
Chapter 2

Theoretical Background

The theoretical background for the determination of the magnetic exchange coupling constants from the first principle of magnetism has been discussed here. Theory for zero field splitting parameters and magnitude are also described in this chapter.

2.1. Introduction

In the previous chapter we have discussed the background of the different qualitative methods of how the ground state of a diradical based magnetic species can be estimated. Although these qualitative methods can estimate the ground state of a diradical very effectively; however, the quantification is necessary. Theoretically the quantification of the magnetic nature of a diradical species have been done by estimating the magnetic exchange coupling constant (J). In diradical species J is mainly the energy difference between the triplet and the singlet states. Positive and negative values of J indicate the ferromagnetism and antiferromagnetism respectively. Nonetheless, as far as the applications of the organic diradical based magnetic species are concerned, after evaluating their magnetic characters, one needs to quantify their biological activity such as applicability as magnetic resonance imaging contrast agent (MRICA), as hyperthermic agent, applicability in optoelectronic devices, in spintronic applications and so on. A point to be mentioned here is that, the quantification of a diradical to be applicable as MRICA can be done by the quantitative estimation of spin spin axial and rhombic zero field splitting (ZFS) parameters D , E and also with the static ZFS magnitude a_2 .

2.2. Quantitative Methods: The Hamiltonian

It is known that the magnetic interaction is electronic spin related phenomenon. In organic ferromagnetic diradicals, electronic spins at two different radical centers are aligned parallel to each other whereas in antiferromagnetic substances spins are aligned in antiparallel fashion.¹ Hence, ferromagnetic substances have high spin ground state. For example, organic ferromagnetic diradicals have triplet ground state in contrary antiferromagnetic diradicals have singlet ground state. This indicates that for a moiety to be ferromagnetic it must have singly occupied molecular orbitals as their HOMO and HOMO-1. We now discuss how this interaction energy can be quantified.

Let us consider a diradical with two unpaired electrons at sites 1 and 2. The isotropic interaction between two spin sites, say S_1 and S_2 , can be best described by Heisenberg effective spin exchange Hamiltonian

$$\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2. \quad (2.1)$$

The eigenfunctions of the Heisenberg Hamiltonian are eigenfunction of \hat{S}^2 and \hat{S}_z where S is the total spin angular momentum and is directly related to the energy difference between the spin eigenstates.

Let the two electrons are in $\Psi_a(r_1)$ and $\Psi_b(r_2)$ where r is the spatial coordinate. For a singlet system, the spin part χ_S will be antisymmetric and for triplet χ_T is symmetric. Electrons being fermionic the total wave function must be antisymmetric under the exchange of coordinates which is written as:

$$\begin{aligned} \Psi_S &= \frac{1}{\sqrt{2}}[\Psi_a(r_1)\Psi_b(r_2) + \Psi_a(r_2)\Psi_b(r_1)]\chi_S \\ \Psi_T &= \frac{1}{\sqrt{2}}[\Psi_a(r_1)\Psi_b(r_2) - \Psi_a(r_2)\Psi_b(r_1)]\chi_T. \end{aligned} \quad (2.2)$$

The singlet and triplet energies are given by

$$\begin{aligned} E_S &= \int \Psi_S^* \hat{H} \Psi_S dr_1 dr_2 \\ E_T &= \int \Psi_T^* \hat{H} \Psi_T dr_1 dr_2. \end{aligned} \quad (2.3)$$

The quantity $(E_S - E_T)$ can be estimated assuming χ_S and χ_T to be normalized,

$$E_S - E_T = 2 \int \Psi_a^*(r_1)\Psi_b^*(r_2)\hat{H}\Psi_a(r_2)\Psi_b(r_1)dr_1dr_2. \quad (2.4)$$

Now, we define exchange integral J as

$$J = \int \Psi_a^*(r_1) \Psi_b^*(r_2) \hat{H} \Psi_a(r_2) \Psi_b(r_1) dr_1 dr_2. \quad (2.5)$$

Here the quantity J is called isotropic interaction parameter or magnetic exchange coupling constant. For diradical systems, when J is negative, $S = 0$ is the ground state with anti-parallel spins resulting an antiferromagnetic interaction. In contrast, when J is positive, $S = 1$ is the ground state with parallel orientation of the electronic spins resulting in a ferromagnetic interaction.

In summary, if the two centers interact with each other then the total spin of the diradical system will be $S=0$ and 1 , i.e., singlet and triplet respectively. Due to the electrostatic reason, energy of the singlet and triplet states are separated by a $2J$ energy gap which is defined as

$$2J = E_{S=0} - E_{S=1}. \quad (2.6)$$

An explanation of eq 2.6 is required here. Considering electronic correlation, one can describe the limiting behavior of a diradical molecule in a weak coupling limit. We note that for a ferromagnetic system in weak coupling limit, the spin polarized description of the lowest energy electronic configuration corresponds to all spin up with $S = 1$ and lowest energy configuration with half spin up and half spin down corresponds to $S = 0$. But for an S value in between 0 and 1 , more than one configuration can be written. Therefore, $S = 1$ correctly describes a state with all radical centers with spin up condition. However, $S = 0$ corresponds to a state in which radical moieties have their magnetic electrons equally distributed among localized spin up and spin down orbitals. Hence $E_{S=1}$ gives correct energy for triplet whereas $E_{S=0}$ gives a poor approximation to energy of singlet state. The magnetic exchange coupling constant can be evaluated by determining the proper singlet and triplet energy values from a multiconfigurational approach. However, quantitative description of spin exchange interaction is a difficult task and computationally very expensive.

Nevertheless, many groups have done theoretical research using multiconfigurational techniques.

2.3. Methodology: The Density Functional Theory (DFT) Based Methods

DFT is the powerful methodology for chemical simulation where the energy of the systems can be defined in terms of its electron probability density (ρ), that is, in DFT formalism the electronic energy E is treated as the functional of the electron density $E(\rho)$, so that one to one correspondence between the total electron density of a system and its electronic energy is made. Notable point is that, compared to the *ab initio* methodology the density functional theory based treatments are easy to use in respect of their time consumption and flexibility. The simplicity of DFT based methods over other pure methods can be understood by considering a system with n electrons. In such systems the wavefunctions have 3 coordinates for each electron and there must be one extra coordinate where spin is included. However, the electron density actually depends on the 3 coordinates and independent of the number of total electrons of the system. As a matter of fact, if complexity in the wavefunction is increased for the large systems the electron density keeps up the same number of variables, irrespective of the size of the system.

The density functional concept for the first time was emerged from the work of Fermi and Thomas in late 1920s,² where the energy of a system is expressed as a function of total electron density. In early 1950s, Slater has made the development of Hartree-Fock method to form Hartree-Fock-Slater³ method which is treated today as an ancestor theory of DFT. However, it is the mid 1960s, when Kohn and Sham⁴ have developed a formalism with the introduction of atomic orbitals then the application of DFT in the field of computational chemistry really sets in motion. The difficulties in the representation of the kinetic energy (KE) of a system are the main problem in earlier DFT formalism. The main essence of Kohn-Sham approach to overcome this problem is that they have splitted the KE functional into two different parts. The first part considered electrons are non-interacting particles and this part is calculated exactly, and in the other part the electron-electron interactions are considered by the introduction of a small correction term.

According to the Kohn-Sham formalism the ground state electronic energy of a system having n electrons and N nuclei is written as

$$E(\rho) = -\frac{1}{2} \sum_{i=1}^n \int \Psi_i^*(r_1) \nabla_i^2 \Psi_i(r_1) dr_1 - \sum_{X=1}^N \int \frac{Z_X}{r_{X_i}} \rho(r_1) dr_1 + \frac{1}{2} \iint \frac{\rho(r_1) \rho(r_2)}{r_{12}} dr_1 dr_2 + E^{XC}[\rho], \quad (2.7)$$

where, Ψ_i 's ($i=1, \dots, n$) are called Kohn-Sham orbitals, KE of the noninteracting electrons are represented by the first term, second term accounts for the nuclear-electron repulsion, whereas the last two terms represent the Coulombic repulsion and exchange correlation term which leads to correction to total kinetic energy of the system respectively.

Within the Kohn-Sham orbital formulations the ground state electron density $\rho(r)$ at a point r can be written as

$$\rho(r) = \sum_{i=1}^n |\Psi_i(r)|^2. \quad (2.8)$$

The importance of Kohn-Sham orbitals lies in the fact that the electron density of the total electronic system is calculated from the above equation. To obtain the Kohn-Sham orbital one needs to solve the Kohn-Sham equation for which the application of variational principle to the electronic energy $E(\rho)$ with the charge density (eq 2.8) is required.

$$\hat{h}_i \Psi_i(r_i) = \varepsilon_i \Psi_i(r_i). \quad (2.9)$$

In the above equation \hat{h}_i and ε_i represent the Kohn-Sham Hamiltonian and respective orbital energy. The Kohn-Sham Hamiltonian has the form

$$\hat{h}_i = -\frac{1}{2} \nabla_i^2 - \sum_{X=1}^N \int \frac{Z_X}{r_{X_i}} + \int \frac{\rho(r_2)}{r_{12}} dr_2 + V^{XC}(r_1), \quad (2.10)$$

where V^{XC} is the functional derivative of the exchange correlation energy and the description of this term causes the major challenge of DFT methodology, which is given by

$$V^{XC}[\rho] = \frac{\delta E^{XC}[\rho]}{\delta \rho}. \quad (2.11)$$

Hence, having known the E^{XC} , the term V^{XC} can be obtained readily. In Kohn-Sham density functional theory starting from the tentative charge density ρ the dependence of E^{XC} on electron density is used to calculate V^{XC} . Once the initial set of Kohn-Sham orbitals is obtained, these orbitals are used to obtain the superior electron density from eq (2.8). Until the density and the E^{XC} meet the certain convergence criteria the process is repeated again and again. At last, from eq (2.7) the electronic energy is calculated.

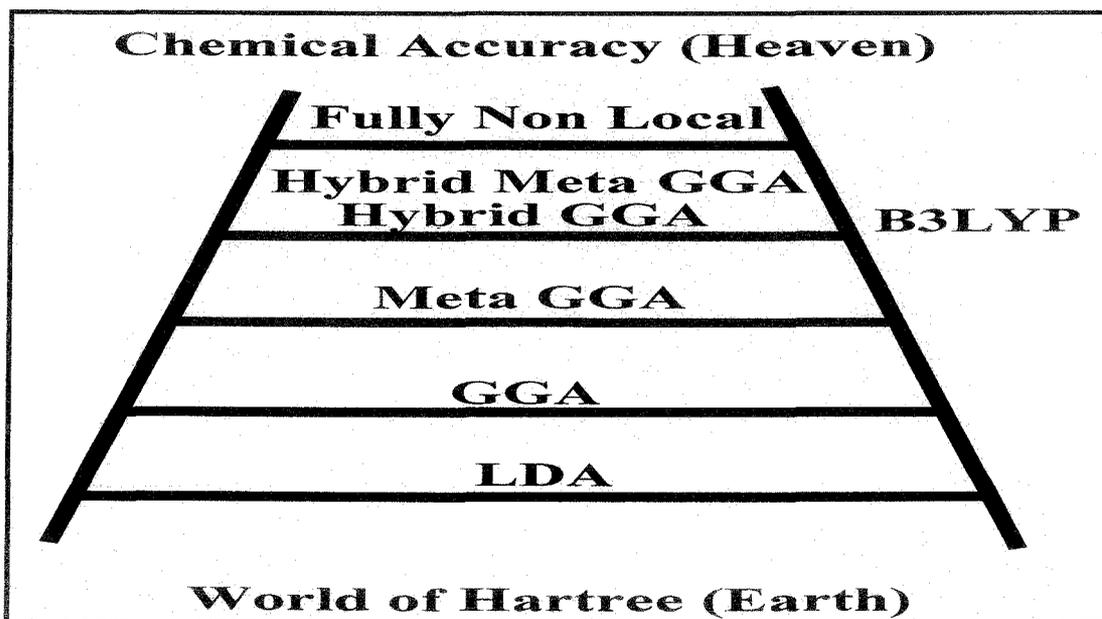
One point to be noted here is that, the exchange correlation energy (E^{XC}) is separated in two terms, namely the exchange term (E^X), the interactions between the electrons having same spin and the correlation term (E^C), the interactions between the electrons having opposite spins. The respective functionals are known as exchange functional and correlation functional correspondingly

$$E^{XC}[\rho] = E^X[\rho] + E^C[\rho]. \quad (2.12)$$

Today, one can find different functionals depending on the variation of different values of exchange and correlation functional. However, Perdew and Schmidt⁵ have successfully represented their vision of the progress of DFT functionals in the form of Jacob's ladder, the famous allusion from the book of *Genesis* (28, 10-12), in a DFT symposium in Menton, France. The ladder has five different rungs depicting the five different generations of DFT functionals (Scheme 2.1). One gets local density approximation (LDA) in the first rung, generalized gradient approximation (GGA) stands in the second rung, meta generalized gradient approximation (M-GGA) remains in the third rung, whereas the hybrid generalized gradient approximation (H-GGA) and hybrid meta generalized gradient approximation (HM-GGA) stand in the fourth rung and the fully nonlocal

approximation remains in the last rung when moving from the lower to the higher steps in the Jacob's ladder. If one climbs up with the ladder one needs to assume more and more sophisticated and complicated approximation and reach the heaven of chemical accuracy. A point to be mentioned here is that, each rung has its own drawbacks and advantages. Although the better rung gives better results than its lower one, however, the choice of functionals somehow depends on the problems in hand.

Scheme 2.1. The vision of Perdew for Jacob's ladder of five generation DFT functionals from the world of Hartree to the heaven of chemical accuracy, with the indication of most popular density functional B3LYP at the fourth rung of the ladder.



The H-GGA functional has possessed a new dimension in the field of density functional study especially after the birth of B3LYP having 20% Hartree-Fock exchange in 1994. The most popular and widely used B3LYP functional contains Becke 3 parameter exchange in addition to Lee-Yang-Parr correlation functional.⁶ There are very few alternatives of B3LYP functional for average quantum chemical problems. If publication is a criterion then from its birth to 2005, the B3LYP is the most accepted one. Many competitive functionals of B3LYP, like M0X suite⁷ of functionals are still mounting. However, it is

expected that the supremacy of popular B3LYP may continue for another 4-5 years or more. At last, the property and obviously the type of the systems under study is the key factor of choosing accurate functionals. All these discussions are nicely portrayed in a nice review of Ramos and coworkers.⁸

2.4. Broken Symmetry: Noodleman's Approach

A reliable and computationally less expensive solution to estimate the exchange coupling constant (J) is provided by Density Functional Theory (DFT) based methodologies. To date, the best technique to calculate the S - T energy gap is the well known broken symmetry (BS) method. This method was developed by Noodleman and coworkers.⁹ In this method, the spin-polarized, triplet state from unrestricted formalism ($\langle S^2 \rangle = 2$ for diradical) and a broken-symmetry (BS) solution is needed. According to Noodleman "when the magnetic orbitals, i.e., the singly occupied orbital of two spin bearing monomers are allowed to interact by overlapping in self-consistent field procedure, a state of mixed spin symmetry and lowered space symmetry is obtained. This is referred to as the mixed spin or broken symmetry state." The BS state is not an eigenstate of \hat{H} . It has the expectation value of $\langle S^2 \rangle$ equal to 1 for a diradical. It is assumed to be an equal admixture of a singlet and a triplet state. States of pure spin symmetry can be retrieved from the BS state using projection operator method. A detailed theoretical description of the BS state is given below.

Following the description of the BS state given by Caballol et al.,¹⁰ we write broken symmetry triplet state in unrestricted formalism as $|T'\rangle = |\dots\phi_A\phi_B\rangle$, where ϕ_A and ϕ_B are the open shell localized spin up orbitals. If one assumes that the spin contamination is small enough to neglect its effect, then one can easily approximate that $|T'\rangle = |T\rangle$ where $|T\rangle$ represents pure triplet. In case of broken symmetry solutions, two types of solutions are possible. These are

$$\begin{aligned} |BS_1\rangle &= |\dots\bar{m}n\rangle \\ |BS_2\rangle &= |\dots m\bar{n}\rangle. \end{aligned} \tag{2.13}$$

The two magnetic orbitals m and n are expressed as

$$\begin{aligned} m &= c_1\phi_A + c_2\phi_B \\ n &= c_2\phi_A + c_1\phi_B, \end{aligned} \quad (2.14)$$

where $(c_1^2 + c_2^2) = 1$. Using these BS solutions one can write the spin adopted singlet function S' (not the pure singlet, S) as

$$|S'\rangle = \frac{|BS_1\rangle + |BS_2\rangle}{\sqrt{2(1 + \langle BS_1|BS_2\rangle)}}, \quad (2.15)$$

where $\langle BS_1|BS_2\rangle$ is the overlap integral between the two non-orthogonal BS Slater determinant. Similarly one can write the triplet with $S_z = 0$ as

$$|T'\rangle = \frac{|BS_1\rangle - |BS_2\rangle}{\sqrt{2(1 - \langle BS_1|BS_2\rangle)}}. \quad (2.16)$$

From the energy expectation values of S' and T' one can express that the intramolecular exchange coupling constant J as

$$J = E_{S'} - E_{T'} = \frac{2(E_{BS} - E_{T'})}{1 + \langle BS_1|BS_2\rangle}. \quad (2.17)$$

Assuming that the spin polarization of the closed shells can be neglected, the quantity $\langle BS_1|BS_2\rangle$ can be approximated as the square of simple overlap integral between the magnetic orbitals $S_{ab} = \langle m|n\rangle$. Hence the J value can be written as

$$J = \frac{(E_{BS} - E_{T'})}{1 + S_{ab}^2}. \quad (2.18)$$

As discussed earlier, in a single determinantal approach, because of the much less spin contamination in the high-spin state, $E_{T'}$ can be approximated by the energy of the triplet state that is achieved from a direct computation i.e., $E_{T'} \approx E_T$. In contrast, the BS state is often found as spin-contaminated. Therefore, to eliminate the effect of spin contamination from the energy of the BS state, spin-projected methods have been applied. Eq (2.18) is valid when there is only one pair of magnetic orbitals.

The BS method was further investigated for various systems with different degrees of overlap between the magnetic orbitals. The following three spin-projected equations are the results obtained from the same basic methodology and valid for different general cases depending on the degrees of overlap between the magnetic orbitals:

$$J^{GND} = \frac{({}^{DFT}E_{BS} - {}^{DFT}E_T)}{S_{\max}^2}, \quad (2.19)$$

$$J^{BR} = \frac{({}^{DFT}E_{BS} - {}^{DFT}E_T)}{S_{\max}(S_{\max} + 1)}, \quad (2.20)$$

$$J^Y = \frac{({}^{DFT}E_{BS} - {}^{DFT}E_T)}{\langle S^2 \rangle_T - \langle S^2 \rangle_{BS}}. \quad (2.21)$$

These three relations differ in their applicability. For a sufficiently small overlap between the magnetic orbitals, eq (2.18) reduces to eq (2.19).^{9,11} This expression is given by Giensberg, Noodleman and Davidson. In another work, Bencini et al.¹² and Ruiz et al.¹³ have proposed an expression for evaluation of J which was further modified by Illas et al.^{14,10} (eq 2.20) for the systems with sufficiently large overlap integral, that generally happens for binuclear transition metal complexes. On the other hand, eq (2.21), can be reduced to eq (2.19) and eq (2.20) in the weak and strong overlap limits respectively, has been derived by Yamaguchi et al.¹⁵ One notable point to be mentioned here is that, in my entire thesis work I

have used eq (2.21), the expression given by Yamaguchi and coworkers¹⁵ for the quantification of magnetic exchange coupling constant (J) values.

2.5. Zero Field Splitting (ZFS) Parameters

The direction dependent magnetic properties of a material are known as magnetic anisotropy. Magnetically isotropic material, in absence of magnetic field has no preferential direction of their magnetic moments; however, in absence of such field magnetically anisotropic materials align their magnetic moments with one of the easy axes. The easy axis means an energetically favorable direction of spontaneous magnetization. The magnetic anisotropy may lead to the splitting of $2S+1$ magnetic sublevels in absence of external magnetic field. This phenomenon is called zero field splitting (ZFS). The magnetic anisotropy also known as ZFS can characterize the geometric and electronic environment of a radical having spin $> 1/2$.¹⁶ The reason for the quantification of the ZFS data, that is, its utility in the biomedical applications (D , E and a_2 the axial and rhombic parameters and magnitude of ZFS respectively) and the theoretical background of ZFS are discussed below.

Rajca and co-workers have synthesized and characterized various nitroxide diradicals and polyradicals. Nonetheless, the most interesting bio-features of these radicals are that they can be used as magnetic resonance contrast agents (MRICAs).¹⁷ To design MRICAs in a rational manner, one needs to know the ZFS parameters. The electron spin correlation time is a leading factor for clearer MRI scans with enhanced contrast. The easy estimation of the electron spin correlation time is possible by the ZFS data.¹⁸ The sign and magnitude of axial ZFS parameter D is crucial in determining different magnetic properties of a system. Rajca and co-workers have established that the diradical and polyradical systems of organic origin can be successfully used as MRICAs.¹⁷ The ZFS arises from two contributions, namely the direct electron-electron magnetic-dipole spin-spin (SS) (to first order in perturbation theory) interaction and the spin-orbit coupling (SOC) (to second order in perturbation theory) of the electronically excited state with the ground state.¹⁶ The second order correction to the total energy, originating entirely from the spin orbit coupling interactions in molecular systems, is estimated with the help of the following expression

$$\Delta_2 = \sum_{\sigma\sigma'} \sum_{ij} M_{ij}^{\sigma\sigma'} S_i^{\sigma\sigma'} S_j^{\sigma'\sigma} \quad (2.22)$$

where different spin degrees of freedoms are represented by σ , and i, j denote coordinate levels x, y and z . However, spin-orbit interaction happens to be dominant in case of heavy metal ion systems; in case of organic systems containing lighter elements, this part contributes a negligible amount to the total magnetic anisotropy of the system.

On the other hand, the SS coupling contribution is the main source of ZFS in case of organic radicals.¹⁹ The ZFS value arising from the SS interactions can be estimated through effective spin Hamiltonian

$$\hat{H}_{ZFS} = \sum_{ij} \mathbf{D}_{ij} \hat{S}_i \hat{S}_j, \quad (2.23)$$

where \mathbf{D}_{ij} is the ZFS tensor, \hat{S}_k is the k 'th Cartesian component of the total electron spin operator. Rearrangement of the \mathbf{D}_{ij} leads to

$$\hat{H}_{ZFS} = D \left(\hat{S}_z^2 - \frac{1}{3} \hat{S}^2 \right) + E \left(\hat{S}_x^2 - \hat{S}_y^2 \right), \quad (2.24)$$

where D and E are axial and rhombic ZFS parameters respectively.²⁰ The spin spin coupling interaction appears as a dipole dipole interaction²¹

$$\hat{H}_{SS} = \frac{\alpha^2}{2} \sum_{i,j} \left[\frac{\vec{s}_i \cdot \vec{s}_j}{r_{ij}^3} - \frac{3(\vec{s}_i \cdot \vec{r}_{ij})(\vec{s}_j \cdot \vec{r}_{ij})}{r_{ij}^5} \right] \quad (2.25)$$

The single ground-state Kohn-Sham determinant approximates the result of the SS coupling part of the ZFS tensor as the expectation over the single determinant, thereby²²

$$D_{kl}^{(SS)} = \frac{g_e \alpha^2}{4 S(2S-1)} \left\langle 0SM_S \left| \sum_i \sum_{j \neq i} \frac{r_{ij}^2 \delta_{kl} - 3(r_{ij})_k (r_{ij})_l}{r_{ij}^5} \times \left\{ 2\hat{S}_{iz} \hat{S}_{jz} - \hat{S}_{ix} \hat{S}_{jx} - \hat{S}_{iy} \hat{S}_{jy} \right\} \right| 0SM_S \right\rangle, \quad (2.26)$$

where α is the fine structure constant, g_e is the gyromagnetic ratio. The operators \hat{S}_{mn} signify n 'th component of m 'th spin vector and r_{ij} is the distance between spins i and j ; k and l run over x , y , and z coordinates. McWeeny and Mizuno expressed the above equation using the spin density matrix as²³

$$D_{kl}^{(SS)} = \frac{g_e}{4} \frac{\alpha^2}{S(2S-1)} \sum_{\mu\nu} \sum_{\kappa\lambda} \{P_{\mu\nu}^{\alpha-\beta} P_{\kappa\lambda}^{\alpha-\beta} - P_{\mu\kappa}^{\alpha-\beta} P_{\nu\lambda}^{\alpha-\beta}\} \times \left\langle \mu\nu \left| r_{12}^{-5} \left\{ \{3r_{12,k} r_{12,l}\} - \delta_{kl} r_{12}^2 \right\} \right| \kappa\lambda \right\rangle. \quad (2.27)$$

Here $P^{\alpha-\beta} = P^\alpha - P^\beta$ is the spin density matrix in the atomic-orbital basis, and $\mu, \nu, \kappa, \lambda$ are the basis functions.¹⁸ The ZFS parameters D and E are determined from the tensor components $D_{kl}^{(SS)}$, in the following way²⁴

$$D = D_{zz} - \frac{1}{2}(D_{xx} + D_{yy}) \quad (2.28)$$

$$E = \frac{1}{2}(D_{xx} - D_{yy}). \quad (2.29)$$

The D and E values are utilized to determine the static ZFS magnitude (a_2) using the formula

$$a_2 = \sqrt{\left(\frac{2}{3} D^2 + 2E^2 \right)}. \quad (2.30)$$

From this a_2 , the longitudinal electron spin relaxation rate $\frac{1}{T_{1e}}$ can be estimated via²⁵

$$\frac{1}{T_{1e}(B_0)} = \frac{2}{5} a_2^2 \tau_R \left[\frac{1}{1 + \omega_0^2 \tau_2^2} + \frac{4}{1 + 4\omega_0^2 \tau_2^2} \right] + \frac{12}{5} a_{2T}^2 \tau' \left[\frac{1}{1 + \omega_0^2 \tau'^2} + \frac{4}{1 + 4\omega_0^2 \tau'^2} \right], \quad (2.31)$$

where B_0 is the external magnetic field, ω_0 is the Larmor frequency, τ_2 and τ' are the reduced spectral densities and a_{2T} is the transient ZFS magnitude.²⁶ Larger a_2 corresponds to a faster relaxation rate $\frac{1}{T_{1e}}$.²⁵

2.6. Conclusions

In this chapter we have discussed the theoretical background for the quantification of the ground state of a diradical based magnetic species. A brief discussion on Hamiltonian relevant to magnetic molecules such as Heisenberg effective spin exchange Hamiltonian is given. We also discuss different studies on this subject density functional theory (DFT) based methods. A brief focus on the development of DFT from Fermi and Thomas (1920) to Kohn and Sham (1965) is also discussed. In recent years broken symmetry (BS) approach in DFT framework has gained much attention for its effectiveness in handling very critical problems with less computational effort. A section of this chapter has been attributed to the BS formalism. Computational methodology on different contemporary research articles is also given. At last, a systematic theoretical discussion on the magnetic anisotropy which is also called zero field splitting (ZFS) as well as the need of its quantification for design a magnetic resonance imaging contrast agents is made. These theoretical methodologies would be followed systematically in this thesis.

2.7. References and Notes

- (1) (a) Coronado, E.; Delhaè, P.; Gatteschi, D.; Miller, J. S. *Molecular Magnetism: From Molecular Assemblies to the Devices*, Eds.; Nato ASI Series E, Applied Sciences, Kluwer Academic Publisher: Dordrecht, Netherland, 1996, Vol. 321. (b) Kahn, O. *Molecular Magnetism*, New York, VCH, 1993. (c) Blundell, S. J. *Magnetism in Condensed Matter*; Oxford University Press: New York, 2001.
- (2) Fermi, E. *Rend. Accad. Naz. Lincei* **1927**, *6*, 602. (b) Thomas, L. H. *Proc. Cambridge Philos. Soc.* **1927**, *23*, 542.
- (3) Hohenberg, P.; Kohn, W. *Phys. Rev. B* **1964**, *136*, 864.
- (4) Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140*, 1133.
- (5) Perdew, J. P.; Schmidt, K. Jacob's ladder of density functional approximations for the exchange-correlation energy. In *Density Functional Theory and Its applications to Materials*; Van Doren, V. E.; Van Alseoy, K.; Geerlings, P. Eds.; AIP Press: New York, 2001.
- (6) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (c) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
- (7) (a) Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Phys.* **2005**, *123*, 161103. (b) Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Theory Comput.* **2006**, *2*, 364. (c) Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215. (d) Zhao, Y.; Truhlar, D. G. *J. Chem. Phys.* **2006**, *125*, 194101. (e) Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157.
- (8) Sausa, S. F.; Fernandes, P. A.; Ramos, M. J. *J. Phys. Chem. A* **2007**, *111*, 10439.
- (9) (a) Noodleman, L. *J. Chem. Phys.* **1981**, *74*, 5737. (b) Noodleman, L.; Baerends, E. J. *J. Am. Chem. Soc.* **1984**, *106*, 2316. (c) Noodleman, L.; Davidson, E. R. *Chem. Phys.* **1986**, *109*, 131. (d) Noodleman, L.; Peng, C. Y.; Case, D. A.; Mouesca, J.-M. *Coord. Chem. Rev.* **1995**, *144*, 199.
- (10) Caballol, R.; Castell, O.; Illas, F.; Moreira I. de P. R.; Malrieu, J. P. *J. Phys. Chem. A*, **1997**, *101*, 7860.
- (11) Ginsberg, A. P. *J. Am. Chem. Soc.* **1980**, *102*, 111.

- (12) (a) Bencini, A.; Totti, F.; Daul, C. A.; Doclo, K.; Fantucci, P.; Barone, V. *Inorg. Chem.* **1997**, *36*, 5022. (b) Bencini, A.; Gatteschi, D.; Totti, F.; Sanz, D. N.; McCleverty, J. A.; Ward, M. D. *J. Phys. Chem. A* **1998**, *102*, 10545.
- (13) Ruiz, E.; Cano, J.; Alvarez, S.; Alemany, P. *J. Comput. Chem.* **1999**, *20*, 1391.
- (14) (a) Martin, R. L.; Illas, F. *Phys. Rev. Lett.* **1997**, *79*, 1539. (b) Caballol, R.; Castell, O.; Illas, F.; Moreira, I. de P. R.; Malrieu, J. P. *J. Phys. Chem. A* **1997**, *101*, 7860. (c) Barone, V.; di Matteo, A.; Mele, F.; Moreira, I. de P. R.; Illas, F. *Chem. Phys. Lett.* **1999**, *302*, 240. (d) Illas, F.; Moreira, I. de P. R.; de Graaf, C.; Barone, V. *Theor. Chem. Acc.* **2000**, *104*, 265. (e) de Graaf, C.; Sousa, C.; Moreira, I. de P. R.; Illas, F. *J. Phys. Chem. A* **2001**, *105*, 11371. (f) Illas, F.; Moreira, I. de P. R.; Bofill, J. M.; Filatov, M. *Phys. Rev. B* **2004**, *70*, 132414.
- (15) (a) Yamaguchi, K.; Takahara, Y.; Fueno, T.; Nasu, K. *Jpn. J. Appl. Phys.* **1987**, *26*, L1362. (b) Yamaguchi, K.; Jensen, F.; Dorigo, A.; Houk, K. N. *Chem. Phys. Lett.* **1988**, *149*, 537. (c) Yamaguchi, K.; Takahara, Y.; Fueno, T.; Houk, K. N. *Theo. Chim. Acta* **1988**, *73*, 337.
- (16) Duboc, C.; Ganyushin, D.; Sivalingam, K.; Collomband, M.; Neese, F. *J. Phys. Chem. A* **2010**, *114*, 10750.
- (17) (a) Olankitwanit, A.; Kathirvelu, V.; Rajca, S.; Eaton, G. R.; Eaton, S. S.; Rajca, A. *Chem. Commun.* **2011**, *47*, 6443. (b) Spagnol, G.; Shiraishi, K.; Rajca, S.; Rajca, A. *Chem. Commun.* **2005**, 5047.
- (18) Tucker, B. J. *Dissertation in Chemistry in the Graduate College of the University of Illinois at Urbana-Champaign*, 2010.
- (19) Zein, S.; Duboc, C.; Lubitz, W.; Neese, F. *Inorg. Chem.* **2008**, *47*, 134.
- (20) Loboda, O.; Minaev, B.; Vahtras, O.; Schimmelpfennig, B.; Ågren, H.; Ruud, K.; Jonsson, D. *Chem. Phys.* **2003**, *286*, 127.
- (21) McGlynn, S. P.; Azumi, T.; Kinoshita, M. *Molecular Spectroscopy of the Triplet State*, Prentice Hall, Engelwood Clins, NJ, 1969.
- (22) Harriman, J. E. *Theoretical Foundations of Electron Spin Resonance*, Academic Press, New York, 1987.
- (23) McWeeny, R.; Mizuno, Y. *Proc. R. Soc., London*, **1961**, *A259*, 554.

- (24) Boča, R. *Theoretical Foundations on Molecular Magnetism*, Elsevier, Netherlands, 1999.
- (25) Benmelouka, M.; Borel, A.; Moriggi, L.; Helm, L.; Merbach, A. E. *J. Phys. Chem. B* **2007**, *111*, 832.
- (26) Belorizkya, E.; Fries, P. H. *Phys. Chem. Chem. Phys.* **2004**, *6*, 2341.