

## **CHAPTER 2**

### **Theoretical background**

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The theoretical background for the estimation of the magnetic exchange coupling constant ( $J$ ) is described in this chapter. The theoretical background for the determination of the transport property of molecules is also discussed here.

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## 2.1 Introduction

The quantification of magnetic nature of molecular systems renders a wide area for theoretical exertion. The magnetic property of a molecule or radical can be estimated by the magnetic exchange coupling constant ( $J$ ). In diradical species  $J$  is quantified by the difference in energy between triplet and the singlet states.

For many electron systems, the Hartree-Fock (HF) method provides a solution of Schrödinger equation based on variational principle. The main limitation of HF method is that the electrons are moving independently, and they have no correlation. After that different post-HF methods such as coupled cluster methods or configuration interaction methods are introduced. Though, an adequate computation of  $J$  can be achieved through Post-HF methods, they are not so popular as they are immensely resource intensive.<sup>1</sup> In recent years density functional theory-based approach is extensively used to compute the magnetic exchange coupling constant.

## 2.2 Density Functional Theory

DFT is the powerful methodology that overcomes the inadequacy of HF and computational cost of post-HF methods by using the electronic density as the basic variable instead of the multi-electronic wave function. In DFT formalism the electronic energy  $E$  of the systems can be expressed as the functional of electron density  $E(\rho)$ . Density functional theory-based methodology is easy to use compared to the *ab initio* methodology due to the low time consumption and flexibility. Besides, for a large system the complexity in the wave function is increased, however the electron density sustains the same number of variables which is independent on the size of the system. In late 1920s,<sup>2</sup> the concept of density functional was emerged for the first time from the work of Fermi and Thomas.

The energy functional have three terms i.e., the kinetic energy (KE), potential energy from the external field and the electron-electron interaction energy and can be written as;

$$E[\rho] = T[\rho] + V_{ext}[\rho] + V_{ee}[\rho]. \quad (2.1)$$

The external potential energy is expressed as

$$V_{ext}[\rho] = \int \hat{V}_{ext} \rho(r) dr. \quad (2.2)$$

Though KE has a common form for every system, the major problem in earlier DFT formalism is the difficulties in representing the KE of a system. In Kohn-Sham approach, the KE functional have split into two different parts to overcome this problem. The first part represents the kinetic energy of non-interacting particles and

this part can be calculated exactly and another part that comes from the introduction of a small correction term due to the electron-electron interactions.

Here we introduce the quantity  $E_{xc}[\rho]$  which is called the exchange-correlation energy and represented as

$$E_{xc}[\rho] = (T[\rho] - T_s[\rho]) + (V_{ee}[\rho] - V_H[\rho]). \quad (2.3)$$

i.e.,  $E_{xc}$  is the sum of the error made by using a non-interacting kinetic energy and by treating the electron-electron interaction classically.

Therefore, the energy functional can be written as

$$E[\rho] = T_s[\rho] + V_{ext}[\rho] + V_H[\rho] + E_{xc}[\rho]. \quad (2.4)$$

The exchange correlation energy ( $E_{xc}$ ) is often decomposed as

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho]. \quad (2.5)$$

Where  $E_x$  is the exchange energy due to the interactions between the electrons with same spin and  $E_c$  is the correlation energy due to the interactions between the electrons having opposite spins. The respective functional are the exchange functional and the correlation functional.

In Kohn-Sham approach the system is composed of  $n$  non-interacting electrons described by a single determinantal wavefunction in  $n$  "orbitals" $\Psi_i$ . The kinetic energy is represented as,

$$T_s[\rho] = -\frac{1}{2} \sum_i^n \langle \Psi_i | \nabla^2 | \Psi_i \rangle. \quad (2.6)$$

The suffix represents that this is the kinetic energy of a system with non-interacting electrons and not the true kinetic energy.

The ground state electron density  $\rho(r)$  can be written as

$$\rho(r) = \sum_i^n |\Psi_i|^2. \quad (2.7)$$

The electron–electron Coulomb interaction which is known as the Hartree energy can be represented in terms of density as

$$V_H[\rho] = \frac{1}{2} \int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} dr_1 dr_2. \quad (2.8)$$

The Kohn-Sham equation needs to solve in order to obtain the Kohn-Sham orbital. For which application of variational principle to the electronic energy  $E(\rho)$  is needed.

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

Here  $\hat{h}_i$  and  $\varepsilon_i$  signify the Kohn-Sham Hamiltonian and the respective orbital energy. The Kohn-Sham Hamiltonian has the form

$$\hat{h}_i = \left[ -\frac{1}{2} \nabla^2 + v_{ext}(r) + \int \frac{\rho(r')}{|r - r'|} dr' + v_{xc}(r) \right] \quad (2.10)$$

Where  $V_{xc}$  is a local potential which is the functional derivative of exchange correlation energy with respect to the density and is given by

$$v_{xc}(r) = \frac{\delta E_{xc}[\rho]}{\delta \rho}. \quad (2.11)$$

After obtaining the initial set of Kohn-Sham orbitals, they are used to get the electron density from eq. (2.7). The process is repeated again and again until the  $E_{xc}$  and the density meet the certain convergence criteria.

### 2.3 Spin Hamiltonian and magnetic exchange coupling constant ( $J$ )

The magnetic exchange interaction between two magnetic centers 1 and 2 is generally expressed by the phenomenological Heisenberg spin Hamiltonian

$$\hat{H} = -2J \hat{S}_1 \cdot \hat{S}_2 \quad (2.12)$$

Where  $\hat{S}_1$  and  $\hat{S}_2$  are the respective spin angular momentum operators and  $J$  is the effective exchange coupling constant between two magnetic sites. For a diradical system, a negative  $J$  value indicates the antiferromagnetic interaction with anti-parallel orientation of the spins ( $S = 0$ ) in the ground state and the positive  $J$  value indicates the ferromagnetic interaction with parallel spins ( $S = 1$ ) in the ground state.

The magnetic exchange coupling constant for a diradical with one unpaired electron on each site can be represented as

$$E_{HS} - E_{LS} = -2J. \quad (2.13)$$

Though the single determinantal wave function properly represent the high spin state of a molecule, it cannot adequately signify the singlet state of a molecule in unrestricted formalism which causes spin contamination in such calculations. Multiconfigurational approach can describe the pure spin states in proper way. Many research groups have done the theoretical study using multiconfigurational techniques. However, these methods are computationally very expensive and are difficult to apply in large systems. The broken symmetry method is the way out of this difficulty.

## 2.4 Broken symmetry approach

Till now broken symmetry (BS) approach is the best technique proposed by Noodleman and coworkers to calculate the  $S$ - $T$  energy gap as well as the magnetic exchange coupling constant ( $J$ ).<sup>3</sup> Though the arguments are given in terms of wavefunction theory, the formalism is mostly applied in DFT framework. To determine the magnetic exchange coupling constant, the triplet state ( $\langle S^2 \rangle = 2$ , in case of diradical) from unrestricted formalism and a broken-symmetry (BS) solution is required. According to Noodleman, a state of lowered space symmetry and mixed spin symmetry is obtained when two singly occupied orbital of spin bearing monomers interact by overlapping in self-consistent field procedure. This state is known as the broken symmetry state.

Following are the three spin-projected equations that differ in their applicability depending on the extent of overlap between the magnetic orbitals. When the interaction between magnetic orbitals are sufficiently small, the expression for evaluating magnetic exchange coupling constant is given by Giensberg, Noodleman and Davidson.<sup>3,4</sup>

$$J = -\frac{E_{HS} - E_{BS}}{S_{max}^2} \quad (2.14)$$

where  $E_{HS}$  and  $E_{BS}$  represents the energies of the high-spin (HS) and BS states respectively.

On the other hand, Bencini et al.<sup>5</sup> and Ruitz et al.<sup>6</sup> have proposed an expression given in eq. 2.15 to estimate  $J$  which is applicable for large interaction with large overlap integral that usually occurs for binuclear transition metal complexes.

$$J = -\frac{E_{HS} - E_{BS}}{S_{max}(S_{max} + 1)} \quad (2.15)$$

However, the spin projected method given by Yamaguchi<sup>7</sup> to evaluate the magnetic exchange coupling constant is given in eq. 2.16 that are applicable for whole range of coupling strengths.

$$J = -\frac{E_{HS} - E_{BS}}{\langle S^2 \rangle_{HS} - \langle S^2 \rangle_{BS}} \quad (2.16)$$

In my thesis work, I have used the eq. 2.16 given by Yamaguchi to determine the magnetic exchange coupling constant ( $J$ ) values.

## 2.5 Electron transport (Density functional method)

A general approach to determine whether a molecule can transport electrical current or not, is to look at their current vs. voltage ( $I$ - $V$ ) profile. As an unbalanced situation arises under an applied bias voltage, the transport phenomena of a system deviate from equilibrium proviso. Therefore, nonequilibrium green's function method (NEGF)<sup>8</sup> is used to address the inadequacy of nonequilibrium behavior of the transport property. In addition to the  $I$ - $V$  plot, the transmission probabilities also give an insight about the transport property of molecular systems.

The standard Kohn-Sham one-electron Hamiltonian (within the nonlocal-pseudopotential approximation) is written as<sup>9</sup>

$$\hat{H} = \hat{T} + \sum_I V_I^{local}(r) + \sum_I \hat{V}_I^{KB} + V^H(r) + V^{xc}(r). \quad (2.17)$$

Where  $I$  is an atom index, the kinetic energy operator  $\hat{T} = -\frac{1}{2}\nabla^2$ , the total Hartree and XC potentials are represented by  $V^H(r)$  and  $V^{xc}(r)$ , the local and nonlocal Kleiman and Bylander (KB) parts of pseudopotential of the atom  $I$  are  $V_I^{local}(r)$  and  $\hat{V}_I^{KB}$ .

In Landauer approach,<sup>10</sup> a single molecule (or in general a nanoscopic structure) is sandwiched between two macroscopic electrodes. The zero-temperature conductance ( $G$ ) is determined by

$$G(V) = \frac{dI(V)}{dV} \quad (2.18)$$

where  $I$  is the current and  $V$  is the bias voltage. The zero-bias conductance (for low voltages) is given by

$$G = G_0 T(E_F) \quad (2.19)$$

Where  $G_0$  is the conductance quantum,  $G_0=2e^2/h$ .  $T$  is the transmission function and often calculated for zero bias. The electronic structure and thus  $T$  may change considerably under a large applied bias. Transmission measures the tendency for an electron to tunnel over the junction.  $E_F$  is the Fermi energy of the electrodes.

Molecular transport properties through electrode-molecule-electrode junction uses the Landauer–Imry–Büttiker approximation,<sup>10</sup> with nonequilibrium Green's functions (NEGF)<sup>8</sup> and spin-unrestricted Kohn-Sham density functional theory (UKSDFT).<sup>11</sup>

In the coherent tunnelling regime (i.e., for short molecular bridges with large gap between the one-particle energy levels and Fermi energies of the electrodes and for low temperature) the current ( $I_s(V)$ ) for electron spins  $s \in \{\alpha, \beta\}$  relates to the transmission function  $T_s(E, V)$  by the following equation<sup>12</sup>

$$I_s(V) = \frac{e}{h} \int_{E_F - \frac{eV}{2}}^{E_F + \frac{eV}{2}} dE T_s(E, V) \quad (2.20)$$

Here  $h$  Planck's constant,  $e$  is the unit charge,  $V$  is the symmetrically applied finite bias voltage,  $E$  is the energy and  $T_s(E, V)$  is the transmission function. The number of electrons on the molecule is supposed to be constant in time. In the Landauer–Imry–Büttiker approximation,<sup>10</sup> zero voltage conductance ( $(dI/dV)_{V=0}$ ) is proportional to  $T(E_F)$ . Therefore, it is reasonable to take integration over  $E_F - \frac{eV}{2}$  to  $E_F + \frac{eV}{2}$ .

In the NEGF approach,  $T_s$  can be calculated from a trace over matrices ( $\Gamma_{L/R,s}$ ) that describes the coupling of central region to the left and right electrodes, and the retarded and advanced Green's functions ( $G_{C,s}^{r/a}$ ) of the electrode-molecule-electrode system<sup>13</sup> as

$$T_s(E, V) = \text{tr}(\Gamma_{R,s} G_{C,s}^r \Gamma_{L,s} G_{C,s}^a) \quad (2.21)$$

The advanced Green's function is the complex conjugate of the retarded Green's function.

For a finite cluster electrode-molecule-electrode System,  $\Gamma_{X,S}$  and  $G_{C,S}^r$  are calculated from the Fock and overlap matrices.<sup>12</sup>

$$\Gamma_{X,S} = 2 \text{Im} [(ES_{XC} - H_{XC,S})^\dagger g_{X,S} (ES_{XC} - H_{XC,S})] \quad (2.22)$$

$$G_{C,S}^r = \left( ES_C - H_{C,S} + i \frac{1}{2} \Gamma_{R,S} + i \frac{1}{2} \Gamma_{L,S} \right)^{-1} \quad (2.23)$$

The overlap and Fock matrices are divided into central, right-electrode and left-electrode regions.  $H_{XC,S}$  and  $S_{XC}$  represent the coupling block of molecule and electrode X in the Fock and overlap matrix, respectively. Whereas the molecule (i.e., “central region”) subblocks of these matrices are designated by the subscript C.  $g_{X,S}$  is the Green’s function matrices of the isolated and infinite electrodes.

In my thesis work, I have calculated the transmission property using the ARTAIOS code developed by Herrmann et al.<sup>12,14,15</sup>

## 2.6 References

- (1) Orio, M.; Pantazis, D. A.; Neese, F. *Photosynth. Res.* **2009**, *102*, 443-453.
- (2) Fermi, E. *Rend. Accad. Naz. Lincei.* **1927**, *6*, 602-607. (b) Thomas, L. H. *Proc. Cambridge Philos. Soc.* **1927**, *23*, 542-548.
- (3) (a) Noodleman, L. *J. Chem. Phys.* **1981**, *74*, 5737-5743. (b) Noodleman, L.; Baerends, E. J. *J. Am. Chem. Soc.* **1984**, *106*, 2316-2327. (c) Noodleman, L.; Davidson, E. R. *Chem. Phys.* **1986**, *109*, 131-143. (d) Noodleman, L.; Peng, C. Y.; Case, D. A.; Mouesca, J.-M. *Coord. Chem. Rev.* **1995**, *144*, 199-244.
- (4) Ginsberg, A. P. *J. Am. Chem. Soc.* **1980**, *102*, 111-117.
- (5) (a) Bencini, A.; Totti, F.; Daul, C. A.; Doclo, K.; Fantucci, P.; Barone, V. *Inorg. Chem.* **1997**, *36*, 5022-5030. (b) Bencini, A.; Gatteschi, D.; Totti, F.; Sanz, D. N.; McCleverty, J. A.; Ward, M. D. *J. Phys. Chem. A* **1998**, *102*, 10545.
- (6) Ruiz, E.; Cano, J.; Alvarez, S.; Alemany, P. *J. Comput. Chem.* **1999**, *20*, 1391-1400.
- (7) (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*, 537-542. (c) Yamaguchi, K.; Takahara, Y.; Fueno, T.; Houk, K. N. *Theo. Chim. Acta* **1988**, *73*, 337.
- (8) Mahan, G. D. *Many-particle Physics*; Plenum Press: New York, **1990**.



- (9) Soler, J. M.; Artacho, E.; Gale, J. D.; García, A.; Junquera, J.; Ordejón, P.; Sánchez-Portal, D. *J. Phys.: Condens. Matter*. **2002**, *14*, 2745-2779.
- (10) (a) Landauer, R. *IBM J. Res. DeV.* **1957**, *1*, 223–231. (b) M. Buttiker, Y. Imry, R. Landauer and S. Pinhas, *Phys. Rev. B*. **1985**, *31*, 6207-6215.
- (11) (a) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140*, 1133–1138. (b) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *136*, 864–871.
- (12) Herrmann, C.; Solomon, G. C.; Ratner, M. A. *J. Am. Chem. Soc.* **2010**, *132*, 3682-3684.
- (13) (a) Caroli, C.; Combescot, R.; Nozieres, P.; Saint-James, D. *J. Phys. C: Solid State Phys.* **1971**, *4*, 916–929. (b) Meir, Y.; Wingreen, N. S. *Phys. Rev. Lett.* **1992**, *68*, 2512–2516.
- (14) Herrmann, C.; Solomon, G. C.; Subotnik, J. E.; Mujica, V.; Ratner, M. A. *J. Chem. Phys.* **2010**, *132*, 024103(1–17).
- (15) Herrmann, C.; Groß, L.; Steenbock, T.; Solomon, G. C. Artaios — a transport code for postprocessing quantum chemical electronic structure calculations, **2008-2014**.