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Radical Pair Dynamics

[1]J. López-Bonilla, [2]G. Torres-Vega, [3]E. López-Sandoval, [3]A. Rodolfo Samana and [2]J.J. Godina-Nava

[1]ESIME-Zacatenco, IPN, Col. Lindavista, CP 07738, CDMX, México
[2]Departamento de Física CINVESTAV-IPN, Ap. Postal 14-740, CP 07000, CDMX, México
[3]Departamento de Ciẽncias Exatas e Tecnológicas, Universidade Estadual de Santa Cruz,
Campus Soane Nazaré de Andrade, Rodovia Jorge Amado, Km 16, Bairro Salobrinho,
45662-900 Ilhus, BA, Brazil, CEP 22290-180, Rio de Janeiro, R. J. Brazil

Abstract: The Lanczos method has been utilized in a wide variety of research areas in the physical sciences, since atomic matters until nuclear physics, inclusive in the condensed matter and engineering. The method is useful to study the collective properties of a many-body system. We use the classical Lanczos algorithm to diagonalize the Hamiltonian that describes the radical pairs spin dynamics. Radical pairs appear quite often in biological processes, and they are sensitive to external magnetic fields. We also give explicit expressions for the calculation of relevant quantities regard the eigen-information for a radical pair system in the damped two-state approximation. The advantage of this method is that it allows the analysis of large systems involving only the needed information.

Key words: Quantum mechanics, Radical pair model dynamics.

INTRODUCTION

Several biological processes such as the photosynthesis, the geomagnetic orientation of bird migration and the enzymatic reactions can be explained throughout the spin polarization in radical interactions [1-3]. In fact, it is known that magnetic field significantly influences the movement of magnetic particles and induces a change in the final product of chemical reactions. Some chemical reactions like as bond hemolysis or with electron transfer usually create radicals in pairs, with some correlation electron spins. The two unpaired electrons spins, one on each radical, are initially either parallel (a triplet state) or anti-parallel (a singlet state), according to the spin multiplicity of the precursors. The chemistry of radical pairs (RP) is controlled not only by their diffusive motions and their inherent reactivity but also, and more important, by the spin-correlation via the requirement to conserve spin angular momentum. The RP participate in important [4] reactions as intermediates in a wide range of photolytic, thermal and radiolytic processes [5, 17]. Their electron spin-dependent reactivity and magnetic interactions give rise to magnetic polarization phenomena observable by nuclear magnetic resonance and electron paramagnetic resonance spectroscopies [6, 7]. The radical pairs also form the basis of the only well-established mechanism the radical pair mechanism (RPM).

Through this mechanism, an external magnetic field affects the interchange between singlet and triplet RP spin states. The weak magnetic interactions such as the hyperfine and Zeeman interaction of the RP are the only interactions that happen [8, 9], influencing the rates and yields of chemical reactions [10]. Physically, magnetic forces induce this spin state interchange. In fact, the coherent oscillatory interchange of singlet and triplet spin states is driven by intermolecular electron-nuclear Fermi interactions (well known in spectroscopy as a hyperfine coupling). The Zeeman resonance only occurs when one of the two radicals has no hyperfine couplings, such that its energy levels are split only by the interactions with the applied magnetic field. These phenomena have been widely exploited to provide detailed insight concerning free radical chemistry and spin physics [11], photosynthetic energy conversion [12], the structure and folding of proteins [13], and enzyme kinetics [14-16]. The possible existence of quantum effects in biological systems is fascinating. Thereby, in this paper, we illustrate the use of the Lanczos algorithm by giving explicit expressions for eigen values, conditions for steady states, the steady populations and transitions between singlet and triplet spin states of an RP coupled to a nuclear spin all immersed into an external magnetic field.

The radical pair dynamics is a technique that establishes the relationship when two radicals react together and how the interchange between singlet and triplet spin states can be carried out. Radical pair dynamics, and its chemistry, is of interest in biological systems. There are molecules like cytochrome P450 that are part of many biological chemical reactions. These molecules give raise to RP that can interact with a magnetic field and give rise to interesting effects.

Corresponding Author: Dr. J. López-Bonilla, ESIME-Zacatenco, IPN, Col. Lindavista, CP 07738, CDMX, México.

In Section 2, we establish the mathematical model for treating the time evolution of an RP coupled to a 1/2 nuclear spin and immersed in an external magnetic field. This system can be extended to more pairs and more nuclei, but in that case, the method should be implemented numerically. The case we present here can be worked out analytically. We also rewrite the evolution equation for the system's density operator in the super-states representation so that we end up with a linear matrix equation amenable to linear algebra methods. We will use the Lanczos algorithm with this model to determinate some properties of the system. The Lanczos algorithm generates a vector space formed by only the necessary information for the calculation of quantities of interest according to those are needed. It is given a matrix representation for the transition operator (the super-state representation), the Lanczos method transforms such matrix into a symmetric tridiagonal form that permits the fast numerical calculation of eigen values usually when the system is large. When the system is small, even we can use the method to describe the behavior of the system analytically. In Sec. 3, we briefly explain how to implement the Lanczos algorithm to the RP system, in the damped two-state approximation. In Sec. 4, as an illustration, we apply the results of the previous sections, to transitions between singlet and spin zero triplet state of a general RP. We evaluate the eigen-information of the system, the realization of steady states, the steady state populations and transition probabilities.

RADICAL PAIR DYNAMICS

The quantum dynamics of a so-called RP coupled to one single 1/2 spin nucleus came described by the Liouville equation:

$$-\hat{\hat{L}}\hat{\rho}(t) = \frac{\partial \hat{\rho}(t)}{\partial t}, \tag{1}$$

where the transition super operator $\hat{\hat{L}}$ acting on the weight density operator $\hat{\rho}(t)$ or strenght function. This term characterizes the global dynamics of the system and is expressed by

$$\hat{\hat{L}} = \frac{i}{\hbar}[\hat{H}, \hat{\rho}] + \frac{1}{2\hbar}\{\hat{\Gamma}, \hat{\rho}\}, \tag{2}$$

where

$$[\hat{H}, \hat{\rho}] = \hat{H}\hat{\rho} - \hat{\rho}\hat{H}, \quad \text{and} \quad \{\hat{\Gamma}, \hat{\rho}\} = \hat{\Gamma}\hat{\rho} + \hat{\rho}\hat{\Gamma}\,. \tag{3}$$

The operator $\hat{H}$ is the Hamiltonian operator of the system given as [17]

$$\hat{H} = \mu_B(g_a S_{1z} + g_b S_{2z})B + A_1 I \cdot S_1 + A_2 I \cdot S_2 - J(r)\left(2S_1 \cdot S_2 + \frac{1}{2}\right). \tag{4}$$

The first two-term describes the Zeeman interaction between the spines of the RP with a magnetic field (MF) B; μ_B is the magnetic moment of the electron, g_a and g_b are the gyro-magnetic factors of the radicals a and b, respectively. The hyperfine constant are A_i for the interaction between the spin of the nucleus, $\hat{I}$, and the spin of the electrons, $\hat{S}_i$, $i = 1,2$.

The exchange interaction between unpaired electrons of the partners is a function of inter-radical distance r between them and expressed by the interchange relation $J(r) = J_0 e^{-\xi r}$ and molecular dynamics modulated it. Thus, the spin dynamics result being a small range function of exchange potential given by the last term of Eq. (4). We are going to use the spin population (SPo) to investigate not only the properties of individual character as the level energies and the Eigen system, but also those collective properties as local density of states and the interchange between singlets and triplets SPo [21]. The production and decay of SPo through the operator $\hat{\Gamma}$ will be modeled, which is diagonal in the spin states spectral representation. The decay of SPo can be due to chemical reaction generating products.

We use the representation of the singlet $|S>$ and triplet states, $|T_->$, $|T_0>$ and $|T_+>$ of the RP electrons and the nucleus spin one half states $|\downarrow>$ and $|\uparrow>$ as the vector basis to study the evolution equation Eq.(1):

$$|a_1>=|S>|\uparrow>,|a_2>=|T_0>|\uparrow>,|a_3>=|T_+>|\uparrow>,|a_4>=|T_->|\uparrow>,$$
$$|a_5>=|S>|\downarrow>,|a_6>=|T_0>|\downarrow>,|a_7>=|T_+>|\downarrow>,|a_8>=|T_->|\downarrow>, \quad (5)$$

Mathematically the action of the Hamiltonian Eq. (4) on these vectors is

$$\widehat{H}|a_1>=J(r)|a_1>+\left(\gamma_{ab}+\frac{\Delta A}{2}\right)|a_2>-\frac{\Delta A}{\sqrt{2}}|a_7>, \quad (6)$$

$$\widehat{H}|a_2>=\left(\gamma_{ab}+\frac{\Delta A}{2}\right)|a_1>-J(r)|a_2>+\frac{\sigma_A}{\sqrt{2}}|a_7>, \quad (7)$$

$$\widehat{H}|a_3>=\left(\eta_{ab}+\frac{\sigma_A}{2}-J(r)\right)|a_3>, \quad (8)$$

$$\widehat{H}|a_4>=-\left(\eta_{ab}+\frac{\sigma_A}{2}-J(r)\right)|a_4>+\frac{\Delta A}{\sqrt{2}}|a_5>+\frac{\sigma_A}{\sqrt{2}}|a_6>, \quad (9)$$

$$\widehat{H}|a_5>=J(r)|a_5>+\left(\gamma_{ab}-\frac{\Delta A}{2}\right)|a_6>+\frac{\Delta A}{\sqrt{2}}|a_4>, \quad (10)$$

$$\widehat{H}|a_6>=\frac{1}{2\sqrt{2}}A_1|a_4>+\left(\gamma_{ab}-\frac{\Delta A}{2}\right)|a_5>-J(r)|a_6>, \quad (11)$$

$$\widehat{H}|a_7>=\left(\eta_{ab}-\frac{\sigma_A}{2}-J(r)\right)|a_7>+\frac{1}{2\sqrt{2}}A_1(|a_2>-|a_1>), \quad (12)$$

$$\widehat{H}|a_8>=\left(-\eta_{ab}+\frac{\sigma_A}{2}-J(r)\right)|a_8>+\frac{1}{2\sqrt{2}}A_2(|a_2>-|a_1>), \quad (13)$$

where

$$\gamma_{ab}=\frac{1}{2}\mu_B(g_a-g_b)B=\frac{1}{2}\mu_B\Delta gB, \quad (A_1-A_2)=2\Delta A, \quad (14)$$

$$\eta_{ab}=\frac{1}{2}\mu_B(g_a+g_b)B, \quad (A_1+A_2)=2\sigma_A. \quad (15)$$

More information respect this spin Hamiltonian and their operational action can be found in the book of Hayashi [17].

At this point, we can use the familiar linear algebra tools to change to so-called super-state representation. In this representation the density operator is replaced for a vector whose index are formed by the product of two indices of the discrete representation $|a_i>$ given by the Eq. (5). If the dimension of the $|a_k>$ representation is N, then the new index have N^2 values. The matrix element of Eq. (1) is

$$-\sum_{j,m} L\,(kl,mj) < a_m|\hat{\rho}|a_j >= \frac{\partial}{\partial t} < a_k|\hat{\rho}|a_l >, \tag{16}$$

where

$$L(kl,mj) = \frac{i}{\hbar}\left(\delta_{jl} < a_k|\hat{H}|a_m > -\delta_{mk} < a_j|\hat{H}|a_l >\right) + \frac{1}{2\hbar}\left(\delta_{jl} < a_k|\hat{\Gamma}|a_m > +\delta_{mk} < a_j|\hat{\Gamma}|a_l >\right). \tag{17}$$

For the case of a damped two-level system, as our application example, the transition matrix $L(kl,mj)$ acquires the form

$$L = \begin{pmatrix} \gamma_1 & -iV^* & iV & 0(18) \\ -iV & -i\Delta E + \frac{1}{2}(\gamma_1+\gamma_2) & 0 & iV(19) \\ iV^* & 0 & i\Delta E + \frac{1}{2}(\gamma_1+\gamma_2) & -iV^*(20) \\ 0 & iV^* & -iV & \gamma_2 \end{pmatrix}, \tag{18}$$

where $V =< a_1|\hat{H}|a_2 >$, $\Delta E =< a_2|\hat{H}|a_2 > -< a_1|\hat{H}|a_1 >$, and $\gamma_i =< a_i|\hat{\Gamma}|a_i >$.

We now elucidate some properties of the RP system using the Lanczos algorithm for that purpose.

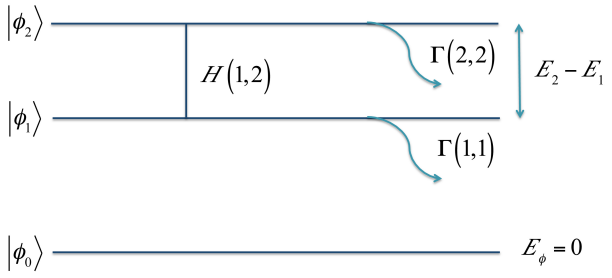

Fig. 1: Two level system to analyze the $S \Leftrightarrow T$ interconversion.

LANCZOS METHOD

Nowadays the Lanczos method is typically used to find in a numerical way the eigen-information of large matrices representing real systems. However, it can also be used to determine relevant collective properties like the dynamics of a physical system [18-20]. The Lanczos method is also employed for solving systems of equations and is associated with the typical eigenvalue problem

$Ax = \lambda x,\ A \in \mathbb{C}^{N\times N},\ x \in \mathbb{C}^N,$

where $\lambda \in \mathbb{R}$, because $A = A^T$, for a large sparse symmetric matrix A. Again, the Lanczos method defines a computational tool which is very efficient to diagonalize a quantum mechanical Hamiltonian [21], more if we are interested in the evaluation of few eigen values and the corresponding eigenvectors. In fact, it is a iterative scheme in which, starting with an

initial vector (chosen from their Hilbert space), converts the eigen value problem associated with a quantum mechanical system into one that evaluate the eigen sytem of a Jacobi matrix, converting it in a real symmetric tridiagonal matrix. The first concept at hand is that we knew that a vector $\vec{P} = \{p_1, p_2, \dots, p_N\}$ is called orthonormal if it satisfied the following conditions:

$$\begin{gathered} p_j^T p_j = 1, \\ \vec{P}^T = \vec{P}^{-1}, \\ Norm(p_j) = \| p_j \|^2 = 1, \\ p_k^T p_j = 0,\ k \neq j. \end{gathered} \tag{19}$$

Ordinarily, the power method is used to find the eigenvector associated with the maximum eigen value, $x^{j+1} = \eta A x^j$, with η a normalization factor to avoid that power be so large, x^{j+1}. When $j \to \infty$, $x^{j+1} \to v_1$, the eigenvector associated with eigenvalue λ_1, satisfying the hierarchy $\lambda_1 > \lambda_2 \geq \lambda_3 \dots \lambda_N$. The maximum eigenvalue is obtained using the Raleigh Quotient

$$R(A, x^j) = \frac{(x^j)^T A x^j}{Norm(x^j)^2}.$$

Case in which we cannot use the QR method because it is inefficient, because QR approach does not maintain the sparsity of the new matrix generated by the iteration process if A is sparse. It is evident that, with this process, we can evaluate only one eigenvector and one eigen value. For this reason, Lanczos method is crucial. One step to arrive the Lanczos method is kept in safe each iteration used by the power method. The result is a set of vectors $\{v,\ Av,\ A^2v, \dots, A^{j-1}v\}$, where each one of this vectors spans the so-called Krylov subspace of a matrix very close to A

$$\mathcal{K}_j(Av) = span\{v, Av, A^2v, \dots, A^{j-1}v\}.$$

After n iterations, $\{v, Av, A^2v, \dots, A^{j-1}v\}$ are linearly independent and x can be generated from this space. Following the power method, after n-iterations we have an eigenvector, the sequence is linearly dependent, but we need a sequence of linearly independent vectors. The main step in the Lanczos method is orthogonalise such vectors. Then, we have N orthonormal vectors $\vec{P} = \{p_1,\ p_2, \dots,\ p_N\}$, taking k elements of this set in a such way that is satisfied the condition $\vec{P}^T\vec{P} = I$. The process implies a projection of the N-dimensional Hamiltonian onto a subspace associated with a chosen starting vector. Now we change A to a tridiagonal matrix F applying a similarly transformation

$$\vec{P}^T A \vec{P} = \mathrm{F} \Rightarrow A\vec{P} = \vec{P}\mathrm{F},$$

thus, we can define the matrix F as

$$\mathrm{F}_{k+1,k} = \begin{pmatrix} \alpha_1 & \beta_1 & 0 & \dots & \dots & \dots & 0 \\ \beta_1 & \alpha_2 & \beta_2 & 0 & \dots & \dots & 0 \\ 0 & \beta_2 & \alpha_3 & \beta_3 & 0 & \dots & \vdots \\ \vdots & 0 & \dots & \dots & \dots & \dots & \vdots \\ \vdots & \dots & \dots & \dots & \dots & \dots & \beta_{k-1} \\ 0 & \dots & \dots & \dots & 0 & \beta_{k-1} & \alpha_k \\ 0 & \dots & \dots & \dots & \dots & 0 & \beta_k \end{pmatrix} \in \mathbb{C}^{k+1,k}.$$

After $k \leq N$ iterations

$$A\vec{P}_k = \vec{P}_{k+1}\mathrm{F}_{k+1,k} = \vec{P}_k\mathrm{F}_{k,k} + \beta_{k+1}q_{k+1}\vec{e}_k^T,$$

$$A \in \mathbb{C}^{N,N},\ \vec{P}_k \in \mathbb{C}^{N,k},\ \vec{P}_{k+1} \in \mathbb{C}^{N,k+1}, \mathrm{F}_{k+1,k} \in \mathbb{C}^{k+1,k}.$$

The $\vec{e}_k$ is the coordinate vector whose kth component is 1 and the other elements are 0. The matrix F represent the orthogonal projection of A onto the subspace spanned by the vectors $\vec{P}_k$ [23]. The conjecture $A\vec{P} = \vec{P}\mathrm{F}$ establish that:

$$A[p_1, p_2, \dots, p_k] = [p_1, p_2, \dots, p_k]\mathrm{F}_k.$$

The left-hand side of the matrix in their first column results in

$$Ap_1 = \alpha_1 p_1 + \beta_1 p_2,$$

by iteration till i-th term results:

$$Ap_i = \alpha_i p_i + \beta_i p_{i-1} + \beta_{i+1} p_{i+1}, \;\; i = 1,2,3, \dots, k.$$

To calculate the scalar coefficientsα_i, β_i, we multiply the above equation by p_i^T obtaining:

$$p_i^T A p_i = p_i^T \beta_i p_{i-1} + p_i^T \alpha_i p_i + p_i^T \beta_{i+1} p_{i+1} = \beta_i p_i^T p_{i-1} + \alpha_i p_i^T p_i + \beta_{i+1} p_i^T p_{i+1}$$

$$= \alpha_i p_i^T p_i, \Rightarrow \alpha_i = p_i^T A p_i.$$

Now multiplying by p_{i+1}^T:

$$p_{i+1}^T A p_i = p_{i+1}^T \beta_i p_{i-1} + p_{i+1}^T \alpha_i p_i + p_{i+1}^T \beta_{i+1} p_{i+1}$$

$$= \beta_i p_{i+1}^T p_{i-1} + \alpha_i p_{i+1}^T p_i + \beta_{i+1} p_{i+1}^T p_{i+1} = \beta_{i+1} p_{i+1}^T p_{i+1}, \Rightarrow \beta_{i+1} = p_{i+1}^T A p_i.$$

Using the following recurrence relation, we use the value of β_i

$$r_i \equiv \beta_i p_{i+1} = Ap_i - \alpha_i p_i - \beta_{i-1} p_{i-1}.$$

We assume that $\beta_i \neq 0 \Rightarrow \beta_i = Norm(r_i)$. We determine the next Lanczos vector p_{i+1} by orthogonalizing the vector Ap_i

$$p_{i+1} = \frac{r_i}{\beta_i}.$$

In summary, we need choose a $vector = p_0$, let $\beta_0 = Norm(p_0)$, initiate iterations and evaluate $p_l = r/\beta_{l-1} \mapsto r = Ap_l \mapsto r = r - p_{l-1}\beta_{l-1} \mapsto \alpha_l = p_l^T r \mapsto r = r - p_l \alpha_l$. If it is necessary orthogonalise, then assign $\beta_l = Norm(r)$ and compute the approximate eigen value of F_l. The step l can acquire values as small as $2\sqrt{N}$ [24]. In theory since $\vec{P}^T \mathrm{P} = I$ and $\beta_{k+1} = 0$ for some $k \leq N$, then the eigenvalue obtained for F_k will be an eigenvalue for A.

A useful feature of this method is that the dimension of the generated vector space can be smaller than the dimension of the original representation of the system, eliminating redundant quantities as in the case of degenerate energy eigen values. In this section, we apply this method to the damped two-level system of Eq. (1) implementing the rules of the Lanczos method into a program written with friendly Mathematica 7.0 software from Wolfram Co.

Following the Lanczos recipe, we choose a starting vectors to generate the dual Lanczos vector space. For this purpose we call $|p_0)$, and $(r_0|$ as two vectors named right and left respectively:

1.- Such vectors will multiply the matrix to diagonalize L by left and right sides respectively, $lp0 = Simplify[L.p_0]$ and $lr0 = Simplify[r_0.L]$.

2.- Calculate the first Lanczos parameter $\alpha_0 = Simplify[r_0.lp0]$, $\beta 12 = Simplify[lr0.lp0 - \alpha_0^2]$,

3.- Evaluate the next Lanczos vectors, $p_1 = Simplify[(lp0 - \alpha_0 p_0)/Sqrt[\beta 12]$, and $r1 = Simplify[(lr0 - \alpha_0 r_0)/Sqrt[\beta 12]$ and so on.

In our problem, we begin with a physical situation that represents a singlet born spin state

$$(r_0| = (1\ 0\ 0\ 0)^T\,, \quad \text{and} \quad |p_0) = \begin{pmatrix}1\\0\\0\\0\end{pmatrix}. \tag{20}$$

The basis vectors $\{(r_s|\}$ and $\{(p_{s'}|\}$ satisfying the orthonormality relation Eq. (19). The rest of Lanczos vectors are calculated using the following recursion relations:

$$\begin{aligned}\beta_{s+1}(r_{s+1}| &= (r_s|(L-\alpha_s) - \beta_s(r_{s-1}|\,,\\ \beta_{s+1}|p_{s+1}) &= (L-\alpha_s)|p_s) - \beta_s|p_{s-1})\,,\end{aligned} \tag{21}$$

the only non-vanishing matrix elements of the transition super operator $\hat{\hat{L}}$ in the dual Lanczos representation are

$$\alpha_s = (r_s|L|p_s), \quad \text{and} \quad \beta_{s+1} = (r_{s+1}|L|p_s) = (r_s|L|p_{s+1})\,, \tag{22}$$

with $\beta_{-1} = 0$. A valuable relationship for the determination of β_{s+1} is

$$\beta_{s+1}^2 = (r_s|L^2|p_s) - \alpha_s^2 - \beta_s^2. \tag{23}$$

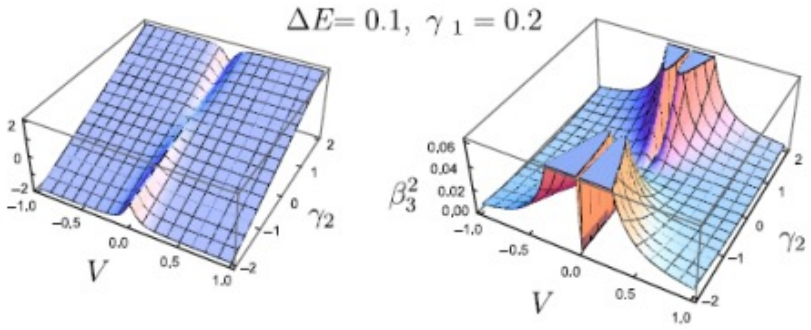

Fig. 2: Values of α_2, and β_3^2 for $\Delta E = 0.1$, and $\gamma_1 = 0.2$. When β_3 becomes zero, the Lanczos space has a dimension of only three and then the dynamic is simpler than for other values.

The result of the application of the Lanczos method to our damped two-level system, Eq. (18), is

$$\begin{aligned}&\alpha_0 = \gamma_1\,, \quad \beta_1^2 = -2|V|^2\,,\\ &(r_1| = \frac{1}{\sqrt{2}|V|}(0\ -V^*\ V\ 0)^T, \quad |p_1) = \frac{1}{\sqrt{2}|V|}\begin{pmatrix}0\\-V\\V^*\\0\end{pmatrix},\\ &\alpha_1 = \frac{1}{2}(\gamma_1+\gamma_2)\,, \quad \beta_2^2 = -(\Delta E)^2 - 2|V|^2\,.\end{aligned} \tag{24}$$

The next set of Lanczos vectors is

$$(r_2| = -\frac{1}{|V|\sqrt{2((\Delta E)^2 + 2|V|^2)}}(0 \;\; V^*\Delta E \;\; V\Delta E \;\; 2|V|^2)^T,$$

$$|p_2) = -\frac{1}{|V|\sqrt{2((\Delta E)^2 + 2|V|^2)}}\begin{pmatrix} 0 \\ V\Delta E \\ V^*\Delta E \\ 2|V|^2 \end{pmatrix}, \tag{25}$$

$$\alpha_2 = \frac{4|V|^2\gamma_2 + (\Delta E)^2(\gamma_1 + \gamma_2)}{2((\Delta E)^2 + 2|V|^2)},$$
$$\beta_3^2 = \frac{(\Delta E)^2|V|^2(\gamma_2 - \gamma_1)^2}{2((\Delta E)^2 + 2|V|^2)^2}.$$

Plots of α_2 and β_3^2 for a particular value of ΔE and γ_1 are shown in Fig. 2. The value of β_s determines the dimension of the Lanczos space. If $\beta_s = 0$ for $s \leq N$, then the dimension is s precisely. Thus, we see that the dynamics of the damped two-level system becomes simpler for some values of the parameters of the model, when $V = 0, \pm\infty$ and when $\gamma_2 = 0$, if $\Delta E = 0.1$ and $\gamma_1 = 0.2$. In fact, a Lanczos space of dimension three appears when $V = 0, \pm\infty$, or when $\gamma_2 = \gamma_1$, or when $\Delta E = 0, \pm\infty$.

The last Lanczos vectors and parameters are:

$$(r_3| = -\frac{1}{\sqrt{(\Delta E)^2 + 2|V|^2}}(0 \; V^* \; V \; \Delta E)^T,$$

$$|p_3) = -\frac{1}{\sqrt{(\Delta E)^2 + 2|V|^2}}\begin{pmatrix} 0 \\ V \\ V^* \\ \Delta E \end{pmatrix}, \tag{26}$$

$$\alpha_3 = \frac{(\Delta E)^2\gamma_2 + |V|^2(\gamma_1 + \gamma_2)}{(\Delta E)^2 + 2|V|^2}, \quad \beta_4^2 = 0.$$

A plot of α_3 for $\Delta E = 0.1$ is shown in Fig. 3.

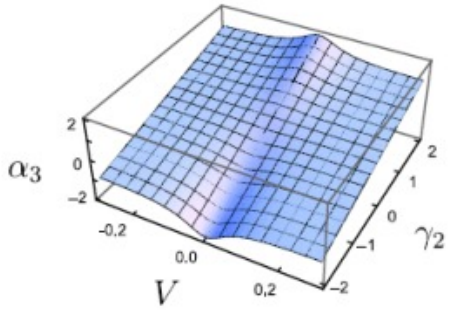

Fig. 3: Values of α_3 for $\Delta E = 0.1$.

THE RADICAL PAIR TRANSITION $S \leftrightarrow T_0$

To exemplify the use of the above algorithm, in this section we determine some properties of the transition $S \leftrightarrow T_0$. In this transition, only the states $|a_1>$ and $|a_2>$, (in Eq. 5), participate and the sub-Hamiltonian to be considered is

$$X_{S\leftrightarrow T_0} = \begin{pmatrix} J & F_1 \\ F_1 & -J \end{pmatrix},$$

where $F_1 = \gamma_{ab} - \frac{\Delta A}{2}$. We also include damping of the states.

For the case in which the radicals are electrons $g_a = g_b$. Thus, the corresponding transition matrix in super-states representation is reduced to the form:

$$\hat{\hat{X}} = \begin{pmatrix} \gamma_1 & \frac{i}{4}\Delta A & -\frac{i}{4}\Delta A & 0 \\ \frac{i}{4}\Delta A & i2J(r) + \frac{1}{2}(\gamma_1+\gamma_2) & 0 & -\frac{i}{4}\Delta A \\ -\frac{i}{4}\Delta A & 0 & -i2J(r) + \frac{1}{2}(\gamma_1+\gamma_2) & \frac{i}{4}\Delta A \\ 0 & -\frac{i}{4}\Delta A & \frac{i}{4}\Delta A & \gamma_2 \end{pmatrix}, \tag{27}$$

moreover, the corresponding Lanczos matrix is:

$$\hat{\hat{X}} = \begin{pmatrix} \gamma_1 & i\frac{\Delta A}{2\sqrt{2}} & 0 & 0 \\ i\frac{\Delta A}{2\sqrt{2}} & \frac{\eta_{12}}{2} & \frac{iR}{2\sqrt{2}} & 0 \\ 0 & \frac{iR}{2\sqrt{2}} & \frac{(\Delta A)^2\gamma_2 + 16J^2(r)\eta_{12}}{R^2} & \frac{2\sqrt{2}\Delta A\, J(r)\, \rho_{12}}{R^2} \\ 0 & 0 & \frac{2\sqrt{2}\Delta A\, J(r)\, \rho_{12}}{R^2} & \frac{64J^2(r)\gamma_2 + (\Delta A)^2\eta_{12}}{R^2} \end{pmatrix}, \tag{28}$$

where we use the following definitions:

$$R = \sqrt{(\Delta A)^2 + 32J^2(r)}\,, \quad \eta_{12} = \gamma_1 + \gamma_2\,,$$
$$\rho_{12} = \gamma_1 - \gamma_2 \tag{29}$$

The eigen values of this matrix are:

$$\lambda_1 = \frac{\eta_{12}}{2} - i\omega\,,$$

$$\lambda_2 = \frac{\eta_{12}}{2} + i\omega \,, \tag{30}$$

$$\lambda_3 = \frac{\eta_{12}}{2} - \gamma_3 \,,$$

$$\lambda_4 = \frac{\eta_{12}}{2} + \gamma_3 \,,$$

where

$$\omega = \frac{1}{2\sqrt{2}}\sqrt{(\Delta A)^2 + 16J^2(r) - \rho_{12}^2 + r_4} \,,$$

$$\gamma_3 = \frac{1}{2\sqrt{2}}\sqrt{r_4 - (\Delta A)^2 - 16J^2(r) + \rho_{12}^2} \,, \tag{31}$$

$$r_4 = \sqrt{(\Delta A)^4 + 2(\Delta A)^2(16J^2(r) - \rho_{12}^2) + (16J^2(r) + \rho_{12}^2)^2} \,.$$

The frequency has a small variation respect γ_1 and γ_2 with a maximum when they are equal. In contrast, the decay rate γ_3 is minimum when $\gamma_2 = \gamma_1$ and experiences a large variation with $\gamma_i \;\; i = 1, 2$.

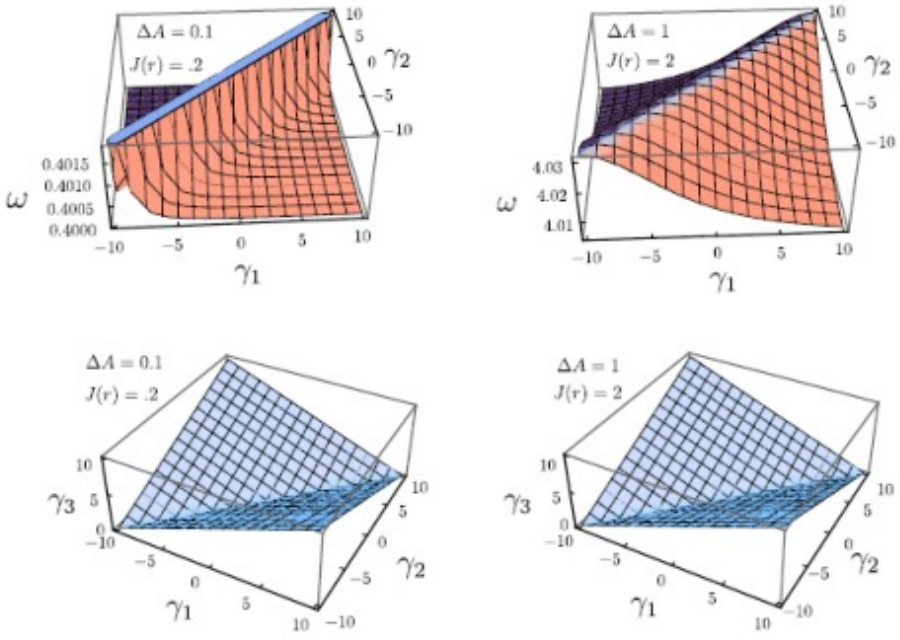

Fig. 4: Frequency ω and decay rate γ_3 for two sets of values of ΔA and $J(r)$.

The eigenvectors are

$$|e_1) = \begin{pmatrix} \frac{\sqrt{(\Delta A)^2 + 32J^2}}{8(\Delta A)^2 J\rho_{12}}[\sqrt{2}(\Delta A)^2\rho_{12} - (-16J^2 - \rho_{12}^2 + r_1)(r_3 + \sqrt{2}\rho_{12})] \\ i\frac{\sqrt{(\Delta A)^2 + 32J^2}}{8(\Delta A)^2 J\rho_{12}}[(\Delta A)^2 + 16J^2 - \rho_{12}^2 + r_1 - \sqrt{2}\rho_{12}r_3] \\ -\frac{1}{8\Delta A J\rho_{12}}[(\Delta A)^2 r_3 + 32J^2(r_3 + \sqrt{2}\rho_{12})] \\ 1 \end{pmatrix} \quad (32)$$

$$|e_2) = \begin{pmatrix} \frac{\sqrt{(\Delta A)^2 + 32J^2}}{8(\Delta A)^2 J\rho_{12}}[\sqrt{2}(\Delta A)^2\rho_{12} + (-16J^2 - \rho_{12}^2 + r_1)(r_3 - \sqrt{2}\rho_{12})] \\ \frac{\sqrt{(\Delta A)^2 + 32J^2}}{8\Delta A J\rho_{12}}[(\Delta A)^2 + 16J^2 - \rho_{12}^2 + r_1 + \sqrt{2}\rho_{12}r_3] \\ \frac{1}{8\Delta A J\rho_{12}}[(\Delta A)^2 r_3 + 32J^2(r_3 - \sqrt{2}\rho_{12})] \\ 1 \end{pmatrix} \quad (33)$$

$$|e_3) = \begin{pmatrix} \frac{\sqrt{(\Delta A)^2 + 32J^2}}{8(\Delta A)^2 J\rho_{12}}[\sqrt{2}(\Delta A)^2\rho_{12} + (16J^2 + \rho_{12}^2 + r_1)(r_2 + \sqrt{2}\rho_{12})] \\ i\frac{\sqrt{(\Delta A)^2 + 32J^2}}{8\Delta A J\rho_{12}}[(\Delta A)^2 + 16J^2 - \rho_{12}^2 - r_1 - \sqrt{2}\rho_{12}r_2] \\ \frac{1}{8\Delta A J\rho_{12}}[(\Delta A)^2 r_2 + 32J^2(r_2 + \sqrt{2}\rho_{12})] \\ 1 \end{pmatrix} \quad (34)$$

$$|e_4) = \begin{pmatrix} \frac{\sqrt{(\Delta A)^2 + 32J^2}}{8(\Delta A)^2 J\rho_{12}}[\sqrt{2}(\Delta A)^2\rho_{12} - (16J^2 + \rho_{12}^2 + r_1)(r_2 - \sqrt{2}\rho_{12})] \\ i\frac{\sqrt{(\Delta A)^2 + 32J^2}}{8\Delta A J\rho_{12}}[(\Delta A)^2 + 16J^2 - \rho_{12}^2 - r_1 - \sqrt{2}\rho_{12}r_2] \\ \frac{1}{8\Delta A J\rho_{12}}[(\Delta A)^2 r_2 + 32J^2(r_2 - \sqrt{2}\rho_{12})] \\ 1 \end{pmatrix}, \quad (35)$$

where

$$r_1 = \sqrt{(\Delta A)^4 + (\Delta A)^2(32J^2 - 2\rho_{12}^2) + (16J^2 + \rho_{12}^2)^2}\,,$$

$$r_2 = \sqrt{\rho_{12}^2 - (\Delta A)^2 - 16J^2 + r_1}\,, \quad (36)$$

$$r_3 = \sqrt{\rho_{12}^2 - (\Delta A)^2 - 16J^2 - r_1}\,,$$

STEADY STATES

We have a steady state when the density operator that involves all information of the system has a time derivative that vanishes, see Eq. (1). In the discrete representation we are working with, the Lanczos representation, $\hat{\hat{L}}\hat{\rho} = 0$ leaving a set of simultaneous equations for the components of the vector $\vec{\rho} = (\rho_1\ \rho_2\ \rho_3\ \rho_4)^T$. The condition for the existence of steady states, $\hat{\hat{L}}\hat{\rho} = 0$, means that the determinant of the Lanczos matrix, $\hat{\hat{X}}$, vanishes, permiting us to find the solution of the constitutive set of simultaneous equations for $\vec{\rho}$. The process results in the condition:

$$\det(\hat{\hat{X}}) = (\Delta A)^2\eta_{12}^2 + 4\gamma_1\gamma_2[16J^2 + \eta_{12}^2] = 0\,. \quad (37)$$

By solving the above equation for γ_2, we get three values for it but the real one is:

$$\gamma_2 = \frac{R_4 - (\Delta A)^2 - 8\gamma_1^2}{12\gamma_1} - \frac{8(\Delta A)^2\gamma_1^2 + 768J^2\gamma_1^2 - (\Delta A)^4 - 16\gamma_1^4}{12\gamma_1 R_4}, \quad (38)$$

where the following definitions were employed:

$$R_4 = (P_1 - (\Delta A)^6 + 64\gamma_1^6 + 96\sqrt{3}r_5)^{1/3}\,,$$

$$P_1 = 4\gamma_1^2\{3(\Delta A)^2[(\Delta A)^2 + 96J^2] + 4\gamma_1^2[576J^2 - 3(\Delta A)^2]\}\,,$$

$$r_5 = J\gamma_1^2\sqrt{4\gamma_1^2 P_2 - (\Delta A)^6 - 16(\Delta A)^4 J^2}\,,$$

$$P_2 = (\Delta A)^2[3(\Delta A)^2 + 4(80J^2 - 3\gamma_1^2)] + 16(16J^2 + \gamma_1^2)^2\,.$$

A plot of γ_2 for steady states is found in Fig. 5. Note that γ_1 and γ_2 have opposite signs. We also observe that these values become enormous around $\gamma_1 = 0$ and $J = 0$.

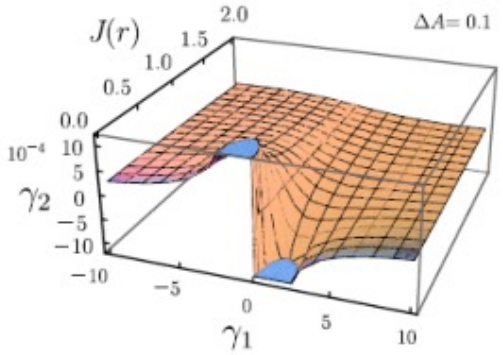

Fig. 5: Values of γ_2 for a steady state, and $\Delta A = 0.1$.

The set of resultant simultaneous equations for ρ is

$$\gamma_1\rho_1 + i\frac{\Delta A}{2\sqrt{2}}\rho_2 = 0\,,$$

$$i\frac{\Delta A}{2\sqrt{2}}\rho_1 + \frac{1}{2}\eta_{12}\rho_2 + \frac{i}{2\sqrt{2}}R\rho_3 = 0\,, \tag{39}$$

$$\frac{i}{2\sqrt{2}}R\rho_2 + \frac{(\Delta A)^2\gamma_2 + 16J^2\eta_{12}}{R^2}\rho_3 + 2\sqrt{2}\frac{\Delta A\, J\rho_{12}}{R^2}\rho_4 = 0\,,$$

$$2\sqrt{2}\frac{\Delta A\, J\rho_{12}}{R^2}\rho_3 + \frac{64J^2\gamma_2 + (\Delta A)^2\eta_{12}}{2R^2}\rho_4 = 0\,.$$

The resultant solution to this system of simultaneous equations, under condition Eq. (38) is

$$\frac{\rho_1}{\rho_4} = R\frac{[(\Delta A)^8 - (\Delta A)^6(12\gamma_1^2 + r_8) + (\Delta A)^4 P_3 - 4(\Delta A)^2\gamma_1^2 P_4 - 32\gamma_1^2(P_5)]}{16\sqrt{2}J\gamma_1^2 r_8 P_6}. \tag{40}$$

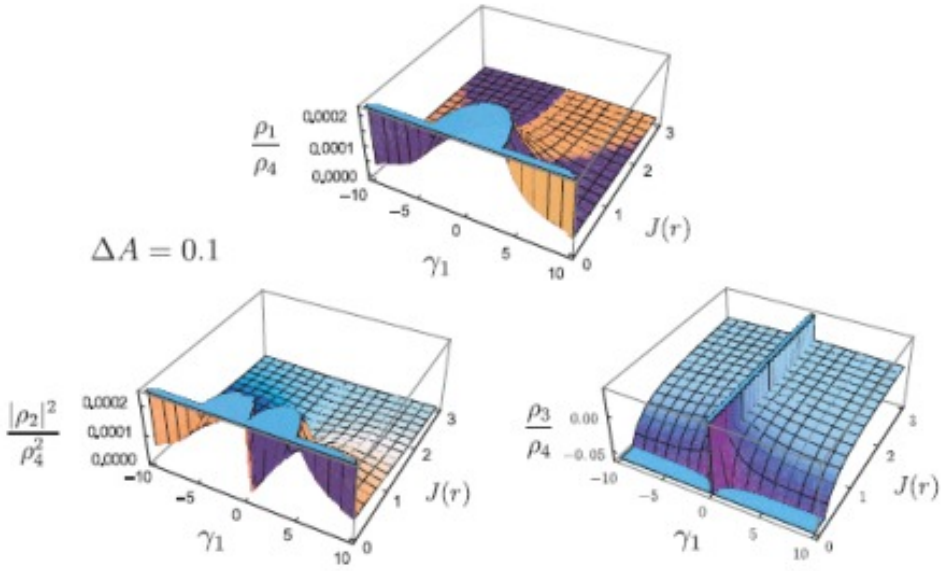

Fig. 6: Values of the different population of spin states, ρ_1/ρ_4, ρ_2/ρ_4 and ρ_3/ρ_4 for a steady state with $\Delta A = 0.1$.

For ρ_2, we have that

$$\frac{\rho_2}{\rho_4} = \frac{i}{R^3}\left\{8Jr_{10}\Delta A - \frac{P_7 P_8}{2Jr_{10}\Delta A}\right\}, \tag{41}$$

where

$$P_3 = 48\gamma_1^4 - 1280J^2\gamma_1^2 + 8\gamma_1^2 r_8 + r_8^2\,,$$

$$P_4 = 16\gamma_1^4 + 16\sqrt{3}Jr_7 + 4\gamma_1^2 r_8 + r_8^2 - 224J^2(r_8 - 4\gamma_1^2)\,,$$

$$P_5 = \sqrt{3}Jr_7(4\gamma_1^2 - r_8) - 6144J^4\gamma_1^2 + 16J^2(40\gamma_1^4 - 8\gamma_1^2 r_8 + r_8^2)\,, \tag{42}$$

$$P_6 = (\Delta A)^4 - 768J^2\gamma_1^2 + 16\gamma_1^4 - 20\gamma_1^2 r_8 + r_8^2 - (\Delta A)^2(8\gamma_1^2 + r_8)\,,$$

$$P_7 = r_{11}(64J^2 + (\Delta A)^2) + (\Delta A)^2\gamma_1\,,$$

$$P_8 = r_{11}((\Delta A)^2 + 16J^2) + 16J^2\gamma_1\,,$$

and ρ_3 is

$$\frac{\rho_3}{\rho_4} = -\frac{64J^2 r_{11} + (\Delta A)^2 r_{12}}{4\sqrt{2} J r_{10} \Delta A}, \tag{43}$$

here we used the following definitions:

$$r_6 = \sqrt{4\gamma_1^2 P_5 - (\Delta A)^4 [(\Delta A)^2 + 16J^2]},$$

$$r_7 = \sqrt{16\gamma_1^2 P_6 - (\Delta A)^4 [(\Delta A)^2 + 4(4J^2 - 3\gamma_1^2)]},$$

$$r_8 = [16\gamma_1^2 P_7 - (\Delta A)^4 ((\Delta A)^2 - 12\gamma_1^2)]^{1/3},$$

$$r_9 = \left[P_8 - (\Delta A)^6 + 64\gamma_1^6 + 96\sqrt{3} J \gamma_1^2 r_6\right]^{1/3}, \tag{44}$$

$$r_{10} = \frac{1}{12\gamma_1 r_8} [(\Delta A)^4 + 8\gamma_1^2 (2\gamma_1^2 - (\Delta A)^2 - 96J^2)],$$

$$r_{11} = \frac{r_9}{12\gamma_1} - \frac{(\Delta A)^2 + 8\gamma_1^2}{12\gamma_1} + r_{10},$$

$$r_{12} = \frac{1}{12\gamma_1 r_9} [\gamma_1^2 (8(\Delta A)^2 + 768J^2 - 16\gamma_1^2) - (\Delta A)^4],$$

$$r_{13} = 2J\Delta A R^3 \left(\gamma_1 + \frac{(\Delta A)^2 + 8\gamma_1^2}{12\gamma_1} + r_{12} - \frac{r_9}{12\gamma_1}\right),$$

where

$$P_5 = 3(\Delta A)^4 + 4(\Delta A)^2 (80J^2 - 3\gamma_1^2) + 16(16J^2 + \gamma_1^2)^2,$$

$$P_6 = 4(16J^2 + \gamma_1^2)^2 + (\Delta A)^2 (80J^2 - 3\gamma_1^2), \tag{45}$$

$$P_7 = 3(\Delta A)^2(24J^2 - \gamma_1^2) + 2(288J^2\gamma_1^2 + 2\gamma_1^4 + 3\sqrt{3}Jr_7)\,,$$

$$P_8 = 4(\Delta A)^2\gamma_1^2[3(\Delta A)^2 + 288J^2\gamma_1^2] + 16\gamma_1^4(576J^2 - 3(\Delta A)^2)\,.$$

A plot of these quantities is found in Fig. 6. Note that these amounts decay very fast when increasing both $J(r)$ and the magnitude of γ_1.

TIME EVOLUTION

We consider a spin-correlated RP evolving under the influence of isotropic electron-nuclear hyperfine interactions and the isotropic Zeeman interactions of the electron spins with a static MF. The coherent evolution of the RP, described by a spin density operator $\hat{\rho}(t)$, is governed by the spin Hamiltonian Eq. (1). The spin evolution arising from the difference in the two electronic g-values and from the nuclear Zeeman interactions is negligible respect the MF applied. We assume that the exchange and dipolar interactions between the radicals and all spin relaxation process may be neglected. According with their spin evolution, the two radicals undergo rapid translational motions and are assumed to recombine in a diffusion-controlled manner whenever they encounter in a singlet state but to be mutually nonreactive in the triplet state. We treat this reactions-diffusion process using the exponential model [24, 25]. In this approach, the two radicals of a spin-correlated pair undergo a single encounter, with a distribution of encounter times given by exponential function $f(t) = ke^{-kt}$, with k is a first-order rate constant. A stochastic Liouville equation will implement the spin evolution in a super-operator basis. Applying MF and including the multiplicity of the spin of the intermediate RP and introducing the spin correlation, we can study the MF influences over the RP. A pair of any spin carriers is a multi-spin system with a manifold of a spin state. The chemical reactions select those of them which are spin-allowed; spin-forbidden states undergo magnetically induced spin conversion. Thus, any multi-spin pair is a spin-selective system. The MF affects the recombination probability of a geminate RP. The effect arises from the time evolution of a coherent state and the spin selectivity of the recombination: RP is created in a triplet electron spin state and only can recombine in the singlet state. Neither the singlet nor the triplet spin states are Eigenstates of the Hamiltonian and the singlet probability, therefore, oscillates in time, since coherences are created during the time evolution. It is introduced the Lanczos vector space where vectors are expanded in a super-operator basis $\{(r_s|\}$, $\{(p_{s'}|\}$ satisfying the relations Eq. (25) to perform the calculation. Using the transition super operator, we obtain the eigen value equation for $|ez_n)$ eigenvectors

$$L|e_n) = \lambda_n|e_n)\,, \quad X|ez_n) = \lambda_n|ez_n)\,,$$
$$(ez_n|L|e_n) = \lambda_n(ez_n|e_n), \tag{46}$$

where any state can be expanded in the super state basis using the orthonormality and closure relations

$$|e_n) = \sum_s |\,p_s)(r_s|e_n)\,, \tag{47}$$

To evaluates the matrix elements of the quantum transition super operator $\hat{L}$, it is used the Eq. (46)

$$\sum_s (\,r_{s'}|L|p_s)(r_s|e_n) = \lambda_n(r_{s'}|e_n)\,, \tag{48}$$

$$(r_{s'}|L|p_{s'-1})(r_{s'-1}|e_n) + (r_{s'}|L|p_{s'})(r_{s'}|e_n) + (r_{s'}|L|p_{s'+1})(r_{s'+1}|e_n) = \lambda_n(r_{s'}|e_n)\,,$$

$$\beta_{s'}(r_{s'-1}|e_n) + (\alpha_{s'} - \lambda_n)(r_{s'}|e_n) + \beta_{s'+1}(r_{s'+1}|e_n) = 0\,,$$

where the Lanczos parameters are evaluated using the following inner products

$$\beta_{s+1}(r_s|p_{s+1}) = (r_s|\hat{L}|p_s) - \alpha_s(r_s|p_s) - \beta_s(r_s|p_{s-1})\,,$$

$$\begin{aligned}\beta_{s+1}(r_{s+1}|p_{s+1}) &= (r_{s+1}|\hat{L}|p_s) - \alpha_s(r_{s+1}|p_s) - \beta_s(r_{s+1}|p_{s-1})\,,\\ \beta_{s+1}(r_{s-1}|p_{s+1}) &= (r_{s-1}|\hat{L}|p_s) - \alpha_s(r_{s-1}|p_s) - \beta_s(r_{s-1}|p_{s-1})\,.\end{aligned} \tag{49}$$

We might be able to compute the eigenvectors of the original matrix by solving the above simultaneous equations. Time evolution of Lanczos vectors is achieved with the help of the eigenvectors of the Lanczos matrix as follows. As above, λ_i are the eigenvalues and $|ez_i)$ the eigenvectors, we have two ways of writing the identity operator,

$$\hat{I} = \sum_s |\,p_s)(r_s|\,, \quad \text{and} \quad \hat{I} = \sum_n |\,ez_n)(ez_n|\,. \tag{50}$$

Therefore,

$$\begin{aligned} e^{-tX_{S\uparrow T_0\uparrow}}|p_s) &= \hat{I}e^{-tX_{S\uparrow T_0\uparrow}}\hat{I}|p_s) = e^{-t\hat{\tilde{X}}}|p_s)\\ &= \sum_n e^{-t\hat{X}}\,|ez_n)(ez_n|p_s) = \sum_n e^{-t\lambda_n}\,|ez_n)(ez_n|p_s)\,,\\ (r_s|e^{-tX_{S\uparrow T_0\uparrow}} &= (r_s|\hat{I}e^{-tX_{S\uparrow T_0\uparrow}}\hat{I} = (r_s|e^{-t\hat{\tilde{X}}}\\ &= \sum_n (\,r_s|e^{-t\hat{\tilde{X}}}|ez_n)(ez_n| = \sum_n e^{-t\lambda_n}\,(r_s|ez_n)(ez_n|\,. \end{aligned} \tag{51}$$

For our RP dynamics model, this quantity can be calculated analytically. In the case of the initial Lanczos vector $p_0(t)$, we find that

$$p_0(t) = \begin{pmatrix} 2y_0^2 e^{-t\eta_{12}/2}A(t) \\ i\dfrac{2y_0^2 e^{-t\eta_{12}/2}}{(\Delta A)^3 J^2}B(t) \end{pmatrix}, \tag{52}$$

where

$$\begin{aligned} A(t) &= a_{11}\cos(\omega t) + a_{12}\sin(\omega t) + a_{13}\cosh(\gamma_3 t) + a_{14}\sinh(\gamma_3 t)\,,\\ B(t) &= a_{21}\cos(\omega t) + a_{22}\sin(\omega t) + a_{23}\cosh(\gamma_3 t) + a_{24}\sinh(\gamma_3 t)\,, \end{aligned} \tag{53}$$

moreover, we have used the following definitions:

$$a_{11} = \frac{1}{64(\Delta A)^4\rho_{12}^2 J^2}[2(\Delta A)^2\rho_{12}^2 Q_1 + (16J^2 + y_1)^2 Q_2]\,,$$

$$a_{12} = -\frac{1}{16\sqrt{2}(\Delta A)^4\rho_{12}J^2}\{(16J^2 + y_1)(16J^2 - (\Delta A)^2 + y_1)\sqrt{y_2 - y_1}\}\,,$$

$$a_{13} = \frac{1}{64(\Delta A)^4\rho_{12}^2 J^2}(Q_3 + Q_4)\,,$$

$$a_{14} = \frac{1}{16\sqrt{2}(\Delta A)^4\rho_{12}J^2}\{(16J^2 + y_3)(16J^2 - (\Delta A)^2 + y_3)\sqrt{y_3 - y_2}\}\,,$$

$$a_{21} = \frac{y_1 - y_2}{32\sqrt{2}\rho_{12}}[(\Delta A)^2 - 2(16J^2 + y_1)]\,, \tag{54}$$

$$a_{22} = -\frac{\sqrt{y_2 - y_1}}{64\rho_{12}^2}[(16J^2 + y_1)(2\rho_{12}^2 + y_1 - y_2) - 2(\Delta A)^2\rho_{12}^2]\,,$$

$$a_{23} = \frac{y_3 - y_2}{32\sqrt{2}\rho_{12}}[(\Delta A)^2 - 2(16J^2 + y_3)]\,,$$

$$a_{24} = \frac{\sqrt{y_3 - y_2}}{64\rho_{12}^2}[2(\Delta A)^2\rho_{12}^2 - (16J^2 + y_3)(2\rho_{12}^2 + y_3 - y_2)]\,,$$

where

$$Q_1 = (\Delta A)^2 - 2(16J^2 + y_1)\,,$$

$$Q_2 = 2\rho_{12}^2 + y_1 - y_2\,,$$

$$Q_3 = 2(\Delta A)^4\rho_{12}^2 - 4(\Delta A)^2\rho_{12}^2(16J^2 + y_3)\,, \tag{55}$$

$$Q_4 = (16J^2 + y_3)^2(2\rho_{12}^2 + y_3 - y_2)\,.$$

The y_i for $i = 0,1,2,3$ represent the populations of the several species in those different spin states. A weak ($<$ 1 mT) MF typically enhances the efficiency of $S \leftrightarrow T$ interchanges (the so called low field effect [26]). For a singlet RP, a weak field reduces the probability of recombination from the singlet state and consequently boosts the number of free radicals that escape from the reaction [27]. To estimate that effect we use the following data: the g factor for the electron is $g_e = 2.002319304$ [28]. The nuclear magnetron (μ_N) is defined with the mass of proton (m_P) as follows:

$$\mu_N = \frac{e\hbar}{2m_P} = 5.05079 \times 10^{-27} JT^{-1},$$
$$m_P = 1.67262 \times 10^{-27} kg\,.$$

The difference between RP energies in the singlet and triplet spin states depends on if exists and not an external magnetic field. When applied magnetic field is absence, singlet-triplet mixing is fast and involves all three triplets sub-states (region I). When the magnetic field is applied, two of the three triplets levels, namely T_{+1} and T_{-1}, become progressively decoupled, restricting $S \leftrightarrow T$ interchanges to the S and T_0 states (region II). In our case, the exchange relation is given by

$J(r) = J_0 e^{-\xi r}$.

The energy of the $|S>$ and $|T_{-}>$ states coincide when

$$-J(r) = J(r) - g\mu_B B\,, \quad \text{i.e.} \quad J(r) = \frac{1}{2} g\mu_B B$$
$$\Rightarrow r_{II} = -\frac{1}{\xi}\ln\left(\frac{g\mu_B}{2J_0}B\right). \tag{56}$$

In the region I we have that

$$J(r_I) = J_0 e^{-\xi r} < \epsilon, \quad \Rightarrow r_I > -\frac{1}{\xi}\ln\left(\frac{\epsilon}{J_0}\right), \tag{57}$$

for some small ϵ.

CONCLUDING REMARKS

In this letter we have been concerned with the determination of local and collective properties of the spin state of a quantum mechanical system ascribed to a RP. We use the Lanczos method to evaluate the Eigen-system and the SPo in the damped two-level system approximation. The method was used to assess the dynamic of the RP system immersed in an MF. In the quantum mechanical model the associated Hilbert space has been projected onto a reduced subspace to obtain the maximum Eigen-system. Mathematically, the physical concepts involved are the distribution of SPo of a vector living into the reduced Hilbert space. In general, the Hamiltonian employed is renormalized in some vague way to take into account, at least partially, the physical information lost because we do not use the whole space [21]. In fact, we use a finite vector space, where is supposed that the Hamiltonian is relevant for our quantum mechanical system.

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