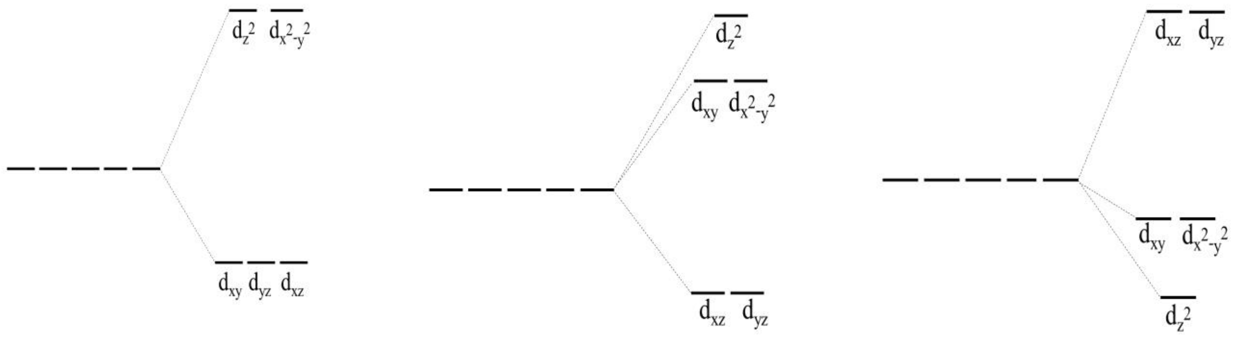
CHAPTER 1

INTRODUCTION

Transition metal ions with unpaired electrons exhibit a rich variety of spectroscopic phenomena. They serve as catalysts and as active site in metalloenzymes that are at the heart of most of the key biochemical processes such as respiration, photosynthesis or nitrogen fixation [1,2]. Electron paramagnetic resonance (EPR) spectroscopy provides information about the oxidation and spin states as well as the coordination geometry and the ligands around the transition-metal ions in their respective complexes. EPR is the leading magnetic technique in order to obtain geometrical and electronic information about these systems. It yields unique information about the nature of open-shell ground state and its dependence on the chemical environment. The more intense ligand–ligand ($\pi \rightarrow \pi^*$) band overshadows the d–d electronic transitions. This makes the spectroscopic data on the electronic properties due to the multiplet structure originating from d^n configuration of the transition metal rather scarce. In this respect Electronic Spin-Resonance (ESR) spectroscopy comes to rescue.

Magnetic anisotropy arises in transition metal complexes with open-shell system. Magnetic anisotropy [3] is the directional dependence of a material's magnetic properties. The magnetic moment of magnetically anisotropic materials will tend to align with an axis which is an energetically favorable direction of spontaneous magnetization [4]. This shows how the magnetic properties depend on the direction of measuring the magnetization. It is the dependence of the internal energy on the direction of spontaneous magnetization. This means that the magnetic properties of the molecule have an oriental dependence. This implies that the response to an external magnetic field depends on the direction in the molecule along which the field is applied, e.g., g-value anisotropy, hard/ easy axes of magnetization, etc. Theoretically calculated magnetochemical parameters can open the perspective of establishing a magnetostructural correlation for magnetic anisotropy that would allow chemists to tune and eventually control various magnetic parameters in transition metal complexes.

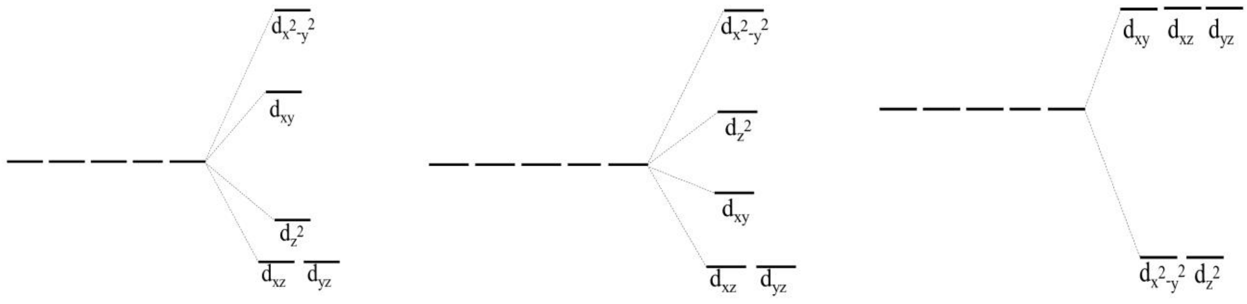
Most transition metal free ions have an orbital angular momentum (except d^5 high-spin). Orbital angular momentum is generally pictured as a circular motion of electrons around the nucleus. In most complexes, the orbital angular momentum appears to have disappeared due to quenching of the orbital moment. Quenching is due to the crystal field splitting of the d-orbitals into in different ways in different symmetries. Figure 1.1 depicts the crystal field splitting diagram.



Octahedral

Pentagonal bipyramidal

Square antiprismatic



Square planar

Square pyramidal

Tetrahedral

Figure 1.1: Crystal field splitting diagram

Transition metal complexes exhibit magnetism which are often paramagnetic, since they have partly occupied d orbitals, and thus possess unpaired electron spins. The paramagnetism of such species makes them amenable to the electron paramagnetic resonance (EPR) experiment, which has been one of the most successful tools in investigating their magnetic properties. From the point of view of coordination chemistry, octahedral d^4–d^7 transition metal complexes can be either low-spin (LS) or high-spin (HS). The former have the maximum number of paired electrons yielding spin ground states $S = 0, \frac{1}{2}$, or 1 (respectively for d^6, d^5,d^7 and d^4), and the latter have the maximum number of unpaired electrons yielding $S = \frac{3}{2}$, 2 or $\frac{5}{2}$ (respectively for d^7, d^4,d^6 and d^5). Magnetic anisotropy can appear when the ground state is at least a spin triplet and the spatial symmetry of the molecule is not too high. The effect is mainly due to spin-orbit coupling. When all the spatial degrees of freedom are quenched, i.e., the ground state is not degenerate and well separated from the excited states, the property is accurately described within the spin Hamiltonian formalism. The resulting Zero Field Splitting (ZFS) parameters can be extracted from various experimental techniques like HF-EPR and also accurately from theoretical calculations. Besides ZFS, g-tensor or g-anisotropy is another parameter that contributes to orbital momentum contribution. It is intrinsically a relativistic property, even for light-element compounds.

A major class of transition metal complexes extensively applied for their magnetic studies and properties are single-molecule magnets (SMMs). In general, SMMs are constituted of several transition metals bearing nonzero local spin moment. They have been investigated by a large scientific community since the discovery of the peculiar magnetic behavior of the so-called Mn_{12} compound in 1991 [5-7]. They have found potential applications in aspects of nanoscale electronics and atomic-scale storage devices as well as chemical catalysts and sensors. Interesting applications of these molecules have been envisaged, such as information storage or quantum computing, and the study of fundamental quantum effects, such as tunneling, coherence, and interference have become possible. Their remarkable properties are the exhibition of the zero-field splitting (ZFS) of the M_S components of the ground spin state and g-anisotropy. Also the interaction of the open-shell electrons with the nucleus give rise to another phenomenon known as hyperfine coupling.

From fundamental theory the g-tensor and D-tensor are important parts of any EPR spectrum. They exhibit details about the radical species present. These two parameters can provide wealth of information on the electronic and geometrical structure of molecules or solids with unpaired electrons. They allow us to enhance our understanding of electronic factors governing the observed spectra. The electronic g tensor is a fundamental quantity of impurity centres in solids which characterizes the magnitude and anisotropy of their magnetic moment in a given electronic state. Designing of single-molecule magnets, which requires a large and negative axial ZFS (D parameter), represents an essential criterion for reaching their desired magnetic characteristics [7,8].

Important models have been developed to study the electronic g-tensor using qualitative or semi-quantitative theoretical treatments since the early days of EPR studies [9].The electronic g-tensor is intrinsically a relativistic property, even for light-element compounds. The theory behind these two parameters were developed very early, but for realistic model, g-tensor and D-tensor calculations using accurate first-principle treatments were developed much later [10–12]. Also density functional theory (DFT) methods were developed for calculation of g-tensor and D-tensor. Therefore, these parameters can be determined straightforwardly from DFT [13] and explicitly correlated *ab initio* calculations [14,15]. These calculations can capture the major changes which are observed upon chemical or structural modification of the concerned radical species [16,17]. This aids to the interpretation of the experimental results.

Besides transition metal complexes, transition metal clusters constitute important single-molecule magnets (SMMs). These clusters which possess high-spin ground state and large negative axial zero-filed splitting have an intrinsic barrier for spin reversal. Consequently they have slow reversal of magnetization. This slow magnetic relaxation observed in low temperatures can be taken to be analogous to superparamagnetic nanoparticles below their blocking temperature.

Theoretical methods such as QM (quantum mechanical), HF (Hartree-Fock), post HF and DFT (Density Functional Method) which allows for economical treatment of electron correlation, provides a strong collaboration between theory and experimental results of molecular properties and hence theoretical methods have been widely used for estimation of EPR parameters as well. There are many evidences where the QM methods have been comprehensively used for assessment of EPR parameters [18−23] and they establish a correlation between experimental and their corresponding EPR results. Also there are instances where DFT is being used to calculate magnetic parameters in organic radicals and transition metal complexes [24−28]. Theoretical studies can provide valuable structural insight into the EPR active species even if there appears no optimal quantitative correlation with the experimental values.

1.1 VARIOUS MAGNETIC PARAMETERS

1.1.1 g-Tensor

The electronic g-tensor is one of the most important parameters of electron paramagnetic resonance spectroscopy (EPR). It contains a wealth of information on the electronic and geometrical structure of molecules or solids with unpaired electrons. The g-tensor is a fundamental quantity of molecules and impurity centers in solids characterizing the magnitude and anisotropy of their magnetic moment in a given electronic state. In transition metal complexes it is of importance in catalysis and metalloenzymes.The electronic g-tensor carries subtle information about electronic structure and geometry of molecules which is essential in determining relation between electronic structure and chemical properties. Generally the electronic g-tensor is dominated by contributions from spin-orbit coupling.

The g-tensor usually requires an adequate treatment of electron correlation. It is calculated as correction, $\mathit{\Delta} g$, to the free electron value. The formalism for calculation of g-tensor can be described as below:

$$g = g_e 1 + \mathit{\Delta} g,$$

where ‘g’ stands for electronic g-tensor, g_e is the g-factor for free electron (2.0023) and Δg is the g-tensor shift. Up to the level of second-order perturbation theory, the g-shift consists of the relevant Breit-Pauli terms:

$$\mathit{\Delta} g = \mathit{\Delta} g_{RMC} + \mathit{\Delta} g_{GC} + \mathit{\Delta} g_{SO/OZ}$$

The first term is of first order and is due to the relativistic mass correction [29]. The second term corresponds to one-electron gauge-correction to the electronic Zeeman effect while the last term denotes one-electron spin-orbit corrections coupled with the Zeeman effect. It is to be studied which among the three terms dominate the total g-shift in a given species. The g tensor is anisotropic when the electron possesses both spin and orbital angular momentum.

In most of the species the “paramagnetic” second-order spin-orbit/orbital Zeeman cross term,$\Delta g_{SO/OZ}$, dominates (except for extremely small Δg -values). The g tensor is anisotropic when the electron possesses both spin and orbital angular momentum. The phenomenological spin Hamiltonian H_{spin} describes the interaction between a magnetic field and the electron spin:

$$H_{spin} = \beta_B \mathbf{B}\mathrm{g}\boldsymbol{S}$$

whereβ_B is the Bohr magneton, $\boldsymbol{B}$ is the magnetic flux density, $\boldsymbol{S}$ is the fictitious electron spin and g is the g-tensor. This matrix H_{spin} can easily be diagonalised using the following unitary transformation:

$$\boldsymbol{E} = \boldsymbol{U}^{\ddagger}\mathbf{HU}$$

where

$$\mathrm{U}=\begin{bmatrix} 1 & 0 & 0 \\ 0 & cos\theta & -isin\theta \\ 0 & -isin\theta & cos\theta \end{bmatrix} \text{ and } \tan(2\theta) = \frac{2\xi\sqrt{3}/2}{\Delta+\xi/2}$$

The components of the g-tensor in the experimental spin Hamiltonian $\beta_B \boldsymbol{B}_g \boldsymbol{S}$ are then easily obtained by calculating the corresponding components of the Zeeman Hamiltonian. $\langle n\Gamma_i \pm \left|\vec{B}.(\vec{l} + 2\vec{s}\right| n\Gamma_i \pm\rangle$. The result for the three relevant Kramers doublet reads:

$|1\Gamma_7\rangle$: $g_{xx} = g_{yy} = g_{\perp} = 0; \qquad g_{zz} = g_{\parallel} = -4$

$|1\Gamma_6\rangle$: $g_{xx} = g_{yy} = g_{\perp} = 2cos^2\theta + 4\sqrt{1.5}sin\theta cos\theta; \qquad g_{zz} = g_{\parallel} = 2cos^2\theta$

$|2\Gamma_6\rangle$: $g_{xx} = g_{yy} = g_{\perp} = 2sin^2 - 4\sqrt{1.5}sin\theta cos\theta; \qquad g_{zz} = g_{\parallel} = 2sin\theta$

When explained in terms of angular momentum in a coordination environment the g-factor is given by:

$$g = 1 + \frac{J(J+1) + (S(S+1) = L(L+1)}{2J(J+1)}$$

where L and S are orbital angular momentum and spin angular momentum, respectively. For a free electron, g-value becomes 2 (S=1/2, L=0, J=1/2). For the free halogen atoms (ns^2np^7) in the gaseous phase g= 4/3 (L=1, S=1/2, J=3/2). These predictions fit well experimentally but in a chemical environment the g-values vary from the theoretically obtained ones [30]. If the orbital motion makes its full contribution to the magnetic moment, then both the orbital angular momentum (L) and spin angular momentum(S) contribute independently. But in reality the orbital contribution is fully or partially quenched depending on the situation [31]. To have an orbital contribution to the magnetic moment, the following conditions must be satisfied:

(i) Condition of degeneracy according to which all the d orbitals which are mutually transformable [32] through the symmetry operation must be degenerate.

(ii) and secondly, the condition of mutual transformability through the symmetry rotation which states that the orbitals must be mutually transformable by rotation about some axis,

$$d_{xy} \Leftrightarrow d_{x^2-y^2} \qquad d_{xz} \Leftrightarrow d_{yz}$$

$$d_{xy} \Leftrightarrow d_{xz} \qquad d_{xy} \Leftrightarrow d_{yz}$$

(with rotation by 90^{o} around the common axis)

Thus it is evident that since $d_{x^2-y^2}$ and d_{z^2} in the 'e' set are not mutually transformable because of their different shapes and hence this set fails to make any orbital contribution. Thirdly we have condition of spin according to which the orbitals must not contain electrons of similar spin.

The first implementation of DFT for calculation of electronic g-tensor with the addition of hybrid functional was reported by Kaupp *et al.* [33]. They studied small main group radicals like H_2O^+, CO^+, etc. and series of transition metal complexes like $[Co(CO)_4]$, $[CrOF_4]^-$ etc. The g-tensors of these species were compared with their experimental values using the local density approximation (VWN functional), the generalized gradient approximation (BP86 functional), as well as B3-type (B3PW91) and BH-type (BHPW91) hybrid functional. Though in case of transition metal complexes significant differences were observed when using different functional but main group radicals showed very little exact-exchange mixing. They had already established that LDA and GGA functionals underestimate the paramagnetic contributions to the g-tensor while using the half-and half functional BHPW91 one can recover 100% of the experimental g-tensor components. For the transition metal complexes B3PW91 hybrid functionals exhibited most satisfactory performance.

Schreckenbach and Ziegler [34] in one study formulated the g-tensor and g-shift based on DFT along with the use of gauge-including atomic orbitals (GIAO). They compared their calculated results with experiment and HF and MRCI calculations of Lushington *et al.* [35,36]. Their method was found to give better result than the HF-based schemes while MRCI was found to be the best for some molecules but with greater computational time. SZ method, as it is called was found to give accurate result for various small first- and second-row radicals but it was less accurate when used for heavier elements.

The electronic g-tensor of d^1 transition metal complexes of V, Cr, Mo, W, Tc and Re was studied by Hrobárik *et al.* [37] using DFT. They assessed the importance of the higher-order SOC by direct comparison of one-, two- and four-component calculations within the same computer program. They used an efficient matrix of Dirac-Kohn-Sham implementation with relativistic kinetic balance basis sets thereby applying four-component DFT to g-tensor.

Malkina coworkers [38] have shown the atomic mean-field approximation provides SOC in absolute agreement with the results obtained using explicit one- and two-electron spin-orbit integrals. For systems containing heavy atoms they used a pseudopotential treatment where quasi-relativistic pseudopotentials are included in the Kohn-Sham calculation whereas appropriate spin-orbit pseudopotentials are used in the perturbational treatment of the *g*-tensors. This approach is shown to provide results in good agreement with the all-electron treatment, at moderate computational cost. Figure 1.2 shows the comparison of calculated and experimental g-shift values for first-row compounds by the authors.

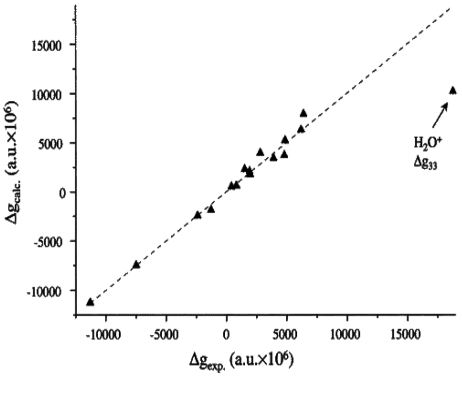


Figure 1.2: Comparison of calculated and experimental g-shift tensor components (ppm) for first-row compounds.

1.1.2 D-tensor

The D-tensor or the Zero-Field Splitting (ZFS) for transition metal complexes is the fundamental quantity which arises when the transition metal ion has a total ground state spin S>1/2 or with more than one unpaired electron [39,40]. This removes the state degeneracy of the system with S>1/2 in absence of magnetic field.

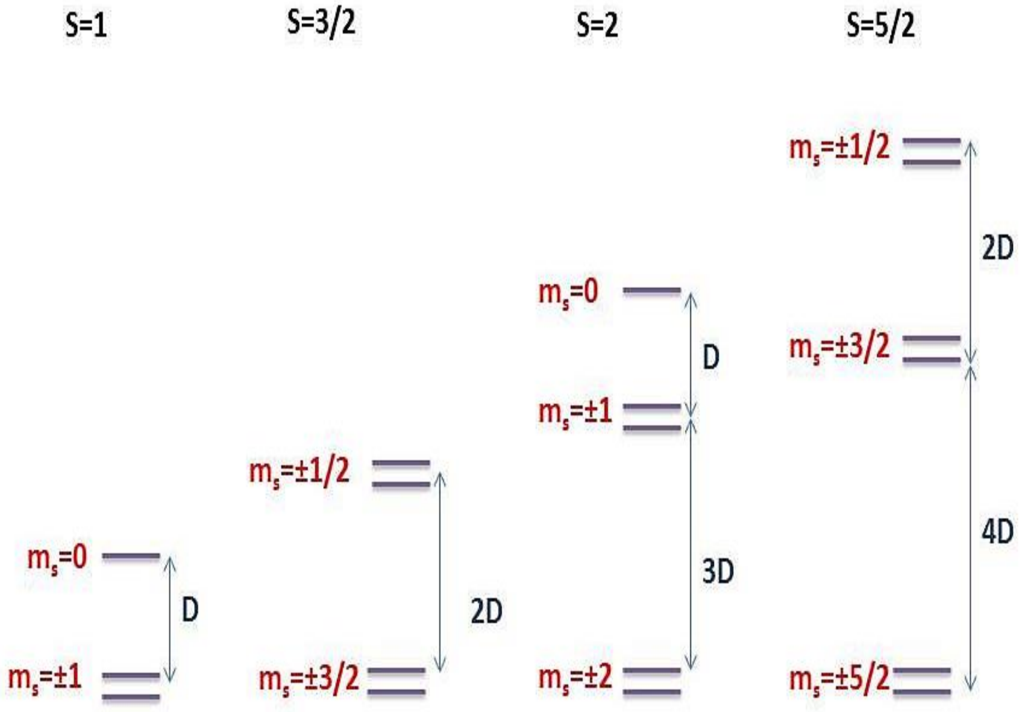


Figure 1.3: Energy level spacing for S=1 to $\frac{5}{2}$ for D<0

The general form of zero-field splitting can be written as:

$$H_{ZFS} = \hat{S}\boldsymbol{D}\hat{S}$$

As a consequence of molecular electronic structure and spin density distribution the degeneracy gets removed. For unpaired electron systems the axial ZFS or the D-tensor removes the microstate degeneracy and produces Kramer’s doublet while the rhombic ZFS, i.e. the E-value splits the Kramer’s doublets. It implies that the ZFS and the D-tensor causes magnetic anisotropy. The energies of spin microstates in unit of D are given by the following equation:

$$E_{m_s} = D\left[\sqrt{S_z^2} - \frac{S(S+1)}{3}\right]$$

The ZFS has a strong influence on the electron spin energy levels and can thus be visible in EPR spectra, in particular at high magnetic field [2]. All the methods for estimating the ZFS make use of the spin Hamiltonian formulation, including the ZFS term. If a coordinate systemis chosen that diagonalizes D, H_{ZFS} can be rewritten as:

$$H_{ZFS} = D\left[S_z^2 - {}^1\!/_3\, S(S+1)\right] + E\left[S_x^2 - S_y^2\right]$$

$$D = D_{zz} - {}^1\!/_2\,(D_{xx} + D_{yy});\ E = {}^1\!/_2\,(D_{xx} + D_{yy})$$

where D_{xx}, D_{yy} and D_{zz} are the diagonal components of the ZFS tensor *D* in its principal axes *xx*, *yy*, and *zz*, respectively. However, for complexes with uniaxial symmetry, the rhombic term vanishes (|*D*|>0, *E*=0).

It is known that the total D-tensor D_{Tot}, or the ZFS has two contributions:[6] a) a first order term which involves the direct dipolar spin-spin (SS) interaction between pairs of electrons and (b) a second order term arising from the spin-orbit coupling (SOC) that introduces some angular momentum into the ground state (assumed orbitally nondegenerate) and which is being picked up by the spin of a second electron. Between the two contributions, the later contributes dominantly towards electronic g-tensor as well as towards D-tensor [41]. The D_{Tot} can be considered as the decomposed form of D_{SS} and D_{SOC}. The major contribution being form the D_{SOC} part, we need to study the spin-orbit coupling part in details. In organic radical the D-tensor tends to be dominated by the direct dipolar spin-spin coupling (SS), and on the other hand, spin-orbit coupling (SOC) dominates in case of open-shell transition metal complexes of relevance in molecular magnetism [42]. In transition metal complexes, D-tensor relies largely on ligand field theory [41].

Though, the contribution from the D_{SS} part was largely discarded, recently detailed calculations have been successfully applied for the prediction of the SS contribution to the ZFS in a variety of systems [43,44].

The interpretation of SOC contribution towards D_{Tot} is mainly carried out on the basis of ligand field theory (LFT) in the literature [45–47]. However, LFT arguments often used to give a qualitative scheme of the involved interactions, but failed at the quantitative level. Therefore, simple arguments have been forwarded in this context.

Many groups have reported the assessment of DFT-based spin-orbit coupling (SOC) approaches viz. Coupled-Perturbed (CP), Pederson-Khanna (PK) and Quasi-restricted Orbital (QRO) methods. Zein *et al.* [48] applied SOC approaches of PK and QRO for studying eighteen experimentally well-characterized four-, five- and six-coordinated complexes of the general formula $[Mn(L)_nL'_2]$ where L' is Cl, Br, I, NCS or N_3 and L is an oligodentate ligand and Mn being in +2 oxidation state. The PK method is found to be more successful than QRO. Also they showed spin-spin (SS) contribution to the axial D-tensor is 30%. As we have seen the D-tensor can be decomposed to spin-spin and spin-flip excited states. Their calculations exhibited that the d-d spin-flip (αβ) and ligand-to-metal charge transfer excited states (ββ) dominate the SOC part of the total D-tensor. It was found that the prediction of the sign of the calculated axial D-tensor is difficult when $\frac{E}{D} > 0.2$.

Frank Neese has done pioneering work in the field of magnetism of transition metal species. In one work Frank Neese [49], derived straightforward response equations that are readily transferable to the SCF-HF or the DFT framework. It was showed that the main additional effort in such calculations arises from the solution of nine sets of nonstandard coupled-perturbed SCF equations. In the ORCA program package [50] developed by Neese *et al.* these equations have been implemented together with the SOMF representation of the SOC operator. The new approach has been tested on a series of diatomic molecules with accurately known D-tensor values and found that it corrects most of the shortcomings of previous DFT-based methods. The slope of the correlation line was found to be unity for the B3LYP and BLYP functions.

The D-tensor values in some six- and five-coordinated Ni(II) complexes were carried out by Kubica *et al.* [51]. They used different levels of theory within the ORCA program package. High-end *ab inito* calculations (CASSCF and NEVPT) were compared with DFT methods. Results obtained with *ab intio* level are quite consistent with experimental data while DFT methods gave functional-dependent data. Figure 1.4 given by the authors shows the D-tensor as a function of geometry distortion in $[Ni(H_2O)_6]^{2+}$ calculated using CASCF, QDPT-CASSCF, NEVPT2, QDPT-NEVPT2 and DFT-B3P.

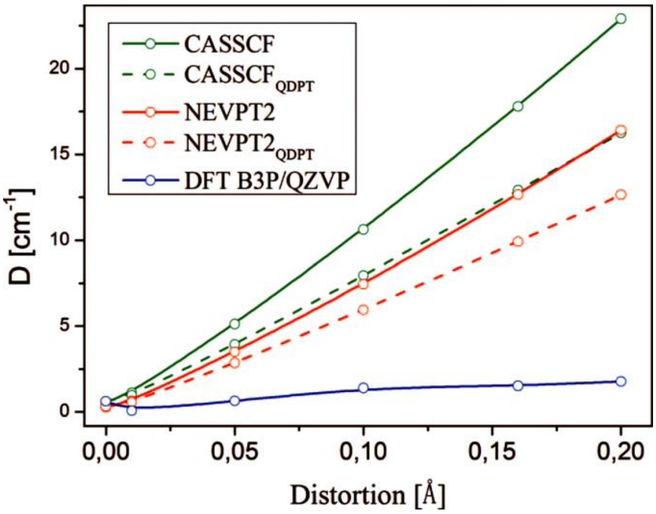


Figure 1.4: The ZFS parameter *D* as a function of geometry distortion in of $[Ni(H_2O)_6]^{2+}$, calculated using various computational methods.

1.1.3 Hyperfine Coupling

All these years the ligand hyperfine couplings in transition metal complexes has also emerged as a trending topic in magnetism. Van Lenthe *et al*. [52] and Munzarova and Kaupp [53−55] have done pioneering work in calculation of hyperfine coupling in transition metal complexes. It has been reported that there is striking resemblance between hypefine coupling and spin-spin couplings. This is accounted by the identical physical mechanisms that cause propagation of spin-polarization via the electronic structure of a molecule [56]. When an open-shell system forms, it leads to a different electronic structure unlike its closed-shell counterpart. The structure thus formed is 1 or 2 bonds away from the center possessing the unpaired electrons [57]. Hence long range spin-spin couplings can be used for prediction and can study the values of hyperfine coupling constants. This approach is being used based on the Dirac vector model [58].

The hyperfine coupling is constituted of three terms: (i) isotopic Fermi Contact term, (ii) the spin dipolar interaction and (iii) the spin-orbit coupling correction. The hyperfine coupling is dominated by the spin-orbit coupling contributions [59−61].

The EPR spin Hamiltonian describes the hyperfine coupling contribution as

$$H^{HFC} = \sum_{N} \sum_{ww`} I_{N,w} A_N^{ww`} S_{w`}$$

Where w and $w`$ are the Cartesian components, $I_{N,w}$ is the nuclear spin vector of the nucleus N, and $S_{w`}$ represents the pseudospin operator of the complex or cluster or the species under study. Mathematically, $A_N^{ww`}$

$$A_N^{ww`} = \frac{\delta^2 E}{\delta I_{N,w} \delta S_{w`}}$$

Here E represents the energy of a molecule under the influence of a nuclear spin generated magnetic field, where the vector potential in Coulomb is denoted by $g_N \beta_N I_n \times \frac{r_N}{r_N^3}$; here g_N and β_N are the g-tensor of the concerned nucleus N and the Bohr magneton of the same, respectively.

In the absence of spin-orbit coupling, the formula for the hyperfine coupling constant is

$$A_N^{ww`} = \frac{g_e \beta_e g_N \beta_N}{2S} \sum_{mn} \gamma_{mn}^{(s)} (F_{N,mn}^{ww`} - S_{N,mn}^{ww`})$$

In this equation, g_e and β_e are the g-tensor and the Bohr magneton of an electron, respectively, m and n are the label atomic orbitals, and $\gamma_{mn}^{(s)}$ is the spin-density matrix. $F_{N,mn}^{ww`}$and $S_{N,mn}^{ww`}$ are the Fermi-Contact and spin-dipolar integrals respectively which are defined by the explicit formulae as below

$$F_{N,mn}^{ww`} = \frac{8\pi\delta_{ww`}}{3} \int \varphi_m(r)\, \delta(r_N) \varphi_n(r) dr$$

and $$S_{N,mn}^{ww`} = \int \varphi_m(r) \frac{3w_N w`_N - |r_N|^2 \delta_{ww`}}{|r_N|^5} \varphi_n(r) dr$$

where$r_N = r - R$ and φ_m is a Gaussian basis function.

In literature, it is evident that in most cases *ab inito* methods are more accurate in prediction of hyperfine coupling theoretically as compared to DFT methods. In most of the work in computation of hyperfine coupling, single-reference many-body perturbation and coupled-cluster methods are shown to provide results with benchmark accuracy [62−67]. When the wave function is described by a single Slater determinant more satisfying close to accurate results are obtained. The complete active space self-consistent field (CASSCF) and multiconfigurational interaction (MRCI) methods are being reported that appear to be computing the hyperfine coupling in more precise manner [68−71] on the other hand, density functional methods can be categorized as relativistic analogues as explanation for the scalar relativistic and spin-orbit effects in case of transition metal complexes [72−76]. DFT methods have also been reported to be used for obtaining benchmark results for prediction of hyperfine coupling constants [77−80].

Theoretically the hyperfine coupling constants are relatively difficult to calculate as compared to g-tensor and D-tensor because it requires the accurate description of core-shell spin polarization without including spin contamination arising from overstated valence shell spin polarization. Besides this, the hypefine coupling constant calculation requires the inclusion of relativistic effects of both scalar (spin-free) as well as spin-orbit relativistic effects. These factors persuade the overestimation or the underestimation of hyperfine coupling phenomenon in transition metals of even 3d series [81]. Therefore, the HFCs are more widely approached by employing quantitative evaluation.

1.2 MAGNETIC PROPERTIES IN METAL CLUSTERS:

Since the discovery of Mn_{12} cluster [82] as a nanoscale magnet, many metal clusters are investigated to be used as single-molecule magnets. Functionalities like optical and magnetic properties, molecular trapping and thermal response have been exhibited by these clusters. The small size and their well dispersive property make them desirable for many applications in the field of magnetism. The reason that these types of nanoclusters are in high demand in this field is that they exhibit different chemical and physical properties as compared to the bulk phases. Metal clusters play a vital role in satisfying the ever increasing demand of high bit density of data storage. The main phenomenon that supports the stability of bits is magnetic anisoptropy. The bit size getting reduced requires higher magnetic anisotropy energy (MAE) per atom. This MAE would keep the magnetization of the metal clusters in specific direction against thermal fluctuations. The magnetic stability of metal clusters is explained by increase in orbital momentum and magnetic anisotropy energy due to lower atomic coordination number; and this exhibited in X-ray magnetic circular dichroism (XMCD) [83]. Now a large series of such clusters are reported to exhibit magnetism. Slow magnetic relaxation in tetranuclear Fe(III) cluster was discussed by Barra *et al*. [84]. They evaluated the projection of single-dipole and dipolar contributions to the ZFS of the ground state. They calculated the D-tensors of three structurally independent Fe(III) centres from coordination geometry and spectroscopic data using overlap model. Waldmann *et al*. [85] studied magnetic anisotropy in cyclic octanuclear Fe(III) cluster. Magnetic anisotropy was calculated exactly to first order, based on a spin-Hamiltonian formalism and the consequent use of all symmetries. Its magnetic parameters were compared to those of several related hexanuclear ferric wheels.

1.3 COMPUTATIONAL METHODS

1.3.1 Basis sets

Mathematically basis set [86] is a collection of vectors which defines a 3D space where the problem to be solved. These are unit vectors$\hat{\imath}$, $\hat{\jmath}$and $\hat{k}$. In quantum chemistry, a basis set is a set of functions in order to create the molecular orbitals that are expanded as a linear combination with coefficients to be determined. Usually these functions are centered on atoms, but those centered in bonds or lone pairs have also been used. Quantum chemical calculations are typically performed within a finite setoff basis functions. These basis functions are usually not the exact atomic orbitals, even for the corresponding hydrogen-like atoms, due to approximations and simplifications of their analytic formulas.

(a) Slater Type Orbitals

Slater type orbitals (STOs) were used as basis functions due to their similarity with the eigen functions of the hydrogen atom. Their general definition is

$$s\zeta_{n.l.m}(r,\theta,\phi) = Nr^{n-1}e^{-\zeta r}Y_l{}^m(\theta,\phi)$$

with N as the normalization constant and $Y_l{}^m(\theta,\phi)$ is the spherical harmonics.

STOs can give direct physical interpretation and thus are naturally good basis for molecular orbitals. From a computational point of view the severe shortcoming is that most of the required integrals to be calculated in the SCF procedure needed in the course drastically decrease the speed of a computation.

(b) Gaussian type orbitals (GTOs)

STOs can be approximated as linear combinations of Gaussian orbitals. Gaussian type orbitals (GTOs) are mathematically defined as

$$G_{i,j,k}^{\alpha,R} = N_{i,j,k}^{\alpha}(x-R_1)^i(y-R_2)^j(z-R_3)^k e^{-\alpha(r-R)^2}$$

where normalization factor R and α are called the center and the exponent of the Gaussian function, respectively. GTOs are not really orbitals but are simpler functions frequently called Gaussian primitives. These Gaussian primitives are usually obtained from quantum calculations like Hartree-Fock or Hartree-Fock along with some correlated calculations. Typically, the exponents are varied until the lowest energy of the atom is obtained. For molecular calculations, these Gaussian primitives have to be contracted, i.e., certain linear combinations of them will be used as basis functions. Such a basis function will have fixed coefficients and exponents. The difference lies in that the variable r in the exponential function is squared. And hence an inaccuracy at the electron density in the nucleus is prevalent giving a marked influence on the results. Today, there are hundreds of basis sets composed of these GTOs. The smallest of these are called minimal basis sets and these are typically composed of the minimum number of basis functions that are required to represent all of the electrons on each atom. A minimum basis set is a single basis function used for each orbital. STO-*n*G, where n is an integer is the most common minimal basis set. This n value represents the number GTOs used to approximate STO for both core and valence orbitals. These usually give poor results insufficient for research quality publication but are much cheaper than their larger counterparts. Commonly used minimal basis sets of this type are: STO-3G, STO-4G and STO-6G.

(c) Extended basis sets

There are several different types of extended basis sets

- Double-Zeta,Triple-Zeta, Quadrapole–Zeta
- Split-valence
- Polarized sets
- Diffuse sets

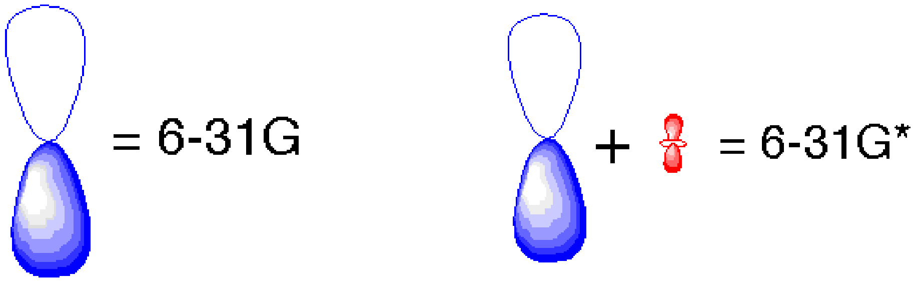
Double-Zeta,Triple-Zeta,Quadrapole-Zeta: The double-zeta basis set is important to us because it treats each orbital separately when the computational calculation is conducted.This gives a more accurate representation of each orbital. In order to do this, each atomic orbital is expressed as the sum of two Slater-type orbitals (STOs). The two equations are the same except for the value of (zeta). The zeta value accounts for how diffuse (large) the orbital is. The two STOs are then added in some proportion. The constant '*d*' determines how much each STO will contribute towards the resulting orbital. Thus, the size of the atomic orbital can range anywhere between the value of either of the two STOs. For example, let's look at the following example of a 2s orbital:

$$\varphi_{2S}(r) = \varphi_{2S}^{STO}(r_1, \zeta_1) + d\varphi_{2S}^{STO}(r_2, \zeta_2)$$

Here each STO represents a different sized orbital because of varying zeta values. The '*d*' stands for the percentage of the second STO adding in. Their linear combination then gives us the atomic orbital. Since each of the two equations is the same, the symmetry remains constant.The triple and quadruple-zeta basis sets work in the similar manner except use three and four Slater equations instead of two.

Split-valence: Often much effort is required to calculate a double-zeta for every orbital. So many scientists simplify by calculating a double-zeta only for the valence orbital. Since the inner-shell electrons aren't that important to the calculation, they are described with a single Slater Orbital. This method is called a split-valence basis set. A few examples of common split-valence basis sets are 3-21G, 4-31G, and 6-31G.

Polarized Sets: In the previous basis atomic orbitals are treated only as '*s*', '*p*', '*d*', '*f*' etc. Although those basis sets are good approximations, a better approximation is taken into account for the fact that sometimes orbitals share qualities of '*s*' and '*p*' orbitals or '*p*' and '*d*', etc. and not necessarily have characteristics of only one or the other. As atoms are brought close together, there is a polarization in the charge distribution (the positive charge is drawn to one side while the negative charge is drawn to the other) which distorts the shape of the atomic orbitals. In this case, '*s'* orbitals begin to have a little of the '*p*' flavor and '*p*' orbitals begin to have a little of the '*d*' flavor. One asterisk (*) at the end of a basis set denotes that polarization has been taken into account in the 'p' orbitals. In Figure 1.5 below shows the difference between the representation of the '*p*' orbital for the 6-31G and the 6-31G* basis sets. The polarized basis set represents the orbital as more than just '*p*', by adding a little '*d*'. Two asterisks (**) depicts that polarization has taken into account the 's' orbitals besides the '*p*' orbitals.



Original 'p' orbital Modified 'p' orbital

Original 's' orbital Modified 's' orbital

Figure 1.5: Pictorial representation of 6-31G, 6-31G* and 6-31G** basis sets.

Diffuse sets: These Gaussians have very small exponents and decay slowly with distance from the nucleus. Diffuse Gaussians are usually of *s* and *p* type. Diffuse functions are necessary for interpretation of anions and weak bonds (e.g. hydrogen bonds) and are frequently used for calculations of properties like dipole moments, polarizability, etc.

1.3.2 Functionals

DFT calculations nowadays are based on the Kohn-Sham approach of which two theorems have been formulated by Hohenberg and Kohn in 1964.

(a) Hohenberg– Kohn Theorem

All the properties of a molecule in a ground state are determined by the ground state electron density

$$E_0 = f[\rho_0(x, y, z)$$

Like energy of ground state can be expressed as above. This means energy is expressed as a function of electron density. Since electron density is itself a function, function of a function is called as functional. It transforms function to a number.

(b) Kohn-Sham theorem

It states that any trial electron density function will give an energy value higher than the true ground state energy.

$$E_t \geq E_0(\rho_0)$$

where E_t stands for energy calculated from trial energy density function. and the trial energy density function must satisfy the condition of

$$\int \rho_r . r . dr = n$$

where n is the number of electrons in the molecule and $\rho_r . r . \geq 0$.

Most commonly used GGA, meta-GGA and hybrid functionals available in ORCA are:

- GGA = BLYP,BP86,PBE,OLYP
- Meta- GGA= TPSS, rev TPSS,MO6-L
- Hybrid-GGA= B3LYP, B3LYP/G,BHLYP,PBEO,B3PW91,O3LYP
- Hybrid meta GGA= TPSSh, rev TPSSh, MO6,MO6-2X, PW6B95
- Range seprated hybrids= LC-BLYHP, CAM-B3LYP,WB97, WB97X,WB97X-D3

1.3.3 Quantum Mechanical Methods

Quantum mechanical methods can be divided into *ab initio* method, density functional method and semi-empirical methods. *Ab initio* methods include Hartree-Fock (HF), Möller-Plesset perturbation theory (MP), Configuration Interaction (CI), Coupled Cluster (CC) method.

1.3.3.1 Ab initio method

The *ab inito* (Latin "from first principles") methods are based on Schrödinger equation [87]. It is approximate solutions of the Schrödinger equation without appealing to fitting to experiment. This method gives a molecule's energy and wavefunction. The wavefunctions and energy levels are obtained by diagonalizing a Fock matrix and is represented by the equation:

$$H = C\varepsilon C^{-1}$$

where the H matrix is an energy-elements matrix, the Fock matrix whose elements are integrals of H_{ij} which are integrals involving $\hat{H}$ and basis function ϕ. This equation shows that the diagonalization of H gives the coefficients or eigen vectors (the columns of C yield the wavefunctions of the molecular orbitals) and the energy levels or eigen values, i.e. the diagonal elements of ε. The equation $H = C\varepsilon C^{-1}$ comes from $HC = SC\varepsilon$ when S is approximated as a unit matrix (simple Hückel method) or when the original Fock matrix is transformed into H using an orthogonalizing matrix calculated from S. The algorithm assembles the Fock matrix H to do a simple or extended Hückel calculation. An *ab inito* calculation is done in this way and the crucial difference compared to the Hückel method is the evaluation of the matrix elements. The Fock matrix elements H_{ij} are not calculated in simple Hückel method. They are set equal to 0 or -1 according to simple rules based on atomic connectivity. While in EHM the H_{ij} are calculated from the relative positions of the orbitals or basis functions. Also the ionization potentials of these orbitals in neither case is H_{ij} calculated from first principles.H_{ij} is explicitly denoted by the formula

$$H_{ij} = \int \phi_i \hat{H} \phi_j dv$$

In *ab inito* method the calculations H_{ij} is calculated from the above equation by performing the integration using explicit mathematical expressions for the basis functions ϕ_i and ϕ_j and the Hamiltonian operator $\widehat{H}$.

The Hartree SCF method

The Hartree-Fock calculation is the simplest kind of *ab inito* calculation. The problem that was addressed arises because of the fact that due to the electron-electron repulsion an exact solution of the Schrödinger equation is not possible with any atom or molecule with more than one electron. For electron one a one-electron Schrödinger equation is solved first where the electron-electron repulsion comes from electron one and an average, smeared out electrostatic field calculated from $\psi_0(2)\psi_0(3), \dots \dots . \psi_0(n)$ due to other electrons in order to apply the Hartree process. The only moving particle in this equation is electron one. Solving this equation gives $\psi_1(1)$. And further solving for electron 2 etc the first cycle of calculation is completed as

$$\psi_1 = \psi_1(1)\psi_1(2)\psi_1(3) \cdots\cdots\cdots \psi_1(n)$$

Repetition of the cycle gives

$$\psi_2 = \psi_2(1)\psi_2(2)\psi_2(3) \cdots\cdots\cdots \psi_2(n)$$

The process is continued for k cycles till a wavefunction ψ_k is obtained. At this stage the field of the k^{th} cycle is essentially the same as cycle k-1. This means the it is consistent with the previous field. Therefore, this Hartree procedure is called the self-consistent field procedure.

1.3.3.2 Density Functional Theory

Density functional theory (DFT) is used to investigate the electronic structure (principally the ground state) of many-body system. With this theory, the properties of a many-electron system can be determined by using functionals which are functions of spatially dependent electron density.

$$\rho(\vec{r}) = N \int \dots . \int |\psi(x_1, x_2 \cdots\cdots x_N)|^2 ds_1 d\vec{x}_2 \cdots\cdots d\vec{x}_N$$

where, $\rho(\vec{r})$ determines the probability of finding any of the N electrons within the volume element dr_1 but with arbitrary spin while the other (N-1) electrons have arbitrary positions and spin in the state presented by ψ. ρ(r) is a non-negative function of only three spatial variables in contrast to wave function (ψ), which is a function of 4N variables (3 spatial variables and 1 spin variable for each electron) for an N electron system. Moreover, unlike the wave-function, the electron density is an observable and can be measured experimentally, e.g. by X-ray diffraction.

Variational Principle in DFT

Second HK Theorem

The functional that delivers the ground state energy of the system, if and only if the input density is the true ground state density.However, there lies a major challenge in DFT and H-K theorem as they do not tell anything regarding the exact form of such functional.

Kohn-Sham equations and energy functional

Kohn and Sham introduced a method based on the Hohenberg-Kohn theorem that helps one to minimise the functional E[ρ(r)] by overall densities containing N electrons. They separated ρ(r) into three parts so that $E[\rho(r)].E$

$$E[\rho] = T_S[\rho] + J[\rho] + E_{xc}[\rho]$$

where, E_{xc} is the exchange correlation energy term and $T_S[\rho]$ represents kinetic energy

$$E_{xc}[\rho] \equiv (T[\rho] - T_S[\rho]) + (E_{ee}[\rho] - J[\rho])$$

Next an approximate form for the functional that describes the dependence of the E_{xc} on the electron density is then used to calculate V_{xc}. This helps the KS equation to be solved giving an initial set of KS orbitals. This set of orbitals is then used to calculate an improved density .This procedure is repeated until the density and the exchange-correlation energy satisfies a convergence criterion.

Effective Core Potentials (ECP)

These basis functions are useful for heavy elements (4th period onwards) that include relativistic effects. As the electrons near the very positive nucleus of a heavy element experience a larger relative attraction than in comparison to lighter elements, which causes the electrons to accelerate close to the speed of light. According to Einstein's theory of general relativity now the core orbitals of a heavy element are contracted relative to the corresponding orbitals in a lighter element. Therefore it is important to choose a basis set that will run a molecule fast without compromising the desired level of accuracy.

1.3.4 ORCA package

The molecules were optimized using Gaussian 09 program, [88] DMol^3 etc. and the magnetic properties are studied using ORCA program package [89].

The g-tensors, d tensors and hyperfine coupling constants were calculated using ORCA program package [89] of 2.9 and 3.0 version. A general purpose quantum chemistry package, ORCA can carry out Density Functional Theory as well as *ab initio* methods like Coupled Cluster method, Møller-Plesset perturbation theory etc. It can study large molecules and transition metal complexes and their spectroscopic properties. ORCA uses standard Gaussian basis functions and is parallelized hence reducing the time for calculation. For optimization, ORCA calculates equilibrium structures (minimum and transition states) using the quasi Newton method (an iterative method) with the well-known BFGS update, the Powell or Bofill update. The optimization is carried out either in redundant internal coordinates (recommended) or Cartesian displacement coordinates. There are a number of standard basis sets for optimization that can be selected from simple 'input' feature. Aldrich's basis sets like TZV and def-2 are being used for optimization calculations. ORCA provides a large range of hybrid functionals like BP86, B3LYP, PW1PW etc.

The output gives information about the g tensor (relativistic mass correction, diamagnetic spin-orbit term, paramagnetic spin-orbit term (OZ/SOC), the isotropic g-value and the orientation of the total tensor. It also gives the information containing contributions spin flip terms contributing towards the total D-tensor. Also ORCA can compute hyperfine coupling constants and its various components.

1.3.4.1 Treatment of Spin-Orbit Coupling:

For convenience, an effective reduced one-electron SOC operator, $h_k^{SO}(i)$, with three spatial components μ=x, y , z is assumed. Previously, the parameterization by Koseki *et al*. [90–92] was used in the ORCA programs

$$h_k^{SO}(i) = \sum_A \xi(r_{iA}) l_k^A(i)$$

where $l_k^A(i)$ is the k^{th} component of the orbital angular momentum operator relative to centre A, and $\xi(r_{iA})$ is a suitable radial operator, i.e.,

$$\xi(r_{iA}) = \frac{\alpha^2}{2} \frac{Z_A^{eff}}{|r_i - R_A|^3}$$

where Z_A^{eff} is a semiempirical nuclear charge for atom A at position R_A. The operator $\hat{h}_k^{SO}$ SO is treated by an accurate mean-field (SOMF) approximation to the full Breit-Pauli SOC operator. The SOMF approachhas been developed by Hess *et al.* [93]. SOMF introduces two further approximations: (a) the neglect of multicenter SOC terms and (b) the use of atomic self-consistent field orbitals and theiraveraged occupation numbers in place of the molecular charge densities.

For the interpretation of the SOC contribution to the total ZFS values various approaches were brought forward, viz., Coupled-Perturbed (CP), Pederson-Khanna (PK) and Quasi-Restricted Orbital (QRO). These simple treatments have been successfully applied to many large high-spin systems. Their mathematical formulation can be derived successfully.

1.3.4.2 Quasi-Restricted Orbitals Approach:

This simple approach seeks a connection to the many-electron treatment. The SOC operator is assumed to be an effective reduced one-electron operator ($h_p^{SO}(i)$) treated by the spin-orbit mean-field (SOMF) approximation [94]. In such a case, the general treatment shows that for a system with ground-state spin S to the second-order-only excited states with total spin $\Delta S = S' - S = 0, \pm 1$ contribute to the D-tensor. Excited states with ΔS=0 correspond to the same-spin excited states and those with $\Delta S = \pm 1$ are referred to as spin-flip excited states [95]. Zein *et al.* have outlined a simple treatment to construct approximate spin eigen-functions from a spin-unrestricted DFT wavefunction [96]. This result was termed as Quasi-restricted Orbital (QRO) treatment since it is based on a set of “quasi-restricted” orbitals that are constructed from the spin-unrestricted natural orbitals [97,98]. They nearly coincide withthe restricted open Kohn-Sham (ROKS) orbitals [99,100]. Their equation is:

$$D_{pq}^{(SOC)} = D_{pq}^{\alpha\alpha} + D_{pq}^{\beta\beta} + D_{pq}^{\alpha\beta} + D_{pq}^{\beta\alpha} = -\frac{1}{4S^2}\sum_{ta} M_{ta}^{pq;\alpha\alpha} - \frac{1}{4S^2}\sum_{it} M_{it}^{pq;\beta\beta} + \frac{1}{2}\frac{1}{S(S-1)}\sum_{t\neq u} M_{tu}^{pq;\alpha\beta} + \frac{1}{2}\frac{1}{(S+1)(2S+1)}\sum_{ia} M_{ia}^{pq;\beta\alpha} \qquad (1)$$

with

$$M_{rs}^{pq;\sigma\sigma'} = \frac{\langle\psi_r|h_p^{SOC}|\psi_s\rangle\langle\psi_s|h_q^{SOC}|\psi_r\rangle}{\epsilon_s^{\sigma'} - \epsilon_r^{\sigma}}$$

where $p, q = x, y, z$ $i, j =$doubly occupied QROs, t,u=singly occupied QROs, and a,b=virtual QROs. The first two terms in equation (1) correspond to the contribution of the same-spin excited states and the $D^{\alpha\beta}$ term corresponds to the spin-flips in the singly occupied molecular orbitals (SOMOs) and $D^{\beta\alpha}$ accounts for the states that arise from the shell-opening excitations [101].

1.3.4.3 *Pederson-Khanna Approach (PK):*

Pederson and Khanna (PK) formulation is based on UKS treatments [102]. They used an uncoupled perturbation theory to develop an equation for calculating the spin-orbit coupling contribution to the D_{Tot}. The D_{SOC} part of the D_{Tot} may then be expressed conveniently as follows:

$$D_{pq}^{(SOC)} = D_{pq}^{\alpha\alpha} + D_{pq}^{\beta\beta} + D_{pq}^{\alpha\beta} + D_{pq}^{\beta\alpha}$$
$$= \frac{1}{4S^2}\left(-\sum_{i_\alpha a_\alpha} M'^{pq}_{i_\alpha a_\alpha} - \sum_{i_\beta a_\beta} M'^{pq}_{i_\beta a_\beta} + \sum_{i_\alpha a_\beta} M'^{pq}_{i_\alpha a_\beta} + \sum_{i_\beta a_\alpha} M'^{pq}_{i_\beta a_\alpha}\right)$$

With $$M'^{pq}_{r_\sigma s_{\sigma'}} = \frac{\left\langle\psi_r^\sigma\middle|h_p^{SOC}\middle|\psi_s^{\sigma'}\right\rangle\left\langle\psi_s^{\sigma'}\middle|h_q^{SOC}\middle|\psi_r^\sigma\right\rangle}{\epsilon_s^{\sigma'} - \epsilon_r^\sigma}$$

1.3.4.4 *Coupled-Perturbed (CP) approach:*

A more general approach for satisfactory SOC contribution to total ZFS is the coupled-perturbed (CP) SCF theory [103,104]. This treatment is based on a single spin-unrestricted determinant formed from HF or KS orbital. In this approach, the perturbed orbitals in the presence of an SOC perturbation are expanded as:

$$\begin{aligned}\psi_i^{pq;\alpha\alpha}(\mathbf{r}) &= \sum_{a_\alpha} M'^{pq}_{i_\alpha a_\alpha}\psi_a^\alpha(\mathbf{r}) + \sum_{a_\beta} M'^{pq}_{i_\beta a_\alpha}\psi_a^\beta(\mathbf{r})\,\psi_i^{pq;\beta\beta}(\mathbf{r}) \\ &= \sum_{a_\alpha} M'^{pq}_{i_\alpha a_\beta}\psi_a^\alpha(\mathbf{r}) + \sum_{a_\beta} M'^{pq}_{i_\beta a_\beta}\psi_a^\beta(\mathbf{r})\end{aligned}$$

$M'^{pq}_{r_\sigma s_{\sigma'}}$ are the components of the mixing coefficients of the spin-up and spin-down orbitals. Frank Neese forwarded that the CP approach along with a hybrid DFT functional leads to a slope of the correlation line (plot of experimental vs. calculated D-values) that is unity [105].

1.3.4.5 *Spin-spin contribution:*

According to McWeeny and Mizuno formula [106] the D_{SS} part of the total D-tensor was estimated on the basis of the ground state Slater determinant, as follows:

$$\begin{aligned}D_{kl}^{(SS)} &= -\frac{g_e^2}{16}\frac{\alpha^2}{S(2S-1)}\sum_{\mu\nu}\sum_{\kappa\tau}\left\{P_{\mu\nu}^{\alpha-\beta}P_{\kappa\tau}^{\alpha-\beta} - P_{\mu\kappa}^{\alpha-\beta}P_{\nu\tau}^{\alpha-\beta}\right\} \\ &\quad \times \left\langle \mu\nu \middle| r_{12}^{-5}\left\{3r_{12,k}r_{12.l} - \delta_{kl}r_{12}^2\right\} \middle| \kappa\tau \right\rangle\end{aligned}$$

where $\boldsymbol{P^{\alpha-\beta}} = P^\alpha - P^\beta$ is the spin density matrix with $P_{\mu n}^\sigma = \sum_{p\sigma} c_{\mu p}^\sigma c_{\nu p}^\sigma$ and c^σ are the MO coefficient matrix of spin σ; α is the fine structure constant ($\sim\frac{1}{137}$ in atomic units); and μ,ν,κ,τ are the atomic basis functions.

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