

5.1: Exchange interaction

Physical origin and consequences of the exchange interaction

If two unpaired electrons occupy SOMOs in the same molecule or in spatially close molecules, the wave functions ψ_1 and ψ_2 of the two SOMOs may overlap. The two unpaired electrons can couple either to a singlet state or to a triplet state. The energy difference between the singlet and triplet state is the exchange integral

$$J = -2e^2 \iint \frac{\psi_1^*(r_1) \psi_2^*(r_2) \psi_1(r_2) \psi_2(r_1)}{|\vec{r}_1 \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 \quad (5.1.1)$$

There exist different conventions for the sign of J and the factor 2 may be missing in parts of the literature. With the sign convention used here, the singlet state is lower in energy for positive J . Since the singlet state S with spin wave function $(|\alpha\beta\rangle - |\beta\alpha\rangle)/\sqrt{2}$ is antisymmetric with respect to exchange of the two electrons and electrons are Fermions, it corresponds to the situation where the two electrons could also occupy the same orbital. This is a bonding orbital overlap, corresponding to an antiferromagnetic spin ordering. Negative J correspond to a lower-lying triplet state, i.e., antibonding orbital overlap and ferromagnetic spin ordering. The triplet state has three substates with wave functions $|\alpha\alpha\rangle$ for the T_+ state, $(|\alpha\beta\rangle + |\beta\alpha\rangle)/\sqrt{2}$ for the T_0 state, and $|\beta\beta\rangle$ for the T_- state. The T_+ and T_- state are eigenstates both in the absence and presence of the J coupling. The states S and T_0 are eigenstates for $J \gg \Delta\omega$, where $\Delta\omega$ is the difference between the electron Zeeman frequencies of the two spins. For the opposite case of $\Delta\omega \gg J$, the eigenstates are $|\alpha\beta\rangle$ and $|\beta\alpha\rangle$. The latter case corresponds to the high-field approximation with respect to the exchange interaction.

For strong exchange, $J \gg \Delta\omega$, the energies are approximately $-(3/4)J$ for the singlet state and $J/4 - \omega_S$, $J/4$ and $J/4 + \omega_S$ for the triplet substates T_- , T_0 , and T_+ , respectively, where ω_S is the electron Zeeman interaction, which is the same for both spins within this approximation. If $J \gg 2\pi\nu_{mw}$, microwave photons with energy $h\nu_{mw}$ cannot excite transitions between the singlet and triplet subspace of spin Hilbert space. It is then convenient to use a coupled representation and consider the two subspaces separately from each other. The singlet subspace corresponds to a diamagnetic molecule and does not contribute to EPR spectra. The triplet subspace can be described by a group spin $S = 1$ of the two unpaired electrons. In the coupled representation, J does not enter the spin Hamiltonian, as it shifts all subspace levels by the same energy. For $J < 0$, the triplet state is the ground state and is always observable by EPR spectroscopy. However, usually one has $J > 0$ and the singlet state is the ground state. As long as $\hbar J$ does not exceed thermal energy $k_B T$ by a large factor, the triplet state is thermally excited and observable. In this case, EPR signal amplitude may increase rather than decrease with increasing temperature. For organic molecules, this case is also rare. If $\hbar J \gg k_B T$, the compound does not give an EPR signal. It may still be possible to observe the triplet state transiently after photoexcitation to an excited singlet state and intersystem crossing to the triplet state.

Weak exchange coupling is observed in biradicals with well localized SOMOs that are separated on length scales between 0.5 and 1.5 nm. In such cases, exchange coupling J decreases exponentially with the distance between the two electrons or with the number of conjugated bonds that separate the two centers of spin density. If the two centers are not linked by a continuous chain of conjugated bonds, exchange coupling is rarely resolved at distances larger than 1.5 nm. In any case, at such long distances exchange coupling is much smaller than the dipole-dipole coupling between the two unpaired electrons if the system is not conjugated. For weak exchange coupling, the system is more conveniently described in an uncoupled representation with two spins $S_1 = 1/2$ and $S_2 = 1/2$.

Exchange coupling is also significant during diffusional encounters of two paramagnetic molecules in liquid solution. Such dynamic Heisenberg spin exchange can be pictured as physical exchange of unpaired electrons between the colliding molecules. This causes a sudden change of the spin Hamiltonian, which leads to spin relaxation. A typical example is line broadening in EPR spectra of radicals by oxygen, which has a paramagnetic triplet ground state. If radicals of the same type collide, line broadening is also observed, but the effects on the spectra can be more subtle, since the spin Hamiltonians of the colliding radicals are the same. In this case, exchange of unpaired electrons between the radicals changes only spin state, but not the spin Hamiltonian.

Exchange Hamiltonian

The spin Hamiltonian contribution by weak exchange coupling is

$$\hat{\mathcal{H}}_{EX} = J \left(\hat{S}_{1x} \hat{S}_{2x} + \hat{S}_{1y} \hat{S}_{2y} + \hat{S}_{1z} \hat{S}_{2z} \right) \quad (5.1.2)$$

This Hamiltonian is analogous to the J coupling Hamiltonian in NMR spectroscopy. If the two spins have different g values and the field is sufficiently high ($g\mu_B B_0/\hbar \gg J$), the exchange Hamiltonian can be truncated in the same way as the J coupling Hamiltonian in heteronuclear NMR:

$$\hat{\mathcal{H}}_{\text{EX, trunc}} = J\hat{S}_{1z}\hat{S}_{2z} \quad (5.1.3)$$

Spectral manifestation of the exchange interaction

In the absence of hyperfine coupling, the situation is the same as for J coupling in NMR spectroscopy. Exchange coupling between like spins (same electron Zeeman frequency) does not influence the spectra. For radicals in liquid solution, hyperfine coupling is usually observable. In this case, exchange coupling does influence the spectra even for like spins, as illustrated in Figure 5.1 for two exchange-coupled electron spins $S_1 = 1/2$ and $S_2 = 1/2$ with each of them coupled exclusively to only one nuclear spin ($I_1 = 1$ and $I_2 = 1$, respectively) with the same hyperfine coupling A_{iso} . If the exchange coupling is much smaller than the isotropic hyperfine coupling, each of the individual lines of the hyperfine triplet further splits into three lines. If the splitting is very small, it may be noticeable only as a line broadening. At very large exchange coupling, the electron spins are uniformly distributed over the two exchange-coupled moieties. Hence, each of them has the same hyperfine coupling to both nuclei. This coupling is half the original hyperfine coupling, since, on average, the electron spin has only half the spin density in the orbitals of a given nucleus as compared to the case without exchange coupling. For intermediate exchange couplings, complex splitting patterns arise that are characteristic for the ratio between the exchange and hyperfine coupling.

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Figure 5.1: Influence of the exchange coupling J on EPR spectra with hyperfine coupling in liquid solution (simulation). Spectra are shown for two electron spins $S_1 = 1/2$ and $S_2 = 1/2$ with the same isotropic g value and the same isotropic hyperfine coupling to a nuclear spin $I_1 = 1$ or $I_2 = 1$, respectively. In the absence of exchange coupling, a triplet with amplitude ratio 1 : 1 : 1 is observed. For small exchange couplings, each line splits into a triplet. At intermediate exchange couplings, complicated patterns with many lines result. For very strong exchange coupling, each electron spin couples to both nitrogen nuclei with half the isotropic exchange coupling. A quintuplet with amplitude ratio 1 : 2 : 3 : 2 : 1 is observed.

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