{K}} \tilde{u}_l^a(r', E_{ij}^a) \right\} Y_m^i\left( r \right) \quad \text{for} \quad \vec{r} \in S_{\alpha} \tag{124}
\]
1.4.3 Determination of Chemical Shielding Tensors

The shielding tensor is composed of nine independent components though symmetry usually reduces this number. As formulated by Ramsey,\textsuperscript{72-74} the nuclear magnetic shielding can be divided into two contributions

\[ \sigma_{\alpha\beta} = \sigma_{\alpha\beta}^{d} + \sigma_{\alpha\beta}^{p} \]  

The first term \( \sigma_{\alpha\beta}^{d} \), the diamagnetic contribution is derived solely from the electronic ground state of the molecule

\[ \sigma_{ss} = \left( \frac{e^{2}}{2m_{e}c^{2}} \right) \left\langle 0 \right| \sum_{i} \frac{y_{i}^{2} + z_{i}^{2}}{r_{i}^{3}} \left| 0 \right\rangle \]  

\( y, z \) and \( r \) refer to the electron position operators with the nucleus at the origin. The second term is referred to as the paramagnetic term and can be written as

\[ \sigma_{ss}^{p} = -\left( \frac{e^{2}}{2m_{e}c^{2}} \right) \sum_{q>0} \frac{\left\langle 0 \right| \sum_{i} \frac{L_{z}}{r_{i}^{3}} \left| q \right\rangle \left\langle q \right| \sum_{i} L_{z} \left| 0 \right\rangle}{E_{q} - E_{0}} \]  

Hamiltonian as a discrepancy between the applied magnetic field and the actual field at the site of the nucleus.

\[ H = \vec{\mu}_{n} \cdot \left( 1 - \frac{\vec{B}}{B_{0}} \right) B_{0} \]  

The origin of the shielding property is electronic and thus requires a knowledge of the electronic solutions to the molecular Hamiltonian. The energy of interaction between the nuclear moment and the shielding field is a very small quantity compared with the electron orbital energies and, therefore, can be safely regarded as a perturbation.

In the presence of a magnetic field, the momentum of an electron transforms into

\[ p = (-i\hbar)(\nabla) - \left( \frac{e}{c} \right) A \]  

Where \( \nabla \) is the gradient operator, and \( A \) is the magnetic vector potential which is related to the magnetic field \( B \) by

\[ B = \nabla \times A \]
For diamagnetic molecules where all electrons are paired, the magnetic interactions owing to the presence of an applied magnetic field are added into the Hamiltonian

\[ H - V = \left( \frac{1}{2m_e} \right) \left[ -i\hbar \nabla - \frac{e}{c} A \right]^2 \]  

Eq. (131) can be expressed in terms of these two vector potentials. For simplicity, we introduce a new quantity:

\[ \Pi = -i\hbar \nabla - \frac{e}{c} A_b \]  

Hence,

\[ H - V = \left( \frac{\Pi^2}{2m_e} \right) - \left( \frac{e}{2m_e c} \right) (\Pi \cdot A_b + A_b \cdot \Pi) + \left( \frac{e^2}{2m_e c^2} \right) A_b^2 \]  

All operators are one-electron operators. For systems involving more than one electron, a sum over all the electrons is required to arrive at the complete expression. The first term on the right hand side of Eq. (134), \( \frac{\Pi^2}{2m_e} \), contains the kinetic energy of the electron

\[ KE = \left[ \left( -\frac{i\hbar}{2m_e} \right) \nabla \right]^2 \]  

The diamagnetic energy

\[ DE = \left( \frac{e^2}{2m_e c^2} \right) A_b^2 \]  

And the Orbital Zeeman energy of the electrons

\[ OZE = (i\hbar) \left( \frac{e}{2m_e c} \right) (\nabla \cdot A_b + A_b \cdot \nabla) \]  

These terms do not have any reference to the nuclear moment \( \mu_n \). Using first order perturbation treatment and collecting terms that match the expressions in Eq. (128) shows that these terms are not relevant for the derivation of the shielding term. Eq. (137),
however, has terms that are linear in the magnetic vector potential $A_0$ of the applied field, which turn out to be significant in a second-order perturbation treatment. Hence, in the first order perturbation treatment, the following is considered as the perturbing Hamiltonian

$$H^{(1)} = \left(\frac{e^2}{2m_e c^2}\right)(A_0 \cdot A_n + A_n \cdot A_0) + \left(\frac{e^2}{2m_e c^2}\right)A_0^2$$  \hspace{1cm} (138)

The second term, which is independent of the applied field and quadratic in the nuclear moment, does not contribute to the shielding. Consequently, the first order correction to the energy becomes

$$E^{(1)} = \frac{e^2}{2m_e c^2} \langle 0 | A_0 \cdot A_n + A_n \cdot A_0 | 0 \rangle$$ \hspace{1cm} (139)

where the Hartree-Fock ground state wavefunction can be used for $<0|$. The magnetic vector potential associated with the field of nuclear magnetic dipole moment $\mu_n$ is defined as

$$A_n (r) = \frac{\mu_n \times r_n}{r_n^3}$$  \hspace{1cm} (140)

Here, $r_n$ has the nucleus as its origin. On the other hand, the magnetic vector potential associated with the applied external magnetic field is defined at any position $r_0$

$$A_0 = \frac{1}{2} B_0 \times r_0$$ \hspace{1cm} (141)

Substituting Eqs. (140) and (141) into (139), we obtain

$$E^{(1)} = \frac{e^2}{2m_e c^2} \mu_n \cdot \langle 0 | \frac{r_0 \cdot r_n}{r_n^3} | 0 \rangle \cdot B_0$$ \hspace{1cm} (142)

Comparing with Eq. (128) this equation displays the diamagnetic component of the shielding property

$$\sigma_d = \left(\frac{e^2}{2m_e c^2}\right) \langle 0 | \frac{j \times r_n \cdot r_n \times i}{r_n^3} | 0 \rangle$$ \hspace{1cm} (143)

It is possible to derive an additional term which is likewise linear in both $B_0$ and the nuclear moment $\mu_n$ via second order perturbation treatment. From Eq. (134), the terms that need consideration are
\[ M = \frac{e}{m_e c} - i h \nabla \cdot A_n \quad \text{and} \quad N = \frac{e}{m_e c} i h \nabla \cdot A_0 \] (144)

The second order term can be expressed as follows

\[ E^{(2)} = \sum_{q>0} \left[ \frac{\langle 0 | M | q \rangle \langle q | N | 0 \rangle}{E_q - E_0} \right] \] (145)

Replacing the magnetic vector potentials via Eqns (140) and (141) and defining two new quantities \( L_0 = -i h (r_0 \times \nabla) \) and \( L_n = -i h (r_n \times \nabla) \) the following expression is derived,

\[ E^{(2)} = \frac{e^2}{2m_e c^2 \mu_m} \cdot \sum_{q>0} \left[ \frac{\langle q | L^z_0 \rangle \langle 0 | L_0 | q \rangle}{E_q - E_0} \right] \cdot B_0 \] (146)

Hence the paramagnetic term is,

\[ \sigma''_q = -\frac{e^2}{2m_e c^2} \cdot \sum_{q>0} \left[ \frac{i \langle q | L^z_0 \rangle \langle 0 | L_0 | q \rangle \cdot j}{E_q - E_0} \right] \] (147)

Essentially, the determination of shielding tensor amounts to the calculation of the first-order term for the diamagnetic part and the second-order term for the paramagnetic part, as embedded in Eqs. (143) and (147), respectively. In the above Ramsey's formulation of the shielding property, it is required to have a knowledge of ground and excited electronic states and their respective energies. The diamagnetic term depends only the ground electronic state, making it straightforward to calculate from an ab initio or first-principles electronic structure calculation. Its dependence on \( r_i^{-1} \) means that is very much a local contribution, arising largely from the core electrons surrounding the nucleus. On the other hand, the paramagnetic term, which depends more on the bonding, is the more difficult one to calculate.\textsuperscript{74}

An important consideration in the calculation of NMR shielding, is the gauge origin problem.\textsuperscript{75,76} Owing to the method of representing an external magnetic field with a vector potential, great latitude is given to the choice of origin. The total shielding which is an observable quantity should be totally independent of the choice of origin. A change in the choice of origin leads to additional terms in both the diamagnetic and paramagnetic
parts. However, these additional terms are exactly equal in magnitude but opposite in sign rendering the total shielding unchanged. Unfortunately, the desired cancellation does not occur in practice because of inherent difficulties in the computation of the paramagnetic term. This is mainly due to the fact that it depends on the integrals involving components of the electronic orbital angular momentum operator, the ground electronic state, and various excited electronic states. Since the calculation of the excited electronic states is formidable, the paramagnetic part is not calculated to the desired level of accuracy required to cancel the extra terms in the diamagnetic part due to a change in gauge origin. This therefore requires a gauge invariant approach to be adopted and, fortunately, there are methods such as IGLO,77 LORG,78 GIAO,51 and IGAIM79 which overcome this difficulty. Of these, we have used the GIAO method for its versatility and faster convergence.

1.4.4 Determination of Electric Field Gradient Tensors

One of the objectives of in the work carried out by the author is the theoretical determination of electric field gradient tensors using quantum chemical methods. This would in turn lead to the determination of the quadrupole interaction parameters, namely, $C_Q = e^2 Q q / h$ and the asymmetry parameter $\eta_Q$, which then become available for comparison with experimentally determined ones. These are related to the components of EFG as

$$C_Q = \chi = \frac{e^2 Q q}{h} = \frac{eQ}{h} V_{aa}^{PAS} , \quad \eta_Q = \frac{V_{aa}^{PAS} - V_{ss}^{PAS}}{V_{zz}^{PAS}}$$

(148)

Where $V_{aa}^{PAS}$ are components of the second-rank tensor describing the electric field gradient at the nucleus of interest in its principal axis frame, and $eQ$ is the nuclear electric quadrupole moment. As already introduced and discussed in Sec. 2.5, the quadrupole moment $(eQ)$ is a nuclear property and is the same for a given nucleus, taken to be NMR-active, irrespective of the environment in which it is present. The EFG, on the other hand, is determined by the charges external to the nucleus and hence is determined by symmetry and the molecular environment. Since the quantity $(eQ)$ is known, the
computational effort is essentially to determine the field gradient tensor $V$ at the nucleus.

In the electric quadrupole interaction, the charge distribution external to the nucleus enters into the calculation as second derivatives of the potential. The EFG tensor is constructed from these second derivatives as

$$V_{\alpha\beta} \equiv \left( \frac{\partial^2 V}{\partial x_\alpha \partial x_\beta} \right)_{r=0} \quad (149)$$

The potential $V$ at the origin due to a point charge $C$ at a distance $r$ away is

$$V = \frac{C}{4\pi \varepsilon_0 r} \quad (150)$$

where $\varepsilon_0$ is the permittivity of free space. Expressing $V$ in terms of Cartesian coordinates $x, y, z$, the second derivatives with respect to those $x, y, z$ i.e. the electric field gradient at the origin, can be easily determined to be (for the $zz$ component),

$$V_{zz} = e \frac{3z^2 - r^2}{r^5} \quad (151)$$

Or in terms of spherical tensor coordinates,

$$V_{zz} = e \frac{3\cos^2\theta - 1}{r^3} \quad (152)$$

Similar expressions may be found for all the other components $V_{\alpha\beta}$ of the electric field gradient tensor.

In a molecule or compound, the distribution of electrons is described by a wavefunction $\psi_e$ (for convenience expressed such that the origin is at the nucleus of interest and normalized). The expectation value of the $zz$ component of the electric field gradient due to this electron distribution, $\langle V_{zz} \rangle_e$ is then given in the normal way:

$$\langle V_{zz} \rangle_e = \langle \psi_e | \hat{V}_z | \psi_e \rangle \quad (153)$$

$$= e\int \psi_e^* \frac{3\cos^2\theta - 1}{r^3} \psi_e r^2 \sin\theta dr d\theta d\phi \quad (154)$$

where $r^2 \sin\theta dr d\theta d\phi$ is the integration volume element.
The contribution to $V_{zz}$ from the distribution of nuclei around the nucleus of interest $\langle V_{zz} \rangle_n$ is determined by assuming the surrounding nuclei act like point charges and using Eqs. (151) - (152). The other components of $V_{\alpha \beta}$ of the electric field gradient tensor can be calculated in a similar manner and the complete electric field gradient tensor formed by summing the electronic and nuclear contributions for each component. It is then a simple matter to diagonalize the resulting tensor to find the electric field gradient in its principal axis frame, $V^{\text{EFG}}$, and its components used to calculate the quadrupole coupling constant and asymmetry according to Eq. (148).

The electronic wavefunction $\psi_e$ needed for calculating the electric field gradient tensor $V^{\text{EFG}}$ can be determined using $ab\text{ initio}$ electronic structure calculations. One potential difficulty with $ab\text{ initio}$ calculations of the quadrupole coupling constant $C_Q$ is that it depends on the nuclear electric quadrupole moment, $Q$, which although a constant for a given nuclear isotope, is for many nuclei, not accurately known. The EFG tensor is a product of the quadrupole moment and the field gradient, and hence, suffers from a propagation in the error in the quadrupole moment. Moreover, the electric field gradient depends only on the ground state electronic structure and arrangement of nuclei in the molecule, and so it is possible to obtain much more accurate calculations of it than of the chemical shielding for instance, which, as described above, depends on excited electronic states in addition to the ground electronic state, and these are significantly more costly to calculate with any degree of accuracy. However, the EFG tensor is much more influenced by nuclei around the nucleus of study than the chemical shielding tensor. Hence, calculation of the EFG requires the coordination spheres to extend further in a cluster calculation and this makes the computational effort formidable. It is in this regard that the periodic approach scores over a cluster approach.

### 1.4.5 Computational Resources

Technological advancement in compute hardware and highly efficient algorithms and user-friendly interface between hardware and software have all brought advanced quantum chemical computing to the chemists' desktop. From the NMR calculations point
of view, a number of software packages are available for the determination of one or more of the NMR interaction tensors. These include: GAUSSIAN\textsuperscript{52}, WIEN\textsuperscript{53}, GAMESS\textsuperscript{83}, ACESII\textsuperscript{84}, ADF\textsuperscript{85}, VASP\textsuperscript{96}, DALTON\textsuperscript{87} and deMon.\textsuperscript{88}

Gaussian software package, especially Gaussian'03, gives access to the theoretical determination of the three important NMR interactions tensors, namely, the chemical shielding, EFG and $J$-coupling. In terms of making NMR calculations available to a large community of researchers, the most significant development in recent years has been the improvement of the Gaussian suite of programs to include a number of methods, namely, HF, DFT, and MP2 electronic approximations as well as single origin, GIAO,\textsuperscript{89,90} IGAIM,\textsuperscript{79} and CSGT methods to deal with the gauge origin dependence problem. GIAO method has, by far, been the method of choice and has been extensively used by a number of NMR groups.

WIEN software package, especially WIEN2k, has been developed by Prof. Blaha and his group in T U Wien, Austria, who have advanced the LAPW method in the periodic calculations. LAPW is well implemented in WIEN2k. Among other properties, WIEN2k can be used for the calculation of the EFG tensor. Within the NMR community, WIEN is becoming increasingly popular, although there are only very few groups who are proficient in using this package. In our work, WIEN2k was chosen to determine EFG tensors with a high degree of numerical accuracy, especially for $^{14}$N and $^{17}$O nuclei.

Gaussian '03 runs on Personal Desktop computers under Windows or Linux operating systems. In our laboratory, we have been able to set up computational facilities under Windows environment, which fully harnessed the power of the Pentium III and IV processors with enhanced RAM and disk storage. For low end calculations, we have used mainly standalone personal computers running with processor speeds upto 3.3 GHz, which were connected using a KVM switch (CS-64A) and a high speed 100 mbps hub. Using this arrangement, we were able to run many jobs simultaneously and also in a serial uninterrupted mode using the batch control file utility in G'03. For calculations at the highest basis level, we have used a Xeon HP xw8200 work station equipped with two processors, 4 GB of high speed RAM and a 120 GB SCSI drive. For the WIEN2k
calculations, we mainly used a sixteen node DEC Alpha main frame central computer facility available at National Chemical Laboratory. In addition, we also set up WIEN2k to run on standalone Pentium IV PCs under Redhat 8.0 Linux operating system.

1.4.6 Computational Details

A flow chart of the steps involved in our G’03 calculations of shielding tensors is shown below. For the cluster approach that we employed, the first step is to choose the molecular fragment cut out from an X-ray determined superstructure using a suitable molecular modeling environment. This was accomplished using Accelrys Materials Studio software. The details of the cluster models used are given later. The Cartesian coordinates are then input along with the choice of the method (HF or DFT) to be employed and the basis set to be used. We have carried out many test calculations on a number of known systems to determine the best choice that is suited for a particular molecule. This will be discussed later. From the G’03 results, we are able to inspect both the diamagnetic and paramagnetic contributions to chemical shielding separately. The G’03 results are obtained as absolute shieldings, which we need to convert to relative shifts for a direct comparison with experimental data. This required us to determine the absolute shielding of the reference compound, used in the experiment, by using the same method and the basis set and using it to estimate the relative shifts. By default, Gaussian uses its "standard orientation", instead of a principal frame for reporting the shielding tensor. The standard orientation consists of shifting the origin to the center on nuclear charge, then rotating the molecule into a standard orientation based upon symmetry rules. However, for the purpose of determining the eigen values, which alone we could determine from experiments on powder samples, a reorientation of the ‘standard frame’ to a crystal specific frame was not necessary. As a further aid to the visualization of Gaussian results, GaussView 3.0 software was used. This allowed us to view the chemical shielding density as seen by a particular nucleus mapped onto the current density isosurface.
We show below a schematic of the various computational steps involved in the theoretical determination of the EFG tensor using the plane wave approach as implemented in WIEN2k. From the X-ray or neutron diffraction determined atomic coordinates, we generate the unit cell as the first step by running the following modules: NN (nearest neighbor distances), SGROUP (spacegroup as well as all pointgroups of non-equivalent sites) and SYMMETRY (symmetry operations). The unit cell thus generated is taken in for further initialization using LSTART (atomic densities), KGEN (k-mesh in the irreducible wedge of the Brillouin zone) and DSTART (superposition of atomic densities). We then initiate the SCF iterations of the Linearized Augmented Plane Wave Method (LAPW), each of which use the following programs in the indicated sequence: LAPW0 (potential generation), ORB (orbital dependent potentials), LAPW1 (eigenvalues and eigenvectors), LAPWSO (spin orbit coupling), LAPW2 (valence charge density expansions), SUMPARA (summation from parallel execution), LAPWDM (density matrix), LCORE (core states) and MIXER (addition and mixing of charge densities). The above steps involved in the EFG calculation are conveniently executed
from a single browser window using the ‘w2web’, a web-based GUI (Graphical User Interface) available with WIEN2k. WIEN2k calculations yield both the asymmetry parameter (\(\eta\)) and the largest component of the field gradient tensor (\(V_{zz}\), in Volt/m\(^2\)), which when multiplied by the quadrupole moment (\(eQ\), in barn) of the nucleus involved gives the quadrupole coupling constant \(C_Q = e^2 qQ/\hbar\) in Hz units.
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