Heitler-London result for $E_s - E_t$, because it is both a starting point for more refined treatments and the source of a nomenclature that pervades much of the subject of magnetism:

The Heitler-London approximation uses the singlet and triplet wave functions (32.14) and (32.13) to estimate the singlet-triplet splitting as

$$E_s - E_t = \frac{(\bar{\psi}_s, H\bar{\psi}_s)}{(\bar{\psi}_s, \bar{\psi}_s)} - \frac{(\psi_t, H\psi_t)}{(\psi_t, \psi_t)}, \tag{32.15}$$

where H is the full Hamiltonian (32.3). In the limit of large spatial separations this splitting can be shown (Problem 4) to reduce simply to

$$\begin{aligned}\frac{1}{2}(E_s - E_t) = \int d\mathbf{r}_1\, d\mathbf{r}_2\, [\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)] \biggl(\frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{e^2}{|\mathbf{R}_1 - \mathbf{R}_2|} \\ - \frac{e^2}{|\mathbf{r}_1 - \mathbf{R}_1|} - \frac{e^2}{|\mathbf{r}_2 - \mathbf{R}_2|} \biggr) [\phi_2(\mathbf{r}_1)\phi_1(\mathbf{r}_2)]. \end{aligned} \tag{32.16}$$

Because this is a matrix element between two states that differ solely through the exchange of the coordinates of the two electrons, the singlet-triplet energy difference is referred to as an *exchange splitting* or, when viewed as a source of magnetic interaction, an *exchange interaction.*[15]

Since the atomic orbital $\phi_i(\mathbf{r})$ is strongly localized in the neighborhood of $\mathbf{r} = \mathbf{R}_i$, the factors $\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_1)$ and $\phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_2)$ in the integrand of (32.16) insure that the singlet-triplet energy splitting will fall off rapidly with the distance $|\mathbf{R}_1 - \mathbf{R}_2|$ between protons.

THE SPIN HAMILTONIAN AND THE HEISENBERG MODEL

There is a way to express the dependence of the spin of a two-electron system on the singlet-triplet energy splitting, which, though unnecessarily complicated in this simple case, is of fundamental importance in analyzing the energetics of the spin configurations of real insulating solids. One first notes that when the two protons are far apart, the ground state describes two independent hydrogen atoms and is therefore fourfold degenerate (since each electron can have two spin orientations). One next considers the protons to be brought a bit closer together, so that there is a splitting ($E_s \neq E_t$) of the fourfold degeneracy due to interactions between the atoms, which is, however, small compared with all other excitation energies of the two-electron system. Under such conditions these four states will play the dominant role in determining many important properties of the molecule,[16] and one often simplifies the analysis by ignoring the higher states altogether, representing the molecule as a simple four-state system. If we do represent a general state of the molecule as a linear combination of the four lowest states, it is convenient to have an operator, known as the spin Hamiltonian,

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[15] One should not, however, be lulled by this nomenclature into forgetting that underlying the exchange interaction are nothing but electrostatic interaction energies, and the Pauli exclusion principle.

[16] For example, the thermal equilibrium properties when k_BT is comparable to $E_s - E_t$, but small enough that no states other than the four are thermally excited.

whose eigenvalues are the same as those of the original Hamiltonian within the four-state manifold, and whose eigenfunctions give the spin of the corresponding states.

To construct the spin Hamiltonian for a two-electron system, note that each individual electron spin operator satisfies $\mathbf{S}_i^2 = \frac{1}{2}(\frac{1}{2} + 1) = \frac{3}{4}$, so that the total spin $\mathbf{S}$ satisfies

$$\mathbf{S}^2 = (\mathbf{S}_1 + \mathbf{S}_2)^2 = \tfrac{3}{2} + 2\mathbf{S}_1 \cdot \mathbf{S}_2. \qquad (32.17)$$

Since $\mathbf{S}^2$ has the eigenvalue $S(S + 1)$ in states of spin S, it follows from (32.17) that the operator $\mathbf{S}_1 \cdot \mathbf{S}_2$ has eigenvalue $-\frac{3}{4}$ in the singlet ($S = 0$) state and $+\frac{1}{4}$ in the triplet ($S = 1$) states. Consequently the operator

$$\mathcal{H}^{\text{spin}} = \tfrac{1}{4}(E_s + 3E_t) - (E_s - E_t)\mathbf{S}_1 \cdot \mathbf{S}_2 \qquad (32.18)$$

has eigenvalue E_s in the singlet state, and E_t in each of the three triplet states, and is the desired spin Hamiltonian.

By redefining the zero of energy we may omit the constant $(E_s + 3E_t)/4$ common to all four states, and write the spin Hamiltonian as

$$\mathcal{H}^{\text{spin}} = -J\mathbf{S}_1 \cdot \mathbf{S}_2, \quad J = E_s - E_t. \qquad (32.19)$$

Since $\mathcal{H}^{\text{spin}}$ is the scalar product of the vector spin operators $\mathbf{S}_1$ and $\mathbf{S}_2$, it will favor parallel spins if J is positive and antiparallel if J is negative.[17] Note that in contrast to the magnetic dipolar interaction (32.1), the coupling in the spin Hamiltonian depends only on the relative orientation of the two spins, but not on their directions with respect to $\mathbf{R}_1 - \mathbf{R}_2$. This is a general consequence of the spin independence of the original Hamiltonian and (one should note) holds without any assumption about its spatial symmetry. One must include terms that break rotational symmetry in spin space (such as dipolar interactions or spin-orbit coupling) in the original Hamiltonian, in order to produce a spin Hamiltonian with anisotropic coupling.[18]

When N is large, rather than merely reexpressing some known results (as when $N = 2$), the spin Hamiltonian contains in highly compact form some exceedingly complex information about the low-lying levels.[19] When N ions of spin S are widely separated,[20] the ground state will be $(2S + 1)^N$-fold degenerate. The spin Hamiltonian describes the splitting of this vastly degenerate ground state when the ions are somewhat closer together, but still far enough apart that the splittings are small compared with any other excitation energies. One can (in a variety of ways) construct an operator function of the $\mathbf{S}_i$ whose eigenvalues give the split levels. What is remarkable, however, is that for many cases of interest the form of the spin Hamiltonian is simply that

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[17] Since J is positive or negative depending on whether E_t or E_s is lower, this simply restates the fact that the spins are parallel in the triplet state and antiparallel in the singlet.

[18] Such anisotropy is of critical importance in understanding the existence of easy and hard directions of magnetization and plays a role in the theory of domain formation. (See page 720.)

[19] In general, this information is not easily extracted, even from a spin Hamiltonian. In contrast to the case $N = 2$ one does not know the low-lying levels from the start, and finding a spin Hamiltonian is only half the problem. There remains the highly nontrivial problem of finding the eigenvalues of that spin Hamiltonian. (See, for example, pages 701–709).

[20] For simplicity we assume that for each ion $J = S$ (i.e., $L = 0$). This restriction is not essential to the development of a spin Hamiltonian.

for the two-spin case, summed over all pairs of ions:

$$H^{\text{spin}} = -\sum J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j. \tag{32.20}$$

We shall not go into the question of when (32.20) can be justified, which is quite a complex matter.[21] However one should note:

1. For only products of pairs of spin operators to appear in (33.20) it is necessary that all magnetic ions be far enough apart that the overlap of their electronic wave functions is very small.
2. When the angular momentum of each ion contains an orbital as well as a spin part, the coupling in the spin Hamiltonian may depend on the absolute as well as the relative spin orientations.

The spin Hamiltonian (32.20) is known as the Heisenberg[22] Hamiltonian, and the J_{ij} are known as the exchange coupling constants (or parameters or coefficients). Extracting information even from the Heisenberg Hamiltonian is, in general, so difficult a task, that it by itself is taken as the starting point for many quite profound investigations of magnetism in solids. One must remember, however, that much subtle physics and quite complex approximations must be delved into before one can even arrive at a Heisenberg Hamiltonian.

DIRECT EXCHANGE, SUPEREXCHANGE, INDIRECT EXCHANGE, AND ITINERANT EXCHANGE

The magnetic interaction we have just described is known as *direct exchange*, because it arises from the direct Coulomb interaction among electrons from the two ions. It often happens that two magnetic ions are separated by a nonmagnetic ion (i.e., one with all electronic shells closed). It is then possible for the magnetic ions to have a magnetic interaction mediated by the electrons in their common nonmagnetic neighbors, which is more important than their direct exchange interaction. This type of magnetic interaction is called *superexchange*. (See Figure 32.2.)

Yet another source of magnetic interaction can occur between electrons in the partially filled f-shells in the rare earth metals. In addition to their direct exchange coupling, the f-electrons are coupled through their interactions with the conduction electrons. This mechanism (in a sense the metallic analogue of superexchange in insulators) is known as *indirect exchange*. It can be stronger than the direct exchange coupling, since the f-shells generally overlap very little.

There are also important exchange interactions in metals among the conduction electrons themselves, often referred to as *itinerant exchange*.[23] To emphasize the great generality of exchange interactions, we give below a brief discussion of itinerant exchange in the case farthest away from the well-localized electrons for which the Heitler-London theory of direct exchange was devised: the free electron gas.

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[21] A very thorough discussion is given by C. Herring (see footnote 14).

[22] In the older literature it is known as the Heisenberg-Dirac Hamiltonian.

[23] A discussion of itinerant exchange is given by C. Herring in *Magnetism*, vol. 4, G. T. Rado and H. Suhl. eds., Academic Press, New York, 1966.