

## *Invited Review*

# Magnetic Orbitals and Mechanisms of Exchange I. Direct Exchange

Jacques Curély\*

Centre de Physique Moléculaire Optique et Hertzienne (C.P.M.O.H.),  
Université Bordeaux 1, 351 Cours de la Libération, F-33405 Talence Cedex, France

Received November 12, 2004; accepted December 6, 2004

Published online April 26, 2005 © Springer-Verlag 2005

**Summary.** The problem of direct exchange is examined in the simplest cases (formal coupling of two electrons initially isolated and hydrogen molecule). Then we consider the general case of a solid characterized by weak overlaps between the atomic orbitals of first-nearest neighbours so that the involved electrons are quasi-localized. We recall the physical origin of spin-orbit coupling. Its influence on direct exchange allows one to revisit *Hund's* rules and to express phenomenological Hamiltonians describing anisotropic couplings as well as the antisymmetrical *Dzialoshinski-Moriya* coupling.

**Keywords.** Direct exchange; Spin-orbit coupling; Anisotropic exchange; *Dzialoshinski-Moriya* coupling; Magnetic orbital.

## Introduction

The idea of exchange coupling within atoms and between atoms has been one of progress marred by many errors and obscurities. It seems instructive to briefly recall here the main facts which have allowed the emergence of this important concept. In 1895 *Curie* reported in his thesis entitled “Magnetic properties of compounds at various temperatures” that these properties could be shared into three distinct groups: diamagnetics, paramagnetics (the term wrongly employed being “weakly magnetics”), and ferromagnetics [1]. But he also wondered if these magnetic behaviours did not belong to a single class. In 1905 *Langevin* proposed a theory of diamagnetism and paramagnetism which gave a good description of *Curie's* results [2]. The most important point was the link between a microscopic variable (*i.e.*, the magnetic moment per atom in presence of an external magnetic field) and a macroscopic one (*i.e.*, the magnetization derived from experiment). In

---

\* E-mail: j.curely@cpmoh.u-bordeaux1.fr

order to understand the existence of ferromagnetism below a characteristic temperature (the *Curie* temperature) *Langevin* suggested at the end of his article that a possible mechanism could be a co-operative phenomenon between permanent microscopic magnetic moments. In 1906 *Weiss* exploited this fruitful idea and introduced the notion of “molecular field”, acting on the atomic magnets and proportional to the net magnetization [3]. In spite of the fact that a possible electrostatic origin of this field was suggested [4], this very origin remained a puzzle for two decades, notably due to the fact that the field magnitude was acknowledged as improbable. In addition attempts to quantify the *Weiss* theory failed [4, 5].

Meanwhile, the experimental determination of gyromagnetic ratios of ferromagnetics in 1915 by *Barnett* [6] showed that the involved magnetic moments must originate in something quite different from orbital motion of electrons. The first convincing explanation has been given by *Landé* in 1922 [7]: these gyromagnetic ratios have the same origin as anomalous *Zeeman* splittings in atoms. With the introduction of the concept of electron spin in 1925, the fundamental origin of magnetism was identified. But, of course, this is the development of Quantum Mechanics which has given an important impetus to the microscopic understanding of magnetism. More particularly, the recognition by *Heisenberg* [8] and *Dirac* [9] that *Pauli*’s exclusion principle (1925) implies that the wave function of a many-electron system must be antisymmetrical under coordinate-spin permutations, has played an important role. Then, the application of *Hund*’s rules for the coupling of spins in atoms [10] has immediately followed [11].

Thus, with the birth of the “*Heisenberg-Dirac*” Hamiltonian expressed in the  $s_i \cdot s_j$  form, the notion of “exchange energy” resulting from a spin–spin interaction has naturally appeared as well as the first microscopic theory of ferromagnetism. Clearly the lowest state of a ferromagnetic interaction is characterized by a parallel alignment of spins. Discussing the sign of exchange energy *Néel* [12] has first introduced the concept of antiferromagnetism, *i.e.*, a state in which two sublattices of spins in a crystal may align themselves antiparallel. Two years later the idea of superexchange first appeared when *Kramers* [13] tried to understand the early adiabatic demagnetization results which indicated that small exchange couplings existed even between ions separated by one or several diamagnetic groups. Finally, to these central themes of the microscopic theory of magnetism in insulators and semiconductors, one may add the basic ideas of the crystal field theory introduced by *Van Vleck* [14].

In the present article we are going to examine the problem of direct exchange in the simplest cases, *i.e.*, formal coupling of two electrons initially isolated and hydrogen molecule. This will allow one to give a general framework which will be illustrated by the determination of the effective exchange Hamiltonian in a solid characterized by weak overlaps between the atomic orbitals involving first-nearest neighbours. Under these conditions, we always deal with *localized electrons*. Then, we examine the physical origin of spin-orbit coupling. Its influence on direct exchange allows one to revisit *Hund*’s rules and to express the phenomenological Hamiltonians describing anisotropic couplings as well as the antisymmetrical *Dzialoshinski-Moriya* coupling.

Consequently, the problem of *double exchange* will not be evoked in this article. Indeed this type of coupling to which *Zener* first focused [15] notably

occurs in mixed-valency oxides. In such compounds, one deals with the coupling of atoms which are identical except for the number of electrons. Then, interchange of the states of ionisation of the two atoms gives a new state degenerate with the initial one. Since these states can resonate, electrons can hop more easily between atoms and a ferromagnetic alignment of the two atomic spins  $\mathbf{S}_i$  and  $\mathbf{S}_j$  is favoured. This coupling is then characterized by a coupling energy linear in  $|\mathbf{S}_i + \mathbf{S}_j|$  rather than in  $\mathbf{S}_i \cdot \mathbf{S}_j$ . Thus, due to the involved mechanism which is completely different from the exchange one, the problem of double exchange naturally appears as out of the scope of the present article (for a complete review see the papers written by *Anderson* and *Hasegawa* [16] and *de Gennes* [17]).

In the following article II we shall examine the important case of *superexchange*. More particularly, since the phenomenological aspects of exchange coupling have been reviewed in article I and have shown their limits of applicability (the corresponding Hamiltonians having no predictive microscopic character), the involved microscopic mechanisms will be detailed in terms of key molecular integrals.

## Direct Exchange

### 1. The Hamiltonian Symmetries and Pauli's Exclusion Principle

Let us consider a system containing  $N$  electrons, each one being labelled by the current index  $i$  ( $i = 1, \dots, N$ ). Each electron is characterized by its position  $\mathbf{r}_i$  (with respect to the atom to which it belongs) and its spin  $s_i$ . If we set  $\mathbf{u}_i = (\mathbf{r}_i, s_i)$ , the corresponding Hamiltonian may be written as Eq. (1) where  $T_i$  is the kinetic energy of each particle  $i$ ,  $V_i$  the corresponding potential energy, and  $U_{i,j}$  the interaction potential between two different electrons  $i$  and  $j$  (Eq. (2)).

$$H(\mathbf{u}_1, \mathbf{u}_2, \dots, \mathbf{u}_i, \dots, \mathbf{u}_j, \dots, \mathbf{u}_N) = \sum_{i=1}^N (T_i + V_i) + \sum_{i \neq j} U_{i,j} \quad (1)$$

$$T_i = -\frac{\hbar^2}{2m} \nabla_i^2, \quad V_i = V(\mathbf{r}_i), \quad U_{i,j} = U(\mathbf{r}_i, \mathbf{r}_j) \quad (2)$$

$H$  is even with respect to the interchange of any two particle indices (double symmetry group for each pair). As a result of group theory we immediately derive that the corresponding eigenstates are either even or odd (Eq. (3)) so that many types of solutions combining all the pair behaviours (symmetry or antisymmetry) are possible.

$$\Psi(\mathbf{u}_1, \mathbf{u}_2, \dots, \mathbf{u}_i, \dots, \mathbf{u}_j, \dots, \mathbf{u}_N) = \pm \Psi(\mathbf{u}_1, \mathbf{u}_2, \dots, \mathbf{u}_j, \dots, \mathbf{u}_i, \dots, \mathbf{u}_N) \quad (3)$$

However *Pauli's* exclusion principle states that the eigenstates which are relevant when dealing with electrons (*i.e.*, fermions characterized by half-integer spins) must be strictly odd with respect to the interchange of any two particle indices (Eq. (4)) thus bringing a considerable restriction to the available solution domain.

$$\Psi(\mathbf{u}_1, \mathbf{u}_2, \dots, \mathbf{u}_i, \dots, \mathbf{u}_j, \dots, \mathbf{u}_N) = -\Psi(\mathbf{u}_1, \mathbf{u}_2, \dots, \mathbf{u}_j, \dots, \mathbf{u}_i, \dots, \mathbf{u}_N) \quad (4)$$

## 2. Formal Coupling of Two Electrons Initially Isolated

Let us consider the formal case of two electrons labelled 1 and 2, respectively, initially isolated and which may couple their spin. We suppose that there is no spin-orbit coupling. As a consequence, the orbital and spin parts of the collective wave function describing the system of coupled electrons are disconnected (Eq. (5)).

$$\Psi(\mathbf{u}_1, \mathbf{u}_2) = \Phi(\mathbf{r}_1, \mathbf{r}_2)\chi(\mathbf{s}_1, \mathbf{s}_2) \quad (5)$$

The Hamiltonian given by Eq. (1) (in which now  $V_1 = V_2 = 0$ ) only determines the orbital contribution (Eq. (6)).

$$H\Phi(\mathbf{r}_1, \mathbf{r}_2) = E\Phi(\mathbf{r}_1, \mathbf{r}_2) \quad (6)$$

*Pauli's* exclusion principle imposes that either  $\Phi(\mathbf{r}_1, \mathbf{r}_2)$  or  $\chi(\mathbf{s}_1, \mathbf{s}_2)$  must be odd (the other one remaining even) with respect to the interchange of indices 1 and 2. If the *Coulomb* repulsion  $U(\mathbf{r}_1, \mathbf{r}_2) = e^2/4\pi\epsilon_0|\mathbf{r}_1 - \mathbf{r}_2|$  between both electrons is small, this contribution to the Hamiltonian  $H$  may be considered as a perturbation. Let  $\Phi_a(\mathbf{r})$  (respectively,  $\Phi_b(\mathbf{r})$ ) be the eigenstate of the Hamiltonian  $H_1 = T_1 = \mathbf{p}_1^2/2m$  (respectively,  $H_2 = T_2 = \mathbf{p}_2^2/2m$ ) characterized by the eigenvalue  $E_a$  (respectively,  $E_b$ ). In this framework, this approximation leads to solve the well-known secular equation  $\det(H-E\mathbf{1})=0$  (where  $\mathbf{1}$  is the identity matrix and  $H = T_1 + T_2 + U(\mathbf{r}_1, \mathbf{r}_2)$ ). In the subspace spanned by the spatially symmetrical and antisymmetrical wave functions  $\Phi_S(\mathbf{r}_1, \mathbf{r}_2)$  and  $\Phi_A(\mathbf{r}_1, \mathbf{r}_2)$  containing functions  $\Phi_a(\mathbf{r}_1)$  and  $\Phi_b(\mathbf{r}_2)$ , we have Eq. (7).

$$\begin{aligned} \Phi_S(\mathbf{r}_1, \mathbf{r}_2) &= \frac{1}{\sqrt{2}}(\Phi_a(\mathbf{r}_1)\Phi_b(\mathbf{r}_2) + \Phi_a(\mathbf{r}_2)\Phi_b(\mathbf{r}_1)) \\ \Phi_A(\mathbf{r}_1, \mathbf{r}_2) &= \frac{1}{\sqrt{2}}(\Phi_a(\mathbf{r}_1)\Phi_b(\mathbf{r}_2) - \Phi_a(\mathbf{r}_2)\Phi_b(\mathbf{r}_1)) \end{aligned} \quad (7)$$

Note that these functions are orthogonal by construction, *i.e.*,  $\langle \Phi_S(\mathbf{r}_1, \mathbf{r}_2) | \Phi_A(\mathbf{r}_1, \mathbf{r}_2) \rangle = 0$ , and are the eigenstates of the permutation operator  $P$  of both particles (Eq. (8)).

$$P\Phi_S(\mathbf{r}_1, \mathbf{r}_2) = +\Phi_S(\mathbf{r}_1, \mathbf{r}_2), \quad P\Phi_A(\mathbf{r}_1, \mathbf{r}_2) = -\Phi_A(\mathbf{r}_1, \mathbf{r}_2) \quad (8)$$

Let us consider the spin part. As the spin states  $|s_1\rangle$  and  $|s_2\rangle$  are disconnected, the collective spin states  $\chi(\mathbf{s}_1, \mathbf{s}_2) = |s_1, s_2\rangle$  may be written as direct products  $|s_1\rangle \otimes |s_2\rangle$ . If one arbitrarily defines a  $z$ -direction in each spin space, *i.e.*, an axis of quantization, we have Eq. (9).

$$\chi(\mathbf{s}_1, \mathbf{s}_2) = |s_1, s_2\rangle = |s_1\rangle \otimes |s_2\rangle = |s_1^z\rangle \otimes |s_2^z\rangle = |s_1^z, s_2^z\rangle = \begin{cases} |\uparrow\uparrow\rangle \\ |\uparrow\downarrow\rangle \\ |\downarrow\uparrow\rangle \\ |\downarrow\downarrow\rangle \end{cases} \quad (9)$$

Even and odd linear combinations of these spin states may be built up. As there is no spin-orbit coupling, the full rotation group operates in each spin space with the representation  $D_{1/2}$  for a spin 1/2 associated with each electron. We have Eq. (10) where  $\oplus$  is the direct sum symbol.

$$D_{1/2} \otimes D_{1/2} = D_0 \oplus D_1 \quad (10)$$

It means that, if we introduce the total spin operators (Eq. (11)) we may define a new basis  $|S, S^z\rangle$  in a  $4 \times 4$  dimensional space from the starting basis  $|s_1, s_2\rangle$  with  $S=0$  ( $S^z=0$ , *singlet* state) and  $S=1$  ( $S^z=0, \pm 1$ , *triplet* state) (Eq. (12)).

$$\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2, \quad S^u = s_1^u + s_2^u, \quad u = x, y, \text{ or } z \quad (11)$$

$$\begin{aligned} |0, 0\rangle &= \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle), & S = 0 \text{ (singlet state)} \\ \left. \begin{aligned} |1, 1\rangle &= |\uparrow\uparrow\rangle, \\ |1, 0\rangle &= \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle), \\ |1, -1\rangle &= |\downarrow\downarrow\rangle \end{aligned} \right\} & S = 1 \text{ (triplet state)} \end{aligned} \quad (12)$$

Thus, the triplet states  $|1, S^z\rangle$  are even with respect to the interchange of indices 1 and 2, while the singlet state  $|0, 0\rangle$  is odd. Consequently, because of *Pauli's* exclusion principle, we have the following symmetries (Eq. (13)).

$$\begin{aligned} S = 1 \quad \chi(s_1, s_2) &= |s_1, s_2\rangle \text{ even, } \Phi(\mathbf{r}_1, \mathbf{r}_2) = \Phi_A(\mathbf{r}_1, \mathbf{r}_2) \text{ odd} \\ S = 0 \quad \chi(s_1, s_2) &= |s_1, s_2\rangle \text{ odd, } \Phi(\mathbf{r}_1, \mathbf{r}_2) = \Phi_S(\mathbf{r}_1, \mathbf{r}_2) \text{ even} \end{aligned} \quad (13)$$

From a physical point of view, a singlet state ( $S=0$ ) will be a non-magnetic state (i.e., a purely diamagnetic state) whereas the triplet state ( $S=1$ ) will be a magnetic one. Now we wish to express the Hamiltonian  $H$  given by Eq. (1) vs. spin operators, exclusively. As  $H$  commutes with the permutation operator  $P$ , its representation in the subspace spanned by the basis functions  $\Phi_S(\mathbf{r}_1, \mathbf{r}_2)$  and  $\Phi_A(\mathbf{r}_1, \mathbf{r}_2)$  is diagonal (Eq. (14)) where  $E_a$  and  $E_b$  are the eigenvalues associated with the eigenstates  $\Phi_a(\mathbf{r}_1)$  and  $\Phi_b(\mathbf{r}_2)$  appearing in  $\Phi_S(\mathbf{r}_1, \mathbf{r}_2)$  and  $\Phi_A(\mathbf{r}_1, \mathbf{r}_2)$  given by Eq. (7); similarly  $u$  and  $j$  are defined by Eq. (15).

$$H = \begin{pmatrix} E_a + E_b + u + j & 0 \\ 0 & E_a + E_b + u - j \end{pmatrix} \quad (14)$$

$$\begin{aligned} u &= \int d\mathbf{r}_1 d\mathbf{r}_2 |\Phi_a(\mathbf{r}_1)|^2 U(\mathbf{r}_1, \mathbf{r}_2) |\Phi_b(\mathbf{r}_2)|^2 \\ j &= \int d\mathbf{r}_1 d\mathbf{r}_2 \Phi_a^*(\mathbf{r}_1) \Phi_b^*(\mathbf{r}_2) U(\mathbf{r}_1, \mathbf{r}_2) \Phi_b(\mathbf{r}_1) \Phi_a(\mathbf{r}_2) \end{aligned} \quad (15)$$

$u$  is the *Hartree* term (or direct term) whereas  $j$  is the *Fock* term (or exchange term).  $j$  is nothing but the electrostatic energy of the charge distribution  $-e\Phi_a^*(\mathbf{r})\Phi_b(\mathbf{r})$  and is positive definite. As a consequence, if we examine Eq. (7) where the spatially symmetrical and antisymmetrical wave functions are defined, we derive that *function*  $\Phi_A(\mathbf{r}_1, \mathbf{r}_2)$  corresponds to the state of lowest energy. Owing to *Pauli's* exclusion principle we must associate the triplet spin state ( $S=1$ , cf. Eq. (12)) characterized by a symmetrical spin function. Under these conditions, the singlet state ( $S=0$  and antisymmetrical spin wave function, cf. Eq. (12)) is associated with a spatially symmetrical wave function  $\Phi_S(\mathbf{r}_1, \mathbf{r}_2)$  and characterizes the state of highest energy. At this step the physical interpretation is easy: the *Coulomb* repulsion between both electrons favours the state with a parallel spin alignment (see comments below about *Hund's* rule). The energy  $J$  (Eq. (16)) is called "exchange energy";  $E_{S,0}$

and  $E_{T,0}$  are the energies associated with the low-lying singlet and triplet states, respectively.

$$J = E_{S,0} - E_{T,0} = 2j \quad (16)$$

As noted by *Herring* [18], it is possible to give a physical picture for describing this quantity. If we consider both electrons at the time origin  $t=0$  and in the initial state  $\Phi_a(\mathbf{r}_1)\Phi_b(\mathbf{r}_2)$ , the potential  $U(\mathbf{r}_1, \mathbf{r}_2)$  achieves a connection with the permuted state  $\Phi_a(\mathbf{r}_2)\Phi_b(\mathbf{r}_1)$  by the bias of the matrix element  $j$ . Over a small time range  $\Delta t$ , the probability amplitude of the permuted state increases as  $j\Delta t$  ( $j > 0$ ). In other words  $j$  measures the initial ratio with which two tagged electrons, placed one in each state, may be exchanged between these states.

It is straightforwardly shown that the spectrum and the eigenvalues of the effective spin Hamiltonian (in  $\hbar$  unit) (Eq. (17)) coincide with those of  $H$  defined by Eq. (1), restricted to the two electrons 1 and 2, with  $V_1 = V_2 = 0$ , the spin operator of which being given by the set of *Pauli*'s matrices  $\boldsymbol{\sigma}_1$  and  $\boldsymbol{\sigma}_2$  (with  $s_i = \hbar\boldsymbol{\sigma}_i/2$ ,  $i = 1, 2$ ).

$$H_{\text{eff}} = E_0 \mathbf{1} - J s_1 \cdot s_2, \quad E_0 = E_a + E_b + u - \frac{j}{2} \quad (17)$$

$\mathbf{1}$  is the  $4 \times 4$  identity matrix. Then, if we express the projector operators  $P_T$  and  $P_S$  on the triplet and singlet states, respectively, we have for spins  $1/2$  (in  $\hbar$  unit) Eq. (18) so that  $H_{\text{eff}}$  (Eq. (19)) corresponds to the electronic Hamiltonian finally concerning the two types of involved states, *i.e.*, the singlet and triplet states.

$$P_T = \frac{3}{4} \mathbf{1} + s_1 \cdot s_2, \quad P_S = \frac{1}{4} \mathbf{1} - s_1 \cdot s_2 \quad (18)$$

$$H_{\text{eff}} = E_0 \mathbf{1} - \frac{j}{2} (P_T - 3P_S) \quad (19)$$

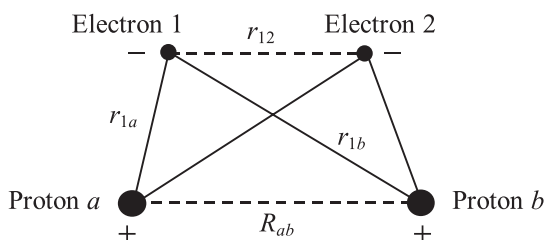
### 3. The Particular Case of Hydrogen Molecule

In 1927 *Heitler* and *London* [19–21] have given the first treatment of the coupling of atoms to form molecules by considering the hydrogen molecule. *Heitler* and *London* have assumed spatial wave functions of the same form, as those given by Eq. (7). But, due to the mass difference between electrons and nuclei, the degrees of freedom may be uncoupled, thus allowing to fix the nuclei positions, say  $\mathbf{R}_a$  and  $\mathbf{R}_b$ . As a consequence, the Hamiltonian describing the motion of the two electrons in the field of the two nuclei may be decomposed into two hydrogenoid contributions and a potential interaction describing the *Coulomb* repulsion between electrons (respectively, between protons) and the attraction with the other proton. This is the well-known *Born-Oppenheimer approximation* [22]. Under these conditions the Hamiltonian may be written as Eq. (20) with  $H_{1a}$ ,  $H_{2b}$ , and  $U_{\text{int}}$  being given by Eq. (21) where the various distances  $r_{1a}$ ,  $r_{1b}$ ,  $r_{2a}$ ,  $r_{2b}$ ,  $r_{12}$ , and  $R_{ab}$  are defined in Fig. 1.

$$H = H_{1a}(\mathbf{r}_1) + H_{2b}(\mathbf{r}_2) + U_{\text{int}}(\mathbf{r}_1, \mathbf{r}_2) \quad (20)$$

$$H_{1a}(\mathbf{r}_1) = \frac{\mathbf{p}_1^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r_{1a}}, \quad H_{2b}(\mathbf{r}_2) = \frac{\mathbf{p}_2^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r_{2b}}$$

$$U_{\text{int}}(\mathbf{r}_1, \mathbf{r}_2) = \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{R_{ab}} + \frac{1}{r_{12}} - \frac{1}{r_{2a}} - \frac{1}{r_{1b}} \right) \quad (21)$$



**Fig. 1.** Description of the distances between protons and electrons in the molecule  $H_2$ ; the dashed lines correspond to repulsive interactions

Let  $\Phi_a(\mathbf{r}_1) = \Phi(\mathbf{r}_{1a})$  and  $\Phi_b(\mathbf{r}_2) = \Phi(\mathbf{r}_{2b})$  be the eigenstates of Hamiltonians  $H_{1a}(\mathbf{r}_1)$  and  $H_{2b}(\mathbf{r}_2)$ , respectively; the corresponding ground state is characterized by the energy  $E_0^*$ . Oppositely to the case of the formal coupling of two electrons where the orbitals are orthogonal by definition, orbitals  $\Phi_a(\mathbf{r}_1) = \Phi(\mathbf{r}_{1a})$  and  $\Phi_b(\mathbf{r}_2) = \Phi(\mathbf{r}_{2b})$  are not orthogonal and allow one to construct the spatially symmetrical and antisymmetrical wave functions of the two electrons (Eq. (22)).

$$\begin{aligned}\Phi_S(\mathbf{r}_1, \mathbf{r}_2) &= \frac{1}{\sqrt{2(1+S^2)}} (\Phi_a(\mathbf{r}_1)\Phi_b(\mathbf{r}_2) + \Phi_a(\mathbf{r}_2)\Phi_b(\mathbf{r}_1)) \\ \Phi_A(\mathbf{r}_1, \mathbf{r}_2) &= \frac{1}{\sqrt{2(1-S^2)}} (\Phi_a(\mathbf{r}_1)\Phi_b(\mathbf{r}_2) - \Phi_a(\mathbf{r}_2)\Phi_b(\mathbf{r}_1))\end{aligned}\quad (22)$$

These functions are eigenfunctions of the permutation operator (see Eq. (8)) and are orthogonal. They have been normalized by introducing the overlap integral  $S$  (Eq. (23)).

$$S = \int d\mathbf{r} \Phi_a^*(\mathbf{r})\Phi_b(\mathbf{r}) \quad (23)$$

The terms of *Hartree* (direct term) and *Fock* (exchange term) are respectively defined as follows (Eq. (24)).

$$\begin{aligned}u &= \int d\mathbf{r}_1 d\mathbf{r}_2 |\Phi_a(\mathbf{r}_1)|^2 U_{\text{int}}(\mathbf{r}_1, \mathbf{r}_2) |\Phi_b(\mathbf{r}_2)|^2 = \int d\mathbf{r}_1 d\mathbf{r}_2 |\Phi_a(\mathbf{r}_2)|^2 U_{\text{int}}(\mathbf{r}_1, \mathbf{r}_2) |\Phi_b(\mathbf{r}_1)|^2 \\ j &= \int d\mathbf{r}_1 d\mathbf{r}_2 \Phi_a^*(\mathbf{r}_1)\Phi_b^*(\mathbf{r}_2) U_{\text{int}}(\mathbf{r}_1, \mathbf{r}_2) \Phi_b(\mathbf{r}_1)\Phi_a(\mathbf{r}_2)\end{aligned}\quad (24)$$

In addition the spatial wave functions  $\Phi_S(\mathbf{r}_1, \mathbf{r}_2)$  and  $\Phi_A(\mathbf{r}_1, \mathbf{r}_2)$  must be multiplied by the spin wave function of the adequate symmetry, as imposed by *Pauli's* exclusion principle (see Eq. (13)). In the subspace spanned by the functions  $\Phi_S(\mathbf{r}_1, \mathbf{r}_2)$  and  $\Phi_A(\mathbf{r}_1, \mathbf{r}_2)$  given by Eq. (22) the secular equation (Eq. (25)) reads as shown by Eq. (26).

$$\langle \Phi_i | H | \Phi_j \rangle = E \langle \Phi_i | \Phi_j \rangle \quad i \text{ or } j = A \text{ or } S \quad (25)$$

$$\begin{pmatrix} 2E_0^* + \frac{u+j}{1+S^2} & 0 \\ 0 & 2E_0^* + \frac{u-j}{1-S^2} \end{pmatrix} = \begin{pmatrix} E_{S,0} & 0 \\ 0 & E_{T,0} \end{pmatrix} \quad (26)$$

Achieving the same reasoning as for the formal coupling of two electrons, we derive Eq. (27) and the associate effective Hamiltonian expressed in terms of spin operators is given by Eq. (28).

$$J = E_{S,0} - E_{T,0} = -2 \frac{uS^2 - j}{1 - S^4} \quad (27)$$

$$H_{\text{eff}} = E_0 \mathbf{1} - J \mathbf{s}_1 \cdot \mathbf{s}_2, \quad E_0 = 2E_0^* + \frac{u - jS^2}{1 - S^4} - \frac{J}{4} \quad (28)$$

Ignoring the first two terms in  $E_0$ , the eigenvalues of  $H_{\text{eff}}$  are  $-J/4$  (triplet state) and  $3J/4$  (singlet state) in  $\hbar$  unit, thus reproducing the electronic spectrum. When the separation between hydrogen atoms is large enough, the overlap  $S$  is small and we have Eq. (29).

$$J \approx 2(j - uS^2) \quad (29)$$

As for a single atom,  $j$  is an electrostatic energy and is positive definite, as  $u$ . Thus,  $J$  appears as the difference of two positive quantities and may be (i) positive,  $E_{S,0} > E_{T,0}$  and the ground state is characterized by a ferromagnetic spin arrangement and a spatially antisymmetrical wave function  $\Phi_A(\mathbf{r}_1, \mathbf{r}_2)$ ; (ii) negative,  $E_{S,0} < E_{T,0}$  and the ground state is characterized by an antiferromagnetic spin arrangement and a spatially symmetrical wave function  $\Phi_S(\mathbf{r}_1, \mathbf{r}_2)$ .

A calculation shows that, for realistic values of the separation distance  $R_{ab}$  between the two protons, case (ii) prevails (antiferromagnetic arrangement). However, for large values  $R_{ab}$ , case (i) now prevails (ferromagnetic arrangement). *Sugiura* [23] has given an exact evaluation of the difference  $E_{S,0} - E_{T,0}$  for the case where  $\Phi_a(\mathbf{r}_1)$  and  $\Phi_b(\mathbf{r}_2)$  are hydrogenic  $1s$  eigenfunctions (Eq. (30)) where  $\gamma = 0.577$  is *Euler's* constant and  $a_H$  is the radius of hydrogen atom (*Bohr* radius).

$$J = E_{S,0} - E_{T,0} \approx \left[ -\frac{56}{45} + \frac{4}{15}\gamma + \frac{4}{15}\ln\left(\frac{R}{a_H}\right) \right] \left(\frac{R}{a_H}\right)^3 \exp\left(-2\frac{R}{a_H}\right) \quad (30)$$

Thus, for reasonable values of  $R$ ,  $J < 0$  (antiferromagnetic arrangement) but  $J > 0$  (ferromagnetic arrangement) at very large  $R$  values because of the logarithm. Unfortunately the latter result contradicts a theorem established by *Courant* [24, Chapter VI, Section 6; 18] which states that the ground state eigenfunction of a semi-bounded *Sturm-Liouville* differential operator, acting in a space of any dimension, must be free from nodes. In other words, *in the  $H_2$  problem, this means that, for any  $R$ , the ground state must be a singlet* (the triplet being characterized by a spatially antisymmetrical wave function). This problem simply comes from the fact that, in the *Heitler-London approximation*, the electron-electron correlations are neglected while using atomic orbitals. The presence of a second atom induces a polarization in the atomic orbitals and increases the probability of finding the electrons between the two protons. In addition, when the two electrons exchange themselves, this event does not occur on the axis joining the two protons because both electrons try to avoid themselves for minimizing their *Coulomb* repulsion.



#### 4. Effective Exchange Hamiltonian for a Solid

We now examine the possible generalization of previous results to a solid when the various overlaps between atomic orbitals are weak [18, 25]. In this respect we must begin by a thorough description of the electronic structure. For an atom  $i$  with  $n_i$  electrons there are  $2^{n_i}$  possible spin functions and for each of these there are  $M_i$  linearly independent coordinate functions of the same energy (which may be transformed by permutations). Thus the partition of  $n = \sum_i n_i$  electrons into sets of  $n_1, n_2, \dots, n_N$  on the various atoms leads to  $\prod_i 2^{n_i} M_i$  independent states. As a consequence the dimensionality of the possible states is  $n! / \prod_i (2^{n_i} M_i / n_i!)$ . Within the space just described, we may define a state  $\overline{\Psi}_k$  of the separated-atom system by the following conditions: (i) electrons  $1, \dots, n_1$  are to be on atom 1, electrons  $(n_1 + 1), \dots, (n_1 + n_2)$  on atom 2, and so forth; (ii) electrons on each atom obey *Pauli's* exclusion principle (*i.e.*, there are in a state antisymmetrical under coordination-spin permutations); (iii) each atom  $i$  is characterized by a particular spin state  $k_i$ , chosen among the  $2S_i + 1$  possible states (the sum  $S_i$  being the total spin of the  $n_i$  electrons).

Now let us define  $\Psi_k$  as the state of the interacting-atom system that corresponds to  $\overline{\Psi}_k$  (Eq. (31)).

$$\Psi_k \rightarrow \overline{\Psi}_k \quad (31)$$

This correspondence is characterized by the following properties: (i) for any spatial symmetry operator  $R$ , or for the time-reversal operator  $K$ , Eq. (31) holds together with Eq. (32); (ii) the scalar product is preserved (Eq. (33)); (iii) the effective Hamiltonian  $H_{\text{eff}}$  relative to the state  $\overline{\Psi}_k$  is the same as that of the Hamiltonian  $H$  relative to the state  $\Psi_k$  so that Eq. (34) is obtained.

$$R\Psi_k \rightarrow R\overline{\Psi}_k, \quad K\Psi_k \rightarrow K\overline{\Psi}_k \quad (32)$$

$$\langle \Psi_k | \Psi_{k'} \rangle = \langle \overline{\Psi}_k | \overline{\Psi}_{k'} \rangle \quad (33)$$

$$\langle \Psi_k | H | \Psi_{k'} \rangle = \langle \overline{\Psi}_k | H_{\text{eff}} | \overline{\Psi}_{k'} \rangle \quad (34)$$

Finally we must make an assumption of localization; the functions  $\overline{\Psi}_k$  of the separated-atom system decrease exponentially when any electron  $m$  is removed to a large distance from the centre  $\mathbf{R}_{i(m)}$  of its own atom  $i(m)$  (Eq. (35)) where  $C$  is an algebraic factor and  $\alpha_{i(m)}$  is the decay constant of the atomic wave function. Due to the fact that overlaps between atomic orbitals are weak, the *Heitler-London approximation* consists in taking for  $\Psi_k$  simply a product of free-atom wave functions (Eq. (36)) where  $\Phi_{k_i}$  is the eigenfunction of atom  $i$  in spin state  $k_i$ . Under these conditions the  $\Psi_k$ s obey the localization condition given by Eq. (35). In addition, as there is no spin-orbit coupling and for satisfying *Pauli's* exclusion principle, each wave function  $\Psi$  must be antisymmetrical under the permutation of coordinates and/or spins and may be symbolically written as shown by Eq. (37).

$$\overline{\Psi}_k \approx C \exp\left(-\sum_m \alpha_{i(m)} |\mathbf{r}_m - \mathbf{R}_{i(m)}|\right) \quad (35)$$

$$\Psi_k \approx \Phi_{k_1}(\mathbf{r}_1, \dots, \mathbf{r}_{n_1}; \mathbf{s}_1, \dots, \mathbf{s}_{n_1}) \Phi_{k_2}(\mathbf{r}_{n_1+1}, \dots, \mathbf{r}_{n_1+n_2}; \mathbf{s}_{n_1+1}, \dots, \mathbf{s}_{n_1+n_2}) \\ \times \dots \times \Phi_{k_N}(\dots, \mathbf{r}_n; \dots, \mathbf{s}_n) \quad (36)$$

$$\Psi_k(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{s}_1, \dots, \mathbf{s}_N) = \mathcal{A} \Phi_k(\mathbf{r}_1, \dots, \mathbf{r}_N) \chi_k(\mathbf{s}_1, \dots, \mathbf{s}_N) \quad (37)$$

$\mathcal{A}$  thus appears as a global antisymmetrizer operator (Eq. (38)) with  $P_{ij}^{(r)}$  and  $P_{ij}^{(s)}$  being given by Eq. (39).

$$\mathcal{A} = \frac{1}{n!} \sum_P \delta_P P_{ij}^{(r)} P_{ij}^{(s)} \quad (38)$$

$$P_{ij}^{(r)} \langle \dots, \mathbf{r}_i, \dots, \mathbf{r}_j, \dots | \Phi_k \rangle = \langle \dots, \mathbf{r}_j, \dots, \mathbf{r}_i, \dots | \Phi_k \rangle \\ P_{ij}^{(s)} \langle \dots, \mathbf{s}_i, \dots, \mathbf{s}_j, \dots | \chi_k \rangle = \langle \dots, \mathbf{s}_j, \dots, \mathbf{s}_i, \dots | \chi_k \rangle \quad (39)$$

For spins 1/2,  $P_{ij}^{(s)}$  may be expressed owing to *Pauli* matrices or *s* matrices by Eq. (40).

$$P_{ij}^{(s)} = \left( \frac{1}{2} \mathbf{1} + 2\mathbf{s}_i \cdot \mathbf{s}_j \right) \quad (40)$$

In Eq. (38)  $\delta_P = +1$  is for even permutations,  $-1$  for odd. Since the projections  $\mathcal{A} \Phi_k$  of the home-base functions characterized by the various spin states  $k$  form a complete set in the subspace of physical interest, the eigenvalues  $E$  of the Hamiltonian  $H$  for the system of interacting atoms are solutions of the secular equation (Eq. (41)).

$$\det[\langle \Phi_k | H \mathcal{A} | \Phi_{k'} \rangle - E \langle \Phi_k | \mathcal{A} | \Phi_{k'} \rangle] = 0 \quad (41)$$

As permutations commute with the Hamiltonian  $H$  given by Eq. (1) and show a group structure, it is easily verified that Eq. (42) may be decomposed as Eq. (43) where  $V_P$  is given by Eq. (44).

$$\langle \Psi_k | H | \Psi_{k'} \rangle = \frac{1}{(n!)^2} \langle \Phi_k | \otimes \langle \chi_k | \sum_{P'} \delta_{P'} P_{ij}^{(r)} P_{ij}^{(s)} H \sum_P \delta_P P_{ij}^{(r)} P_{ij}^{(s)} | \Phi_{k'} \rangle \otimes | \chi_{k'} \rangle \quad (42)$$

$$\langle \Psi_k | H | \Psi_{k'} \rangle = \frac{1}{n!} \langle \chi_k | \sum_P \delta_P V_P P_{ij}^{(s)} | \chi_{k'} \rangle \quad (43)$$

$$V_P = \langle \Phi_k | H | P_{ij}^{(r)} \Phi_{k'} \rangle \quad (44)$$

Thus the secular equation given by Eq. (41) and which determines the solid energy spectrum is equivalent to the secular equation in spin space (Eq. (45)) where  $S_P = \langle \Phi | P_{ij}^{(r)} \Phi \rangle$  is the overlap integral.

$$\det \left[ \sum_P \delta_P (V_P - \varepsilon S_P) P_{ij}^{(s)} \right] = 0 \quad (45)$$

Let us examine the secular equation given by Eq. (41). The permutations  $P = P_{ij}^{(r)} P_{ij}^{(s)}$  which do not move any electron to a new atom form a subgroup  $G_0$  of the group  $G$  of all permutations, such as  $\dim G_0 = \prod_i n_i!$ . The corresponding contribution to Eq. (41) is diagonal, as expected. The largest non-trivial terms in

Eq. (41) are those for which  $P_s$  interchange a single pair of electrons between neighbouring atoms. The  $P_s$  which interchange electrons between far and far atoms give smaller contributions. This is due to the fact that a large number of the coordinate integrations in the scalar product  $\langle \Phi_k | H | \Phi_{k'} \rangle$  involves overlap integrals of the form given by Eq. (35). Under these conditions, expressing  $P_{ij}^{(s)}$  owing to Eq. (40) allows one to write the  $kk'$  matrix element as shown by Eq. (46) where  $n_i$  and  $n_j$  represent the number of electrons involved in permutations between sites  $i$  and  $j$  and where  $\bar{E}_\phi$  is the mean energy  $\langle \Phi_k | H | \Phi_k \rangle$  (the same for all  $k$ ).

$$(\bar{E}_\phi - E)\delta_{kk'} - \sum_{i>j} n_i n_j \langle \Phi_k | (H - E) | P_{ij}^{(r)} \left( \frac{1}{2} \mathbf{1} + 2\mathbf{s}_i \cdot \mathbf{s}_j \right) | \Phi_{k'} \rangle + \dots \quad (46)$$

The remainder term represented by ellipses refers to the contribution from higher-order permutations characterized by an exponential decay law (*cf.* Eq. (35)).

If we consider the dependence of  $\Phi_k$  on the coordinates and spins of the  $n_1$  electrons of atom 1, exclusive permutations of the  $n_1$  coordinates will transform  $\Phi_k$  like a function belonging to an irreducible representation  $D_1$  of the permutation group of  $n_1$  objects, characterized by the dimension  $M_1$ . According to *Wigner* [26],  $\Phi_k$ , which is antisymmetrical under simultaneous permutations of the  $n_1$  coordinates and the corresponding spins, may be written as shown by Eq. (47) where the functions  $\varphi_\xi$  form an orthonormal basis for the irreducible representation  $D_1$ .

$$\Phi_k = \frac{1}{\sqrt{M_1}} \sum_{\xi=1}^{M_1} \varphi_\xi(\mathbf{r}_1, \dots, \mathbf{r}_{n_1}) \chi_\xi(\mathbf{s}_1, \dots, \mathbf{s}_{n_1}) \quad (47)$$

The spin functions  $\chi_\xi$  form a corresponding basis for the associated representation  $\bar{D}_1 = \delta_p D_1$ . At this step, one must remark that, if  $\Phi_k$  is to transform under rotations of the first  $n_1$  spins, like the  $k_1$ th basis state of the irreducible representation of the rotation group characterized by spin  $S_1$ , then each function  $\chi_\xi = \chi_{\xi_1}$  must show this property. As a consequence, it is appropriate to write  $\chi_{\xi_1}$  as  $\chi_{k_1 \xi_1}$  for recalling that its form is determined by its rotational symmetry (quantum number  $k_1$ ) and its permutational symmetry (quantum number  $\xi_1$ ).

Repeating this reasoning to the other  $N - 1$  atoms of the solid allows one to write finally Eq. (48) where  $n$  is the total number of involved electrons.

$$\Phi_k = \frac{1}{\sqrt{\prod_{i=1}^N M_i}} \sum_{\xi_1=1}^{M_1} \dots \sum_{\xi_N=1}^{M_N} \varphi_{\xi_1 \dots \xi_N}(\mathbf{r}_1, \dots, \mathbf{r}_n) \chi_{k_1 \xi_1} \dots \chi_{k_N \xi_N} \quad (48)$$

The last task is to express the term of Eq. (46) containing the product  $\mathbf{s}_i \cdot \mathbf{s}_j$  in terms of spins  $\mathbf{S}_i \cdot \mathbf{S}_j$  of the complete atoms. Owing to *Wigner-Eckart* theorem we may write Eq. (49) with conditions being given by Eq. (50) and where  $\mathbf{S}_i$  is the sum of the spins of all the  $n_i$  electrons belonging to atom  $i$ .

$$\langle k_i \xi_i | \mathbf{s}_i | k_i' \xi_i' \rangle = f_i(\xi_i, \xi_i') \langle k_i \xi_i | \mathbf{S}_i | k_i' \xi_i' \rangle \quad (49)$$

$$f_i(\xi_i, \xi_i') = f_i^*(\xi_i', \xi_i), \quad \sum_{\xi_i=1}^{M_i} f_i(\xi_i, \xi_i) = \frac{M_i}{n_i} \quad (50)$$

This is owing to this argument that *Van Vleck* established the present model [27]. Under these conditions, when the wave functions are non-degenerate, the spin-dependent part of the matrix element given by Eq. (46) may be rewritten as Eq. (51) so that the effective Hamiltonian is described by Eq. (52) in the spin space; as previously noted  $\overline{E_\phi}$  is the mean energy  $\langle \Phi_k | H | \Phi_k \rangle$  (the same for all  $k$ ),  $\Delta \overline{E_\phi}$  is the  $k$ -dependent term which arises from the factor  $\frac{1}{2} \mathbf{1}$  in Eq. (46) and  $J_{ij}$  is given by Eq. (53).

$$-2 \sum_{i>j} \langle \chi_k | \mathbf{S}_i \cdot \mathbf{S}_j | \chi_{k'} \rangle \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \Phi_k (H - E) P_{ij}^{(r)} \Phi_{k'} \quad (51)$$

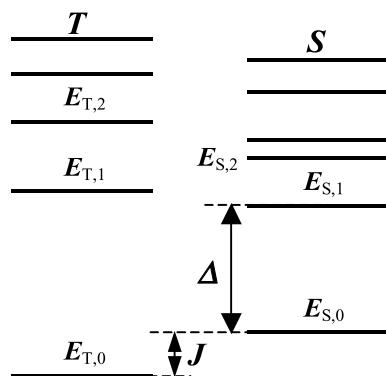
$$H_{\text{eff}} = (\overline{E_\phi} + \Delta \overline{E_\phi}) \mathbf{1} - 2 \sum_{i>j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \quad (52)$$

$$J_{ij} = \frac{n_i n_j}{M_i M_j} \sum_{\xi_i=1}^{M_i} \sum_{\xi'_i=1}^{M_i} \sum_{\xi_j=1}^{M_j} \sum_{\xi'_j=1}^{M_j} f_i(\xi_i, \xi'_i) f_j(\xi_j, \xi'_j) \\ \times \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \langle \varphi_{\dots \xi_i \dots \xi_j \dots}^* | (H - \overline{E_\phi}) | P_{ij}^{(r)} \varphi_{\dots \xi'_i \dots \xi'_j \dots} \rangle_{\text{other } \xi} \quad (53)$$

Thus,  $J_{ij}$  is determined by the coordinate functions  $\varphi_{\xi_1 \dots \xi_N}$  and the symmetries of the problem. The angular brackets mean that the  $\xi_k$ s of atoms other than  $i$  and  $j$  are to be taken the same in  $\varphi^*$  and in  $\varphi$ .

### 5. Concluding Remarks

We have previously seen that the spin–spin exchange coupling has a strictly orbital origin [28]. Furthermore the exchange coupling has appeared as a consequence of the interplay between *Pauli*'s exclusion principle and various energy terms. Thus, any term  $T_1, \dots, V_1, \dots$ , and/or  $U_{12}, \dots$  may contribute to the exchange coupling through the energy difference  $E_{S,0} - E_{T,0}$ , where  $E_{S,0}$  and  $E_{T,0}$  are the respective energies of the singlet and triplet states (see Fig. 2 where the excited states are also reported, the ground state being the triplet). If  $\Delta = E_{S,1} - E_{S,0}$  is the difference



**Fig. 2.** Description of a commonly encountered molecular energy level spectrum; the singlet and triplet spectra have been artificially separated

between the energies of the ground state and the first excited state in the singlet spectrum, the use of the spin–spin Hamiltonian  $-Js_i \cdot s_j$ , with here  $J = E_{S,0} - E_{T,0}$ , is submitted to the two conditions: (i)  $J \ll \Delta$  and (ii)  $kT \ll \Delta$  where  $T$  is the absolute temperature and  $k$  the *Boltzmann's* constant.

In the particular case of the hydrogen molecule, we have seen that the ground state (which is diamagnetic) correspond to the case  $E_{S,0} < E_{T,0}$  and the discussion led by *Sugiura* [23] sets the problem of the sign of  $J$ . At this step we must mention that the energy level spectrum described in Fig. 2 corresponds to a case often encountered in molecular systems. In addition the following spin Hamiltonian (Eq. (54)) may be conventionally employed ( $J > 0$  corresponds to an antiferromagnetic arrangement  $-E_{T,0} > E_{S,0}$  – whereas  $J < 0$  corresponds to a ferromagnetic one  $-E_{T,0} < E_{S,0}$ ).

$$H = E_0 \mathbf{1} + Js_1 \cdot s_2, \quad J = -(E_{S,0} - E_{T,0}) \quad (54)$$

However, in any case, the order of magnitude as well as the sign of  $J$  will be the major answers to the questions concerning the exchange problem. Thus, we may suspect that slight modifications in the crystal structure (for instance due to the *Jahn-Teller* effect [29]) or in the molecular one (crystallized or solvated state) will have strong effects on the exchange coupling and, correlatively, on the magnetic behaviour.

Finally, for evoking the complexity of exchange coupling, we must examine the property of additivity which must be followed by the exchange Hamiltonian. Let us consider, for instance, the problem of four interacting electrons and let us specifically examine the exchange coupling between electrons 1 and 2. The effect of electrons 3 and 4 is treated through the effective (mean) potentials  $\delta V(\mathbf{r}_1)$  and  $\delta V(\mathbf{r}_2)$  “seen” by electrons 1 and 2 (*Hartree-Fock approximation*). Under these conditions the general Hamiltonian for electrons 1 and 2 may be written as Eq. (55) where  $T_i$  and  $V_i$  are given by Eq. (2) and  $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ .

$$H(\mathbf{r}_1, \mathbf{r}_2) + \delta H(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i=1}^2 (T_i + V_i) + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \delta V(\mathbf{r}_1) + \delta V(\mathbf{r}_2) \quad (55)$$

The energies of the even and odd low-lying solutions allow one to define the effective exchange constant  $J_{12}$  between spins  $s_1$  and  $s_2$ . Through  $\delta H(\mathbf{r}_1, \mathbf{r}_2)$   $J_{12}$  depends on the mean distribution (orbital functions) of electrons 3 and 4, which depends itself on the relative orientation of spins  $s_3$  and  $s_4$  (Eq. (56)).

$$J_{12} = J_{12}(s_3 \cdot s_4) \quad (56)$$

Hence the exchange Hamiltonian may be written as Eq. (57).

$$H_{\text{ex}}(s_1, s_2) = -J_{12}(s_3 \cdot s_4) s_1 \cdot s_2 \quad (57)$$

Of course this argument holds for the six distinct electron pairs and, clearly, the situation is quite intricate. Thus, in the present restricted approach, the general Hamiltonian will be as shown by Eq. (58).

$$H_{\text{ex}}(s_1, s_2, s_3, s_4) = \sum_i \sum_{j \neq i} H_{\text{ex}}(s_i, s_j) \quad (58)$$

In addition, as soon as spin-orbit couplings appear, the simplified form taken by the spin–spin exchange Hamiltonian will become more and more complicated [30].

In the general case, several contributions to the Hamiltonian may co-exist and compete. As a consequence, it will be necessary to introduce higher-order couplings involving mechanisms for which more than two spins will interact. Due to their specific character, this aspect will not be evoked in the present article in spite of the fact that the importance of these couplings has been pointed out since the beginning of the sixties. A special review has been achieved by *Herring* [18].

In this respect, let us recall that, from an experimental point of view, it was difficult to find a clear evidence of the existence of higher-order couplings, except for the bi-quadratic term [31]. General four-spin exchange has been investigated intensively since the problem of solid  $^3\text{He}$  [32]. Indeed, from NMR experiments, *Osheroff et al.* [33] observed that the low-temperature spin state of solid  $^3\text{He}$  is a state in which ferromagnetic planes show up–up–down–down spin sequences along one of the cubic axes. This new type of structure has been interpreted by *Roger et al.* [34] as a strong evidence of planar four-spin interactions, large in magnitude. At the beginning of the eighties, other examples were investigated in high field magnetism, by analyzing anomalous magnetization measurements on compounds such as  $\text{NiS}_2$  [35] or  $\text{C}_6\text{Eu}$  [36]. These results were also interpreted as further examples of four-spin exchange interactions in addition to the usual two-spin exchange. A complete review of the four-spin exchange and its application has been achieved by *Yosida* [37].

## The Problem of Spin-Orbit Coupling

### 1. Physical Origin

In the absence of interactions all the magnetism of electrons may be described by the *Dirac* equation (1928) which rules out the quantum relativistic motion of an electron in static fields  $\mathbf{E} = -\nabla U$  and  $\mathbf{B} = \text{curl}\mathbf{A}$  (where  $U$  and  $\mathbf{A}$  are the scalar and vectorial potentials, respectively) [38]. As the electrons involved in a solid structure are characterized by a small velocity with respect to the light celerity  $c$  ( $v/c \sim 10^{-2}$ ) we must consider the non-relativistic limit of the *Dirac* equation. This specific work has been achieved in Appendix. In a first step, it allows one to derive the *Pauli* equation (Eq. (59)) (1927) where  $\mathbf{p} = -i\hbar\nabla$  represents the impulsion operator,  $q = -e < 0$ , the charge of electron,  $\boldsymbol{\sigma}$ , the set of  $2 \times 2$  *Pauli*'s matrices and  $\mathbf{1}$ , the  $2 \times 2$  identity matrix. Thus,  $\varphi$  appears as a 2-component eigenfunction. If we introduce the spin operator  $s = \hbar\boldsymbol{\sigma}/2$ , each  $\varphi$ -component takes into account the eigenvalue of the operator  $s^z$  along the  $z$ -axis of quantization, *i.e.*,  $\pm 1/2$  (in  $\hbar$  unit). Then, the *Pauli* equation differs from the non-relativistic *Schrödinger* equation by the presence of an extra term, *i.e.*, the spin magnetic moment (Eq. (60)) (in  $\hbar$  unit) where  $\mu_B$  is the *Bohr* magneton and  $q = -e$ .

$$\left\{ \left[ \frac{1}{2m} (\mathbf{p} - q\mathbf{A})^2 + qU \right] \mathbf{1} - \frac{q\hbar}{2m} \boldsymbol{\sigma} \cdot \mathbf{B} \right\} \varphi = i\hbar \frac{\partial \varphi}{\partial t} \quad (59)$$

$$\mu_s = 2\mu_B s, \quad \mu_B = \frac{q\hbar}{2m} \quad (60)$$

In Appendix we have achieved the  $1/c$ -expansion of the *Dirac* equation up to  $1/c^2$ . We have the following Hamiltonian (Eq. (61)) with  $H_0$ ,  $V(\mathbf{r})$ ,  $H_S$ , and  $H_{so}^e$  being given by Eq. (62).

$$H = H_0 + V(\mathbf{r})\mathbf{1} + H_S + H_{so}^e + o\left(\frac{1}{c^3}\right) \quad (61)$$

$$H_0 = \frac{1}{2m}(\mathbf{p} - q\mathbf{A})^2\mathbf{1}, \quad V(\mathbf{r}) = qU(\mathbf{r})$$

$$H_S = -g_S\mu_B\mathbf{s} \cdot \mathbf{B}, \quad H_{so}^e = -\frac{\mu_B}{2mc^2}\boldsymbol{\sigma} \cdot (\mathbf{E} \times (\mathbf{p} - q\mathbf{A})) \quad (62)$$

$g_s = 2$  is called the *Landé* factor of electron. Thus, from the  $1/c$ -expansion of the *Dirac* equation, we may derive the following conclusions: (i) the electronic spin has a relativistic origin and the corresponding contribution appears at zeroth order so that a ‘‘classical’’ interpretation may be given; (ii) the spin-orbit interaction described by the Hamiltonian  $H_{so}^e$  has a purely relativistic origin and appears as a second-order perturbation.

For a potential  $V(\mathbf{r})$  characterized by a spherical symmetry, the electric field is  $\mathbf{E} = -\frac{\mathbf{r}}{qr} \frac{dV(r)}{dr}$ . As a consequence, in the simplest case of a vanishing magnetic field  $\mathbf{B}(\mathbf{A} = \mathbf{0})$ , the spin-orbit Hamiltonian may be rewritten under the form of Eqs. (63) or (64).

$$H_{so}^e = \frac{\hbar}{4m^2c^2r} \frac{dV(r)}{dr} \boldsymbol{\sigma} \cdot (\mathbf{r} \times \mathbf{p}) \quad (63)$$

$$H_{so}^e = \lambda^e(r)\boldsymbol{\ell} \cdot \mathbf{s}, \quad \lambda^e(r) = \frac{1}{2m^2c^2r} \frac{dV(r)}{dr}, \quad \boldsymbol{\ell} = \mathbf{r} \times \mathbf{p}, \quad \mathbf{s} = \frac{\hbar}{2}\boldsymbol{\sigma} \quad (64)$$

## 2. The Atomic Spin-Orbit Coupling

For an atom composed of  $N$  electrons, the spin-orbit Hamiltonian is simply given by Eq. (65).

$$H_{so} = \sum_{i=1}^N \lambda^e(r_i)\boldsymbol{\ell}_i \cdot \mathbf{s}_i, \quad \lambda^e(r_i) = \frac{1}{2m^2c^2r_i} \frac{dV(r_i)}{dr_i}, \quad V(r_i) = -\frac{Ze^2}{4\pi\epsilon_0r_i} \quad (65)$$

If we define the total orbital momentum  $\mathbf{L} = \sum_{i=1}^N \boldsymbol{\ell}_i$  and the total spin momentum  $\mathbf{S} = \sum_{i=1}^N \mathbf{s}_i$ ,  $\mathbf{L}$  and  $\mathbf{S}$  are no more constants of motion, separately, due to the fact that the spin momentum of each electron is coupled to its orbital momentum. However the total momentum  $\mathbf{J} = \mathbf{L} + \mathbf{S}$  becomes the new constant of motion as well as its projection  $M_J = M_L + M_S$  along the  $z$ -axis of quantization. In addition, owing to *Wigner-Eckart* theorem which states that, inside each multiplicity  $J$ , all the vectorial operators have identical matrix elements *via* a multiplicative constant, Eq. (65) may be replaced by Eq. (66).

$$H_{so} = \lambda\mathbf{L} \cdot \mathbf{S} \quad (66)$$

This result has an important consequence. Indeed, if we consider the coupling relation  $\mathbf{J} = \mathbf{L} + \mathbf{S}$ , the orbital momentum  $\mathbf{L}$  acts in a space  $\mathcal{E}_L$  (with  $\dim \mathcal{E}_L =$

$2L + 1$ ) and the spin momentum  $\mathbf{S}$  in a space  $\mathcal{E}_S$  (with  $\dim \mathcal{E}_S = 2S + 1$ ). Consequently, the total momentum  $J$  acts in the tensorial product space  $\mathcal{E}_J = \mathcal{E}_L \otimes \mathcal{E}_S$  (with  $\dim \mathcal{E}_J = (2L + 1) \times (2S + 1)$ ). A basis of this new space is given by Eq. (67).

$$|LM_L SM_S\rangle = |LM_L\rangle \otimes |SM_S\rangle \quad (67)$$

Another basis may be built up by means of linear combinations of the previous states so that the eigenstates of  $J$  and  $J^z$  are involved. These states are labelled  $|JM_J\rangle$  and are given by Eq. (68).

$$|JM_J\rangle = \sum_{M_L=-L}^{+L} \sum_{M_S=-S}^{+S} |LM_L SM_S\rangle \langle LM_L SM_S | JM_J\rangle \quad (68)$$

These eigenstates are orthogonal and real by construction so that we may also write Eq. (69) where the coefficient (Eq. (70)) is a *Clebsch-Gordan* coefficient [39]. Thus, the spin-orbit coupling splits  $(2J + 1)$  times each initial multiplet characterized by the set  $\{LM_L SM_S\}$ . As just seen, the spaces  $\mathcal{E}_L$  (which is linked to the crystallographic lattice) and  $\mathcal{E}_S$  (spin space) are coupled so that the relation of the type  $\Phi(\mathbf{r}_i)\chi(s_i)$  given by Eq. (5) is no longer valid ( $\Phi(\mathbf{r}_i)$  and  $\chi(s_i)$  being eigenfunctions of the crystallographic and spin spaces, respectively).

$$|LM_L SM_S\rangle = \sum_{J=|L-S|}^{L+S} \sum_{M_J=-J}^{+J} |JM_J\rangle \langle JM_J | LM_L SM_S\rangle \quad (69)$$

$$\langle JM_J | LM_L SM_S\rangle = \langle LM_L SM_S | JM_J\rangle = C_{LM_L SM_S}^{JM_J} \quad (70)$$

### 3. Hund's Rules [40]

Magnetic properties of solids depend on the total spin and, in some cases (rare earths) on the orbital momentum of the ions involved. Thus, *Hund's* rules try to explain such a kind of situation in which the *Coulomb* repulsion (in the *Hartree-Fock* approximation) and *Pauli's* exclusion principle must be considered simultaneously. For this reason, we shall see in the following article II that these rules, which seem at first sight as out of the scope of the present article, will be understood owing to a more refined physical interpretation.

In a first step we must calculate the energy difference between successive multiplets, *i.e.*, first-nearest neighbour multiplets characterized by a different  $J$  value. We have Eq. (71) and we must normally solve the secular equation (Eq. (72)) for calculating  $E_J$ .

$$\mathbf{L} \cdot \mathbf{S} = \frac{1}{2}(J^2 - L^2 - S^2) \quad (71)$$

$$\det[\langle JM_J | \lambda \mathbf{L} \cdot \mathbf{S} | JM_J\rangle - E_J \langle JM_J | JM_J\rangle] = 0 \quad (72)$$

At zeroth-order approximation the matrix associated with the operator  $\lambda \mathbf{L} \cdot \mathbf{S}$  is diagonal so that the right part of Eq. (71) may be expressed owing to the eigen-



values of operators  $J^2$ ,  $\mathbf{L}^2$  and  $\mathbf{S}^2$ , respectively, (Eq. (73)) where  $\mathbf{1}$  is the identity matrix (with  $\dim \mathbf{1} = (2L + 1) \times (2S + 1)$ ).

$$\mathbf{L} \cdot \mathbf{S} = \frac{1}{2}[J(J + 1) - L(L + 1) - S(S + 1)]\mathbf{1} \quad (73)$$

As all the multiplet components have identical  $L$  and  $S$  values but different  $J$ s, we have for first-nearest neighbour levels characterized by  $J$  and  $J - 1$  (Eq. (74)).

$$\Delta E_{J,J-1} = \lambda J \quad (74)$$

This is the well-known *Landé's interval rule* (1923).  $\lambda$  may be either positive or negative. If  $\lambda > 0$  the low-lying level component of the multiplet is characterized by the lowest  $J$  value, *i.e.*,  $J = |L - S|$  (normal multiplet). But, if  $\lambda < 0$ , the low-lying level is the one for which  $J = L + S$  (reversed multiplet). The sign of  $\lambda$  may be easily determined for normal atomic states (*i.e.*, non-excited ones) if the electronic configuration is such that the external shell is incomplete. If a shell characterized by the quantum number  $\ell$  is at most half-filled, the number of electrons is such as  $z \leq 2\ell + 1$ . Due to *Pauli's* exclusion principle, these electrons cannot be characterized by a similar set of quantum numbers. As a consequence all the spins must be parallel and the total spin is  $S = S_{\max} = z/2$  ( $M_S = z/2$ ). Substituting  $s_i = S/z$  in Eq. (65) we have Eq. (75) where  $\lambda^e$  is given by Eq. (65).

$$H_{\text{so}} = \frac{\lambda^e}{z} \mathbf{L} \cdot \mathbf{S} = \frac{\lambda^e}{2S} \mathbf{L} \cdot \mathbf{S}, \quad \lambda = \frac{\lambda^e}{2S} > 0 \quad (75)$$

In addition  $L = M_L = \ell + (\ell - 1) + \dots + \ell - (z - 1) = z(2\ell - z + 1)/2$ . But, if the shell is more than half-filled, one may proceed as follows. For a complete shell all the spins are paired so that the total spin is  $\mathbf{S} = \mathbf{0}$ , thus formally imposing  $H_{\text{so}} = 0$ . As a consequence we must consider the holes of the unfilled shell and  $H_{\text{so}}$  may be written as  $H_{\text{so}} = -\sum_{i=1}^N \lambda^e(r_i) \boldsymbol{\ell}_i \cdot \mathbf{s}_i$ . In addition the total spin and orbital momenta are  $\mathbf{S} = -\sum_{i=1}^N \mathbf{s}_i$  and  $\mathbf{L} = -\sum_{i=1}^N \boldsymbol{\ell}_i$ , respectively. Then, using the same process previously described, we easily obtain  $\lambda = \lambda^h/2S = -\lambda^e/2S < 0$ . *Hund's* rules may be derived:

- (i) For the ground state configuration, the  $S$  value is equal to the maximum possible value  $S_{\max}$  compatible with the exclusion principle (Eq. (76)).

$$S = S_{\max} \quad (76)$$

- (ii) For the ground state configuration, the  $L$  value is equal to the maximum possible value  $L_{\max}$  compatible with condition (i) and the exclusion principle (Eq. (77)).

$$L = L_{\max} \quad (\text{for } S = S_{\max}) \quad (77)$$

- (iii) The eigenvalue of the total orbital momentum  $J = \mathbf{L} + \mathbf{S}$  is  $J = |L - S|$  if the shell is at most half-filled ( $\mathbf{L}$  and  $\mathbf{S}$  are antiparallel) and  $J = L + S$  if the shell is more than half-filled ( $\mathbf{L}$  and  $\mathbf{S}$  are parallel).

These rules were derived by *Hund* in 1925 when calculating the magnetic moments of ions of rare earths (in good agreement with the corresponding

experimental data, except in two cases explained later by *Van Vleck*). This result has constituted an important success for the young Quantum Mechanics.

#### 4. Domain of Validity for the Spin-Orbit Coupling

We have seen in Appendix that the spin-orbit coupling arises from the  $1/c$ -expansion of *Dirac* equation (at second order). In addition, in the construction scheme of atomic (or ionic) energy levels, it has been admitted that the electronic orbital momenta as well as the corresponding spins may add separately in order to form the total orbital momentum  $\mathbf{L}$  and the total spin  $\mathbf{S}$ . This assumption is only possible with weak relativistic effects inside each atom (or ion). In other words, the energy level differences appearing in the fine structure must remain small with respect to the level differences characterized by different couples  $(L, S)$ . This is the *Russel-Saunders approximation* (1925), also called *LS coupling*.

In fact, the application domain of this approximation is restricted. The spectrum levels of light atoms are constructed on the basis of the *LS* scheme. But, as the atomic number  $Z$  increases, relativistic interactions increase and the *Russel-Saunders* approximation is no longer valid. In addition it is worth noticing that this approximation is not also valid for excited electronic states characterized by a great  $n$  value. If the electrostatic interaction of such an electron with the other electrons is weak, the relativistic interactions inside this inner atomic part do not decrease. Oppositely, when the relativistic interaction is important with respect to the electrostatic one (notably, for the part involving a *LS* dependency of energy), one cannot speak of orbital momentum and spin, separately, because these quantities are not conserved. Thus, when spin-orbit coupling is strong, as it is in heavy atoms, one uses *jj* coupling. In this scheme, the orbital and spin angular momenta of individual electrons couple to give a total angular momentum  $\mathbf{j}$ , and these combined angular momenta couple to give a total angular momentum  $\mathbf{J}$ . Under these conditions,  $\mathbf{l}$  and  $\mathbf{s}$  precess rapidly around  $\mathbf{j}$ , and the various  $\mathbf{j}$ s precess slowly around their resultant  $\mathbf{J}$ . In this scheme,  $\mathbf{L}$  and  $\mathbf{S}$  are not specified and lose their significance. For more details on the various coupling schemes and their experimental domain of existence, one may consult the book written by *Condon and Shortley* [41].

#### 5. The Dzialoshinski-Moriya Coupling [42]

Before detailing the origin of this coupling let us examine the case of a single transition ion and, more particularly, the origin of the anisotropy energy. In this respect, let us recall that, for transition ions, the mean value of orbital momentum in the ground state labelled  $|0\rangle$  is null due to the time reversal symmetry. In addition, as the spin-orbit contribution remains small, the perturbation theory may be employed. At this step, one could think that, for an isolated ion, magnetism is due to the presence of spin, in the ground state. In fact, some excited states show an orbital momentum and contribute, at second order in the perturbation theory, to this magnetism. For fixing ideas let us compare these different contributions in the simplest case of an isolated transition ion. In this purpose one may use an effective Hamiltonian acting on the spin states of the subspace  $|0\rangle$ . At second order we have for the corresponding eigenvalue  $E_{\text{eff}}$  (Eq. (78)) where  $H_{\text{so}}$  is defined by

Eq. (64),  $g_L$  and  $g_S$  are *Landé* factors, respectively, associated with the orbital and spin momenta and are given by the well-known formula (Eq. (79))

$$E_{\text{eff}} = \langle 0 | (H_Z + H_{\text{so}}) | 0 \rangle, \quad H_Z = -(g_L \mathbf{L} + g_S \mathbf{S}) \mu_B \mathbf{B} \quad (78)$$

$$g_J = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$$

$$g_L = 1 \quad (S=0, J=L), \quad g_S = 2 \quad (L=0, J=S) \quad (79)$$

Noting that the spin Hamiltonian  $H_S = -g_S \mu_B \mathbf{S} \cdot \mathbf{B}$  does not act at second order in perturbation theory, Eq. (78) may be expanded as Eq. (80) so that the effective Hamiltonian may be written as Eq. (81) with  $A_{ij}$  being given by Eq. (82).

$$E_{\text{eff}} = -\langle 0 | g_S \mu_B \mathbf{S} \cdot \mathbf{B} | 0 \rangle - \sum_n \frac{|\langle n | (g_L \mu_B \mathbf{L} \cdot \mathbf{B} + \lambda \mathbf{L} \cdot \mathbf{S}) | 0 \rangle|^2}{E_n - E_0} \quad (80)$$

$$H_{\text{eff}} = -g_S \mu_B \mathbf{S} \cdot \mathbf{B} - g_L \mu_B \lambda \sum_{i,j} A_{ij} S_i B_j - \lambda^2 \sum_{i,j} A_{ij} S_i S_j - (g_L \mu_B)^2 \sum_{i,j} A_{ij} B_i B_j \quad (81)$$

$$A_{ij} = \sum_n \frac{\langle 0 | L_i | n \rangle \langle n | L_j | 0 \rangle}{E_n - E_0} \quad (82)$$

Tensor  $A$  has generally three eigenaxes and three associated eigenvalues. As a consequence the *Landé* factor is also a tensor:  $g_{ij} = g_S \delta_{ij} - g_L \lambda A_{ij}$ . In addition the last term in Eq. (81) allows one to explain the paramagnetic *Van Vleck* contribution to the susceptibility and also represents the fine structure (or ionic anisotropy).

After having identified the origin of the single ion anisotropy energy, the case of paired ions may be examined. It differs from the single ion case by the introduction of an exchange term between ions  $A$  and  $B$  carrying the spins  $\mathbf{S}_1$  and  $\mathbf{S}_2$ , respectively. A treatment similar to the single ion may be achieved in perturbation theory by starting from the Hamiltonian (Eq. (83)) where  $J$  is the exchange energy (the definition of which will be specified below),  $H_{\text{so},i}$  and  $H_{Z,i}$  (with  $i = 1$  or  $2$ ) are given by Eqs. (66) and (78). Under these conditions it is very easy to show that the second-order perturbation energy which is bilinear in the spin-orbit coupling and the exchange interaction is written as follows (Eq. (84)) where  $n, n'$  represent the ground orbital states and  $m, m'$  the excited orbital states of the two ions 1 and 2 at the points  $A$  and  $B$  in a crystal, characterized by the positions  $\mathbf{R}_1$  and  $\mathbf{R}_2$ .

$$H = -J \mathbf{S}_1 \cdot \mathbf{S}_2 + H_{Z,1} + H_{\text{so},1} + H_{Z,2} + H_{\text{so},2} \quad (83)$$

$$\sum_m \left\{ \frac{\langle n | \lambda \mathbf{L}_1 \cdot \mathbf{S}_1 | m \rangle 2J(mn'n'n') \mathbf{S}_1 \cdot \mathbf{S}_2}{E_n - E_m} + \frac{2J(nn'mn') \mathbf{S}_1 \cdot \mathbf{S}_2 \langle m | \lambda \mathbf{L}_1 \cdot \mathbf{S}_1 | n \rangle}{E_n - E_m} \right\}$$

$$+ \sum_{m'} \left\{ \frac{\langle n' | \lambda \mathbf{L}_2 \cdot \mathbf{S}_2 | m' \rangle 2J(m'n'n'n) \mathbf{S}_1 \cdot \mathbf{S}_2}{E_{n'} - E_{m'}} + \frac{2J(n'nmm'n) \mathbf{S}_1 \cdot \mathbf{S}_2 \langle m' | \lambda \mathbf{L}_2 \cdot \mathbf{S}_2 | n' \rangle}{E_{n'} - E_{m'}} \right\} \quad (84)$$

$J(nn'mm')$  is the exchange integral (Eq. (85)) with  $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ ,  $\varphi_n(\mathbf{r} - \mathbf{R})$  being the ground orbital wave function of the ion at  $\mathbf{R}$ , etc. . .

$$J(nn'mm') = \int d\mathbf{r}_1 d\mathbf{r}_2 \varphi_n^*(\mathbf{r}_1 - \mathbf{R}_1) \varphi_{n'}^*(\mathbf{r}_2 - \mathbf{R}_2) \frac{e^2}{4\pi\epsilon_0 r_{12}} \varphi_m(\mathbf{r}_2 - \mathbf{R}_1) \varphi_{m'}(\mathbf{r}_1 - \mathbf{R}_2) \quad (85)$$

When the ground state is non-degenerate, the matrix elements of the orbital angular momentum  $\mathbf{L}$  in Eq. (84) are purely imaginary and Eq. (84) may be rewritten as Eq. (86) which gives Eq. (87).

$$2\lambda \sum_m \frac{J(nn'mm')}{E_n - E_m} \langle n | \mathbf{L}_1 | m \rangle [\mathbf{S}_1, (\mathbf{S}_1 \cdot \mathbf{S}_2)] + 2\lambda \sum_{m'} \frac{J(nn'mm')}{E_{n'} - E_{m'}} \langle n' | \mathbf{L}_2 | m' \rangle [\mathbf{S}_2, (\mathbf{S}_1 \cdot \mathbf{S}_2)] \quad (86)$$

$$2i\lambda \left[ \sum_m \frac{J(nn'mm')}{E_n - E_m} \langle n | \mathbf{L}_1 | m \rangle - \sum_{m'} \frac{J(nn'mm')}{E_{n'} - E_{m'}} \langle n' | \mathbf{L}_2 | m' \rangle \right] \cdot (\mathbf{S}_1 \times \mathbf{S}_2) \quad (87)$$

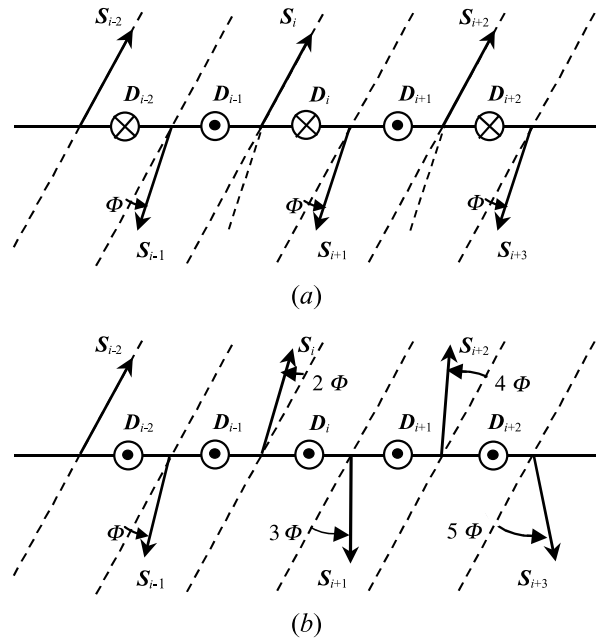
As a consequence we can define the *Dzialoshinski-Moriya* Hamiltonian (Eq. (88)).

$$H_{\text{DM}} = \mathbf{D} \cdot (\mathbf{S}_1 \times \mathbf{S}_2) \quad (88)$$

$\mathbf{D}$  is called the *Dzialoshinski-Moriya* vector.

The following rules to determine the direction of  $\mathbf{D}$  are easily obtained from symmetry considerations for two ions located at points  $A$  and  $B$  [43]:

- (i) When a centre of inversion is located at the midpoint of segment  $AB$ ,  $\mathbf{D} = \mathbf{0}$ .
- (ii) When a mirror plane perpendicular to  $AB$  bisects  $AB$ ,  $\mathbf{D} \parallel$  mirror plane.



**Fig. 3.** Top view of (a) a canted spin chain structure (alternating  $\mathbf{D}$ ), (b) a helical spin chain structure (regular  $\mathbf{D}$ ), at 0 K (XY plane favoured) [44]

- (iii) When there is a mirror plane including  $A$  and  $B$ ,  $\mathbf{D} \perp$  mirror plane.
- (iv) When a two-fold rotation axis perpendicular to  $AB$  passes through the midpoint of  $AB$ ,  $\mathbf{D} \perp$  two-fold axis.
- (v) When there is an  $n$ -fold axis ( $n \geq 2$ ) along  $AB$ ,  $\mathbf{D} \parallel AB$ .

Finally, concerning the spin arrangements involved in the presence of a *Dzialoshinski-Moriya* coupling in a crystal, we shall deal with a spin canting arrangement if  $\mathbf{D}$  shows a regular alternating direction along a crystal row and a helical one if  $\mathbf{D}$  has a regular direction, from site to site (see Fig. 3).

### A Need of Predictive Character for the Exchange Hamiltonian

We have seen that a general Hamiltonian may be written between two magnetic centres  $A$  and  $B$  as Eq. (89), the ellipses representing the possible contribution of higher-order couplings.

$$H = -J\mathbf{S}_A \cdot \mathbf{S}_B + \mathbf{S}_A(A)\mathbf{S}_B + \mathbf{D} \cdot (\mathbf{S}_A \times \mathbf{S}_B) + \dots \quad (89)$$

We have established that this Hamiltonian is a purely phenomenological one.  $J$  appears as the difference between the first low-lying energy levels;  $(A)$  is the anisotropy tensor and  $\mathbf{D}$  the *Dzialoshinski-Moriya* vector. These two latter contributions come from the presence of spin-orbit coupling whereas higher-order couplings (omitted here for clarity) have a completely different origin. This class of phenomenological Hamiltonian, valid for the low-lying energy levels, is characterized by a set of specific eigenvalues. However, it has *no predictive character with respect to the microscopic mechanisms involved*. In the following article II we shall examine the problem of superexchange and, after recalling the phenomenological model proposed by *Anderson*, we shall introduce a description of this phenomenon by the bias of a microscopic Hamiltonian. The concept of *magnetic orbital* will be used. A comparison will be made between this Hamiltonian and a phenomenological one: a correspondence will be then achieved for expressing  $J$  vs. *key molecular integrals*, thus notably allowing to discuss its true sign.

### Appendix

Let us consider the relativistic *Dirac* equation (Eq. (A1)) [38] with  $\mathbf{p} = -i\hbar\nabla$  and further conditions given by Eq. (A2) where  $\mathbf{1}$  is the  $2 \times 2$  identity matrix,  $\sigma^u$  is a  $2 \times 2$  *Pauli* matrix, and  $q = -e < 0$  represents the charge of electron.

$$\{c\boldsymbol{\alpha} \cdot (\mathbf{p} - q\mathbf{A}) + \beta mc^2 + qU\mathbf{1}'\}\psi = i\hbar \frac{\partial \psi}{\partial t} \quad (A1)$$

$$\mathbf{1}' = \begin{pmatrix} \mathbf{1} & 0 \\ 0 & \mathbf{1} \end{pmatrix}, \quad \beta = \begin{pmatrix} \mathbf{1} & 0 \\ 0 & -\mathbf{1} \end{pmatrix}, \quad \alpha^u = \begin{pmatrix} 0 & \sigma^u \\ \sigma^u & 0 \end{pmatrix}, \quad u = x, y, \text{ or } z \quad (A2)$$

As  $\beta$  and  $\alpha^u$  are  $4 \times 4$  matrices it means that  $\psi$  is a wave function characterized by four components; their physical meaning will be given later. As the relativistic

energy contains the rest energy  $mc^2$ , the following transformation (Eq. (A3)) allows one to rewrite the *Dirac* equation as Eq. (A4).

$$\psi = \psi' \exp\left(-i\frac{mc^2}{\hbar}t\right) \quad (\text{A3})$$

$$\{c\boldsymbol{\alpha} \cdot (\mathbf{p} - q\mathbf{A}) + \beta mc^2 + qU\mathbf{1}'\}\psi' = \left(i\hbar\frac{\partial}{\partial t} + mc^2\right)\psi' \quad (\text{A4})$$

If we decompose the 4-component wave function  $\psi'$  under the form  $\psi' = \begin{pmatrix} \varphi' \\ \chi' \end{pmatrix}$  where  $\varphi'$  and  $\chi'$  are 2-components wave functions, we have the system of coupled equations (Eqs. (A5a) and (A5b)).

$$c\boldsymbol{\sigma} \cdot (\mathbf{p} - q\mathbf{A})\chi' = \left(i\hbar\frac{\partial}{\partial t} - qU\right)\varphi' \quad (\text{A5a})$$

$$c\boldsymbol{\sigma} \cdot (\mathbf{p} - q\mathbf{A})\varphi' = \left(i\hbar\frac{\partial}{\partial t} - qU + 2mc^2\right)\chi' \quad (\text{A5b})$$

As we consider the non-relativistic limit, it means that, if  $\varepsilon$  is the ‘‘classical’’ eigenvalue corresponding to the operator  $i\hbar\partial/\partial t$ , we have  $\varepsilon \ll mc^2$  as well as  $|q|U \ll mc^2$ . We then derive Eq. (A6) and by reporting in Eq. (A5a) Eq. (A7).

$$\chi' = \frac{1}{2mc}\boldsymbol{\sigma} \cdot (\mathbf{p} - q\mathbf{A})\varphi' \quad (\text{A6})$$

$$\frac{1}{2m}(\boldsymbol{\sigma} \cdot (\mathbf{p} - q\mathbf{A}))^2\varphi' = \left(i\hbar\frac{\partial}{\partial t} - qU\right)\varphi' \quad (\text{A7})$$

Using the property of *Pauli* matrices we may write Eq. (A8) where  $\mathbf{a}$  and  $\mathbf{b}$  are arbitrary vectors.

$$(\boldsymbol{\sigma} \cdot \mathbf{a}) \cdot (\boldsymbol{\sigma} \cdot \mathbf{b}) = \mathbf{a} \cdot \mathbf{b} + i\boldsymbol{\sigma} \cdot (\mathbf{a} \times \mathbf{b}) \quad (\text{A8})$$

Here we have  $\mathbf{a} = \mathbf{b} = \mathbf{p} - q\mathbf{A}$ , with  $\mathbf{p} = -i\hbar\nabla$ ; but  $[\mathbf{p}, \mathbf{A}] \neq \mathbf{0}$  implies  $\mathbf{a} \times \mathbf{b} \neq \mathbf{0}$  so that Eq. (A9) is valid.

$$\begin{aligned} (\boldsymbol{\sigma} \cdot (\mathbf{p} - q\mathbf{A}))^2 &= (\mathbf{p} - q\mathbf{A})^2 \mathbf{1} - q\hbar\boldsymbol{\sigma} \cdot (\mathbf{A} \times \nabla + \nabla \times \mathbf{A}) \\ &= (\mathbf{p} - q\mathbf{A})^2 \mathbf{1} - q\hbar\boldsymbol{\sigma} \cdot \mathbf{curl}\mathbf{A} \end{aligned} \quad (\text{A9})$$

Finally we may write Eq. (A10)

$$(\boldsymbol{\sigma} \cdot (\mathbf{p} - q\mathbf{A}))^2 = (\mathbf{p} - q\mathbf{A})^2 \mathbf{1} - q\hbar\boldsymbol{\sigma} \cdot \mathbf{B}, \quad \mathbf{B} = \mathbf{curl}\mathbf{A} \quad (\text{A10})$$

so that by reporting in Eq. (A7) we obtain Eq. (A11).

$$H\varphi' = \left\{ \left[ \frac{1}{2m}(\mathbf{p} - q\mathbf{A})^2 + qU \right] \mathbf{1} - \frac{q\hbar}{2m}\boldsymbol{\sigma} \cdot \mathbf{B} \right\} \varphi' = i\hbar\frac{\partial\varphi'}{\partial t} \quad (\text{A11})$$

This equation is called ‘‘*Pauli* equation’’ (1927) and the quantity  $\mu_B = q\hbar/2m$  is the *Bohr* magneton. Equation (A11) differs from the non-relativistic *Schrödinger* equation by the presence of the last term in the Hamiltonian which has the form of a potential energy of a magnetic dipole in an external field. In addition the physical

interpretation of the 2-component eigenfunction  $\varphi'$  clearly appears: each component corresponds to the eigenvalue of the operator  $s^z$ , *i.e.*,  $\pm 1/2$ . For this reason  $\varphi'$  is called a *spinor*. The particular study of the *Dirac* equation without external fields has allowed to give a deepest interpretation of functions  $\varphi'$  and  $\chi'$ : they correspond to electrons with positive energy (moving forwards in time) or negative one (moving backwards in time). The case of negative energy has finally led to the concept of positron (or antielectron).

If we reconsider Eq. (A6) we see that  $\chi' \sim \varphi'/c$ . As a consequence the density function  $\rho = \psi\psi^* = \varphi'\varphi'^* + \chi'\chi'^*$  may be assimilated to  $\rho \approx \varphi'\varphi'^*$  in a first step, as in the non-relativistic *Schrödinger* equation. But, for assuming a  $1/c$  expansion at second order of *Pauli* equation given by Eq. (A11), the contribution  $\chi'\chi'^*$  must be considered. For simplifying the discussion only the external electric field  $\mathbf{E}$  exists,  $\mathbf{A} = \mathbf{0}$  and  $\chi' \sim i\hbar\boldsymbol{\sigma} \cdot \nabla\varphi'/2mc$ . We now have for the density function Eq. (A12).

$$\rho = |\varphi'|^2 + |\chi'|^2 = |\varphi'|^2 + \frac{\hbar^2}{4m^2c^2} |\boldsymbol{\sigma}\nabla\varphi'|^2 \quad (\text{A12})$$

Of course this expression differs from *Schrödinger's* one. So we must search for a function  $\varphi_{Sch}$  such as given by Eq. (A13).

$$\int d\tau \varphi_{Sch}\varphi_{Sch}^* = \int d\tau \left( \varphi'\varphi'^* + \frac{\hbar^2}{4m^2c^2} (\nabla\varphi'^* \cdot \boldsymbol{\sigma})(\boldsymbol{\sigma} \cdot \nabla\varphi') \right) \quad (\text{A13})$$

Integrating by parts leads to Eq. (A14).

$$\begin{aligned} \int d\tau (\nabla\varphi'^* \cdot \boldsymbol{\sigma})(\boldsymbol{\sigma} \cdot \nabla\varphi') &= - \int d\tau \varphi'^* (\boldsymbol{\sigma} \cdot \nabla)(\boldsymbol{\sigma} \cdot \nabla)\varphi' \\ &= - \int d\tau \varphi'^* \Delta\varphi' = - \int d\tau \varphi' \Delta\varphi'^* \end{aligned} \quad (\text{A14})$$

Thus we derive Eq. (A15)

$$\int d\tau \varphi_{Sch}\varphi_{Sch}^* = \int d\tau \left( \varphi'\varphi'^* - \frac{\hbar^2}{8m^2c^2} (\varphi'^* \Delta\varphi' + \varphi' \Delta\varphi'^*) \right) \quad (\text{A15})$$

so that  $\varphi_{Sch}$  and  $\varphi'$  are given by Eq. (A16).

$$\varphi_{Sch} = \left( 1 + \frac{\mathbf{p}^2}{8m^2c^2} \right) \varphi', \quad \varphi' = \left( 1 - \frac{\mathbf{p}^2}{8m^2c^2} \right) \varphi_{Sch} \quad (\text{A16})$$

For simplifying and, as we are in the classical limit, we consider that a stationary state is reached, *i.e.*, the operator  $-i\hbar\partial/\partial t$  must be replaced by the energy  $\varepsilon$  (the rest energy being omitted). Under these conditions, the function  $\chi'$  given by Eq. (A5b) may be rewritten as Eq. (A17).

$$\chi' = \frac{1}{2mc} \left( 1 - \frac{\varepsilon - q\mathbf{U}}{2mc^2} \right) (\boldsymbol{\sigma}\mathbf{p})\varphi' \quad (\text{A17})$$

Then, reporting in Eq. (A5a) with the substitution given by Eq. (A16) and omitting the terms of order greater than  $1/c^2$  leads to the *Schrödinger* equation  $H\varphi_{Sch} = \varepsilon\varphi_{Sch}$  with  $H$  being given by Eq. (A18).

$$H = \left[ \frac{\mathbf{p}^2}{2m} + q\mathbf{U} - \frac{\mathbf{p}^4}{8m^3c^2} \right] \mathbf{1} + \frac{q}{4m^2c^2} \left\{ (\boldsymbol{\sigma}\mathbf{p})\mathbf{U}(\boldsymbol{\sigma}\mathbf{p}) - \frac{1}{2}(\mathbf{p}^2\mathbf{U} + \mathbf{U}\mathbf{p}^2)\mathbf{1} \right\} \quad (\text{A18})$$

Noting that if  $E = -\nabla\mathbf{U}$  (Eq. (A19)) the Hamiltonian may be written as Eq. (A20).

$$\begin{aligned} (\boldsymbol{\sigma}\mathbf{p})\mathbf{U}(\boldsymbol{\sigma}\mathbf{p}) &= \mathbf{U}\mathbf{p}^2 + (\boldsymbol{\sigma}\mathbf{p}\mathbf{U})(\boldsymbol{\sigma}\mathbf{p}) = \mathbf{U}\mathbf{p}^2 + i\hbar(\boldsymbol{\sigma}\mathbf{E})(\boldsymbol{\sigma}\mathbf{p}) \\ \mathbf{p}^2\mathbf{U} - \mathbf{U}\mathbf{p}^2 &= -\hbar^2\Delta\mathbf{U} + 2i\hbar\mathbf{E} \cdot \mathbf{p} \end{aligned} \quad (\text{A19})$$

$$H = \left[ \frac{\mathbf{p}^2}{2m} - \frac{\mathbf{p}^4}{8m^3c^2} + q\mathbf{U} \right] \mathbf{1} - \frac{q\hbar}{4m^2c^2} \boldsymbol{\sigma} \cdot (\mathbf{E} \times \mathbf{p}) - \frac{q\hbar^2}{8m^2c^2} \text{div } \mathbf{E}\mathbf{1} \quad (\text{A20})$$

The first two terms correspond to the expansion of the kinetic energy  $\sqrt{(pc)^2 + (mc^2)^2} - mc^2$  whereas the quantity  $q\mathbf{U}$  is the potential energy. The third term represents the spin-orbit interaction. The last term including the factor  $\text{div } \mathbf{E}$  is called the *Darwin* contribution (1928) and only differs from zero at the points carrying the charges which create the external electric field  $\mathbf{E}$ . Thus, when  $\mathbf{A} = \mathbf{0}$ , the Hamiltonian reduces to Eq. (A21) with conditions being given by Eq. (A22).

$$H = (H_0 + V(\mathbf{r}))\mathbf{1} + H_{\text{so}}^e + o\left(\frac{1}{c^3}\right) \quad (\text{A21})$$

$$H_0 = \frac{\mathbf{p}^2}{2m}, \quad V(\mathbf{r}) = q\mathbf{U}(\mathbf{r}), \quad H_{\text{so}} = -\frac{\mu_B}{2mc^2} \boldsymbol{\sigma} \cdot (\mathbf{E} \times \mathbf{p}) \quad (\text{A22})$$

When  $\mathbf{A} \neq \mathbf{0}$ , a similar reasoning leads to Eq. (A23) with now conditions being given by Eq. (A24).

$$H = (H'_0 + V(\mathbf{r}))\mathbf{1} + H_S + H_{\text{so}}^e + o\left(\frac{1}{c^3}\right) \quad (\text{A23})$$

$$H'_0 = \frac{1}{2m}(\mathbf{p} - q\mathbf{A})^2, \quad H_S = -g_S\mu_B\mathbf{S} \cdot \mathbf{B}, \quad H_{\text{so}}^e = -\frac{\mu_B}{2mc^2} \boldsymbol{\sigma} \cdot (\mathbf{E} \times (\mathbf{p} - q\mathbf{A})) \quad (\text{A24})$$

## References

- [1] Curie P (1895) *Ann Chim Phys (Paris)* **5**: 289
- [2] Langevin P (1905) *J Phys (Paris)* **4**: 678; (1905) *Ann Chim Phys (Paris)* **5**: 70
- [3] Weiss P (1906) *Comptes Rendus Acad Sci (Paris)* **143**: 1136; (1907) *J Phys (Paris)* **6**: 661; (1908) *Physik Z* **9**: 358
- [4] Debye P (1925) In: Marx E (ed) *Handbuch der Radiologie*, vol IV. Akad Verlagsges, Leipzig, p 597; Weiss P (1914) *Ann Phys (Paris)* [9] **1**: 134
- [5] Rozansky D (1926) *Physik Z* **27**: 779
- [6] Barnett SJ (1915) *Phys Rev* **6**: 239; (1935) *Rev Mod Phys* **7**: 129



- [7] Landé A (1922) *Z Physik* **11**: 353
- [8] Heisenberg W (1926) *Z Physik* **38**: 411
- [9] Dirac PAM (1926) *Proc Roy Soc* **A112**: 661
- [10] Hund F (1927) *Linienspektren und periodisches System der Elemente*. Springer, Berlin
- [11] Heisenberg W (1926) *Z Physik* **39**: 499
- [12] Néel L (1932) PhD Thesis, chap VIII. Masson, Paris
- [13] Kramers HA (1934) *Physica* **1**: 182
- [14] Van Vleck JH (1932) *The Theory of Electric and Magnetic Susceptibilities*, chap XI. Oxford University Press, London New York
- [15] Zener C (1951) *Phys Rev* **82**: 403
- [16] Anderson PW, Hasegawa H (1955) *Phys Rev* **100**: 675
- [17] de Gennes PG (1960) *Phys Rev* **118**: 141
- [18] Herring C (1966) Magnetism. In: Rado GT, Suhl H (eds), vol IIB. Wiley, New York, p 1
- [19] Heitler W, London F (1927) *Z Physik* **44**: 455
- [20] Heitler W (1927) *Z Physik* **46**: 47; (1928) **47**: 835; (1928) **51**: 805
- [21] London F (1928) *Z Physik* **46**: 455; (1928) **50**: 24
- [22] Born M, Oppenheimer JR (1927) *Ann Physik* **84**: 457
- [23] Sugiura Y (1927) *Z Physik* **45**: 484
- [24] Courant R, Hilbert D (1931) *Methoden der Mathematischen Physik*. 2<sup>nd</sup> ed, Springer, Berlin; (1953) *Methods of Mathematical Physics*. Wiley, New York
- [25] Stevens KWH (1976) *Phys Rep* **24C**: 1
- [26] Wigner EP (1931) *Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atom-spektren*. Vieweg, Braunschweig; (1959) *Group Theory and its Application to the Quantum Mechanics of Atomic Spectra*. Academic Press, New York
- [27] Van Vleck JH (1934) *Phys Rev* **45**: 405
- [28] Kahn O (1987) *Structure and Bonding* **68**: 89
- [29] Jahn HA, Teller E (1937) *Proc Roy Soc (London)* **A161**: 220; Bates CA (1978) *Phys Rep* **35**: 187
- [30] Hartmann-Boutron F (1968) *J Phys (Paris)* **29**: 212; Van Vleck JH (1962) *Revista de Matematicas y Fisica Teorica (Tucuma, Argentina)* **14**: 189
- [31] Harris EA, Owen J (1963) *Phys Rev Lett* **11**: 9
- [32] McMahan AK, Wilkins JW (1975) *Phys Rev Lett* **35**: 376; Hetherington JH, Willard FDC (1975) *Phys Rev Lett* **35**: 1442
- [33] Osheroff DD, Cross MH, Fisher DS (1980) *Phys Rev Lett* **44**: 792
- [34] Roger M, Derlieu JM, Hetherington JH (1980) *J Phys Lett* **41**: L-139
- [35] Yosida K, Inagaki S (1981) *J Phys Soc Japan* **50**: 3268
- [36] Suematsu H, Ohmatsu K, Yoshizaki R (1981) *Solid State Commun* **38**: 1103; Suematsu H, Ohmatsu K, Sugiyama K, Sakakibara T, Motokawa M, Date M (1981) *Solid State Commun* **40**: 241
- [37] Yosida K (1980) *Suppl of Prog Theor Phys* **69**: 475
- [38] Dirac PAM (1928) *Proc Roy Soc (London)* **A117**: 610; (1930) **A126**: 360; Boča R (1999) *Theoretical Foundations of Molecular Magnetism*, chap IV and references therein. Elsevier, Amsterdam
- [39] Varshalovich DA, Moskalev AN, Khersonskii VK (1988) *Quantum Theory of Angular Momentum*. World Scientific, Singapore
- [40] Hund F (1925) *Z Physik* **33**: 855
- [41] Condon EU, Shortley GH (1935) *The Theory of Atomic Spectra*. Cambridge University Press
- [42] Dzialoshinski IE (1957) *Sov Phys JETP* **6**: 821; (1957) **6**: 1259; Moriya T (1960) *Phys Rev* **120**: 91
- [43] Moriya T (1962) Magnetism. In: Rado GT, Suhl H (eds), vol I. Wiley, New York, p 85
- [44] Curély J, Georges R (1994) *Phys Rev* **B49**: 12839; Curély J (1995) *Physica* **B205**: 31