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Covalent-bond fluctuations measure the direction of the magnetic field

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Abstract

The fluctuations of a covalent bond implies transitions between singlet and triplet spin states. In the presence of a magnetic field the spin states are mixed and the singlet-triplet transitions induce oscillations of the populations of these two types of states. The amplitude of these "spin-rotation" (or "spin-flip") oscillations depends on the direction of the magnetic field, while their frequency is governed by the Zeeman splitting energy. Since the covalent-bond fluctuations imply variations of the distance between the molecular partners, the oscillating transitions generate local polarization currents.

Fluctuations. Covalent-bond electron pair may fluctuate between their singlet (s) and triplet (t) states. The kinetics of the populations $N_{s,t}$ is described by the equations

$$\begin{aligned} \tfrac{dN}{dt} &= wN_t - wN_s \ , \\ \tfrac{dN_t}{dt} &= wN_s - wN_t \ , \end{aligned} \tag{1}$$

where w is the number of transitions per unit time. The solution of this system of equations is

$$\begin{aligned} N_s &= \tfrac{1}{2}\left(N + De^{-\int_0^t wdt'}\right) \ , \\ N_t &= \tfrac{1}{2}\left(N - De^{-\int_0^t wdt'}\right) \ , \end{aligned} \tag{2}$$

where $N = N_s + N_t$ is the initial number of molecules and $D = N_s^0 - N_t^0$ is the initial difference between the two populations.

The spin states of the electron pair are

$$\begin{aligned} \chi_s &= \tfrac{1}{\sqrt{2}}\left(\alpha_1\beta_2 - \alpha_2\beta_1\right) \ , \\ \chi_t^0 &= \tfrac{1}{\sqrt{2}}\left(\alpha_1\beta_2 + \alpha_2\beta_1\right) \ , \\ \chi_t^1 &= \alpha_1\alpha_2 \ , \ \chi_t^{-1} = \beta_1\beta_2 \ , \end{aligned} \tag{3}$$

where α, β are the spin-up, spin-down states along the z-direction for the electron 1 and electron 2. The upper labels indicate the magnetic number. We assume the triplet states degenerate, with energy W, and measure the energies from the singlet-state energy; *i.e.*,

$$H_0\chi_s = 0 \ , \ H_0\chi_t^{0,\pm 1} = W\chi_t^{0,\pm 1} \ , \tag{4}$$

where H_0 is the spin hamiltonian. The difference W in energy may arise from an exchange energy (usually of the order of $10meV$), or a spin-spin coupling, induced by a spin-orbital coupling (fine structure); in this latter case W is a fraction of the atomic energy term, the fraction being of the order of the fine structure constant squared. This gives a value $W \simeq 10^{-4}eV$.

A magnetic field $\boldsymbol{H}$ generates an interaction

$$U = \mu\boldsymbol{\sigma}\boldsymbol{H} \ , \tag{5}$$

where μ is the Bohr magneton, $\boldsymbol{\sigma} = \boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_2$ and $\boldsymbol{\sigma}_{1,2}$ are the Pauli matrices. This interaction conserves the spin, such that the singlet state and the energy E_s are unchanged,

$$\widetilde{\chi}_s = \chi_s \ , \ E_s = 0 \ , \tag{6}$$

but it splits up the triplet state, which becomes

$$\widetilde{\chi}_t^0 = \cos\theta\chi_t^0 - \frac{1}{\sqrt{2}}\sin\theta\left(e^{i\varphi}\chi_t^1 - e^{-i\varphi}\chi_t^{-1}\right) \ , \ E_t^0 = W \tag{7}$$

and

$$\begin{gathered}\widetilde{\chi}_t^1 = \cos^2\tfrac{\theta}{2}e^{i\varphi}\chi_t^1 + \sin^2\tfrac{\theta}{2}e^{-i\varphi}\chi_t^{-1} + \tfrac{1}{\sqrt{2}}\sin\theta\chi_t^0 \ , \\ E_t^1 = W + 2\mu H \ , \end{gathered} \tag{8}$$

$$\begin{gathered}\widetilde{\chi}_t^{-1} = -\cos^2\tfrac{\theta}{2}e^{-i\varphi}\chi_t^{-1} - \sin^2\tfrac{\theta}{2}e^{i\varphi}\chi_t^1 + \tfrac{1}{\sqrt{2}}\sin\theta\chi_t^0 \ , \\ E_t^{-1} = W - 2\mu H \ , \end{gathered} \tag{9}$$

where the angles θ, φ define the direction of the magnetic field; we assume $W \gg 2\mu H$. This is the well-known Zeeman splitting.

Density matrix. Let us denote by $A_n e^{\frac{i}{\hbar}E_n t}$ the transition amplitudes from the triplet state $n = 0, \pm 1$ to the singlet state, where $E_n = E_t^n$ given above. The number of transitions per unit time to the singlet state is given by

$$w_{ts} = \sum_{nm} \rho_{nm} A_n^* A_m e^{\frac{i}{\hbar}(E_m - E_n)t} \ , \tag{10}$$

where ρ_{nm} is the density matrix.

The density matrix of the electron pair is $\rho = \rho_1\rho_2$. For an unpolarized electron ρ_i, $i = 1, 2$, is a diagonal matrix with elements $1/2$, both for the spin up and the spin down. In magnetic field the Zeeman splitting $\pm\mu H$ generates a Boltzmann distribution $e^{\pm\mu H/T}/\left(e^{\mu H/T} + e^{-\mu H/T}\right)$, where T is the temperature, such that the density matrix becomes a statistical matrix. Since $\mu H \ll T$, the statistical matrix can be written as

$$\rho_i = \frac{1}{2}\begin{pmatrix} 1-p & 0 \\ 0 & 1+p \end{pmatrix} \ , \ p = \mu H/T \ , \ i = 1, 2 \ , \tag{11}$$

where p is the polarization parameter ($H > 0$). This is valid for spin states along the direction of the field. For our reference frame we need to rotate the polarization by angles $-\theta$ and $-\varphi$, such that the matrix becomes

$$\rho_i = \frac{1}{2}\begin{pmatrix} 1 - p\cos\theta & p\sin\theta e^{i\varphi} \\ p\sin\theta e^{i\varphi} & 1 + p\cos\theta \end{pmatrix} \ . \tag{12}$$

Also, we note that the spin states in our reference frame are changed in the presence of the interaction $\mu\boldsymbol{\sigma}_i\boldsymbol{H}$.

Since $p \ll 1$ we use the approximation

$$\rho = \rho_1\rho_2 \simeq \frac{1}{4}\begin{pmatrix} 1-2p\cos\theta & 2p\sin\theta e^{i\varphi} \\ 2p\sin\theta e^{i\varphi} & 1+2p\cos\theta \end{pmatrix} \ , \tag{13}$$

i.e. we limit ourselves to the first order in the parameter p.

For ρ_{nm} we need the matrix elements of the matrix ρ given above between the states $\widetilde{\chi}_t^{0,\pm1}$ given by equation (7) to (9). In order to do this we need the matrix elements of the matrix ρ for the states $\chi_t^{0,\pm1}$ given by equations (3). We get

$$\begin{gathered} \rho\chi_t^0 = \tfrac{1}{2}p\cos\theta\chi_s + \tfrac{1}{4}\chi_t^0 + \tfrac{1}{2\sqrt{2}}p\sin\theta\left(e^{i\varphi}\chi_t^1 + e^{-i\varphi}\chi_t^{-1}\right) \ , \\ \rho\chi_t^1 = \tfrac{1}{4}\left(1-2p\cos\theta\right)\chi_t^1 + \tfrac{1}{2\sqrt{2}}p\sin\theta e^{-i\varphi}\left(\chi_t^0+\chi_s\right) \ , \\ \rho\chi_t^{-1} = \tfrac{1}{4}\left(1+2p\cos\theta\right)\chi_t^{-1} + \tfrac{1}{2\sqrt{2}}p\sin\theta e^{i\varphi}\left(\chi_t^0-\chi_s\right) \ ; \end{gathered} \tag{14}$$

it is noteworthy that the singlet state occurs in the action of the statistical matrix, as expected. Now it is easy to get the action of the statistical matrix upon the states $\widetilde{\chi}_t^{0,\pm1}$, and, finally, the matrix elements

$$\begin{gathered} \rho_{00} = 1/4 \ , \ \rho_{0\pm1} = \pm\tfrac{1}{2\sqrt{2}}p\sin 2\theta \ , \\ \rho_{11} = \tfrac{1}{4}\left(1-2p\cos 2\theta\right) \ , \ \rho_{-1-1} = \tfrac{1}{4}\left(1+2p\cos 2\theta\right) \ , \\ \rho_{1,-1} = 0 \ . \end{gathered} \tag{15}$$

Transition rate. By making use of the matrix elements of the statistical matrix in equation (10), the transition rate from the triplet states to the singlet state becomes

$$\begin{gathered} w_{ts} = \tfrac{1}{4}\left[|A_0|^2 + (1-2p\cos 2\theta)|A_1|^2 + (1+2p\cos 2\theta)|A_{-1}|^2\right] + \\ +\tfrac{1}{\sqrt{2}}p\sin 2\theta|A_0|\left[|A_1|\cos\left(\tfrac{2\mu H}{\hbar}t+\alpha_1\right) - |A_{-1}|\cos\left(\tfrac{2\mu H}{\hbar}t+\alpha_{-1}\right)\right] \ , \end{gathered} \tag{16}$$

where the phases $\alpha_{\pm1}$ are defined by $A_{\pm1} = |A_{\pm1}|e^{i\alpha_{\pm1}}$ (and $A_0 = |A_0|$). A similar transition rate exists from the singlet state to the triplet states, the only difference being the change of sign of the phases $\alpha_{\pm1}$,

$$\begin{gathered} w_{st} = \tfrac{1}{4}\left[|A_0|^2 + (1-2p\cos 2\theta)|A_1|^2 + (1+2p\cos 2\theta)|A_{-1}|^2\right] + \\ +\tfrac{1}{\sqrt{2}}p\sin 2\theta|A_0|\left[|A_1|\cos\left(\tfrac{2\mu H}{\hbar}t-\alpha_1\right) - |A_{-1}|\cos\left(\tfrac{2\mu H}{\hbar}t-\alpha_{-1}\right)\right] \ . \end{gathered} \tag{17}$$

The net transition rate between the singlet state and the triplet states, *i.e.* the w which enters equation (1), is the difference

$$\begin{gathered} w = w_{ts} - w_{st} = \\ = -\sqrt{2}p|A_0|\left(|A_1|\sin\alpha_1 - |A_{-1}|\sin\alpha_{-1}\right)\sin 2\theta\cos\tfrac{2\mu H}{\hbar}t \ . \end{gathered} \tag{18}$$

The states ±1 differ by the spin orientation: very likely, $|A_1| = |A_{-1}|$. Also, when changing the spin orientation the singlet wavefunction changes the sign. Consequently we may assume that the two phases differ by π. By using these assumptions, we get

$$w = -2\sqrt{2}p|A_0A_1|\sin\alpha_1\sin 2\theta\cos\frac{2\mu H}{\hbar}t \ . \tag{19}$$

The time dependence of the populations given by equations (2) is

$$N_{s,t} = \frac{1}{2}\left(N \pm De^{\frac{\sqrt{2}\hbar}{T}|A_0A_1|\sin\alpha_1\sin 2\theta\cos\frac{2\mu H}{\hbar}t}\right) \;; \tag{20}$$

it is worth noting that the small parameter p is replaced by $\hbar\,|A_0A_1|\,/T$, which may attain relatively high values. For instance, at room temperature and for an electronic energy of a few meV we get $\hbar\,|A_0A_1|\,/T$ of the order of 10^{-2}.

However, it is likely that the exponent in equation (20) is sufficiently small to warrant the approximations

$$\begin{aligned} N_s &= N_s^0 + \tfrac{1}{2}\left(N_s^0 - N_t^0\right)\cdot\tfrac{\sqrt{2}\hbar}{T}\,|A_0A_1|\sin\alpha_1\sin 2\theta\cos\tfrac{2\mu H}{\hbar}t \;, \\ N_t &= N_t^0 - \tfrac{1}{2}\left(N_s^0 - N_t^0\right)\cdot\tfrac{\sqrt{2}\hbar}{T}\,|A_0A_1|\sin\alpha_1\sin 2\theta\cos\tfrac{2\mu H}{\hbar}t \;. \end{aligned} \tag{21}$$

The populations of the two states oscillate in antiphase; these oscillations may generate local polarization currents. The oscillation amplitude depends on the direction of the magnetic field (angle θ); its maximum value is attained for $\theta = \pm\pi/4$. For a mean magnetic field $0.5Gs$ of the Earth the oscillation frequency is approximately $10MHz$.

An excited state may be generated by photoexcitation, followed by a singlet state, which, in turn, decays to a triplet state. The transition rate is then given by equation (17); its general form is

$$w_{st} = a + pb\sin 2\theta\cos(2\mu Ht/\hbar) \;, \tag{22}$$

where a, b are some coefficients and the phase α_1 is put equal to zero. The kinetic equation is $dN_s/dt = -w_{st}N_s$, with the solution

$$N_s = N_s^0 e^{-at} e^{-\frac{b\hbar}{T}\sin 2\theta\sin(2\mu Ht/\hbar)} \simeq N_s^0 e^{-at}\left(1 - \frac{b\hbar}{T}\sin 2\theta\sin(2\mu Ht/\hbar)\right) \;. \tag{23}$$

The singlet state may generate a chemical reaction, with some reaction constant, such that the total reaction yield includes a term

$$-\frac{b\hbar}{T}\sin 2\theta\int_0^\infty e^{-at}\sin(2\mu Ht/\hbar) = -\frac{b\hbar}{T}\sin 2\theta\frac{2\mu H/\hbar}{a^2 + (2\mu H/\hbar)^2} \;. \tag{24}$$

This term has a minimum value for $\mu H/\hbar \simeq a$(compare with Ref. 1).

References

[1] T. Ritz, S. Adem and K. Schulten, "A model for photoreceptor-based magnetoreception in birds", Biophys. J. **78** 707-718 (2000).