

Daniel C. Mattis

# The Theory of Magnetism I

Statics and Dynamics

With 58 Figures

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However, we are anticipating too far ahead, and it is important to develop the plot gradually.

Suffice it to say that there is in general no guarantee that the levels will fan out in the desired manner, and in many substances they do not do so and therefore defy simple-minded descriptions. Hopefully, a detailed analysis based on physically admissible approximations to the Schrödinger equation will give us some sharper criteria. It is to this task that we turn our attention in this and subsequent chapters.

## 2.2 Hydrogen Molecule

We study molecules first to appreciate some of the difficulties which are absent in our subsequent study of the atom. But these are by now almost classical subjects on which many books have been written. The actual treatment will therefore be addressed to the students who are yet unacquainted with, or have forgotten atomic and molecular physics ("quantum chemistry", as it is now known). The more experienced reader can omit all but a few remarks towards the end of the chapter concerning subjects with which he might be less familiar. The method with which we break ground was invented by *Heitler and London*<sup>2</sup> shortly after the discoveries of Schrödinger, *Heisenberg* [2.2] and *Dirac* [2.1] gave impetus to the quantitative study of the many-body problem in quantum theory. It is still the simplest approach to the problems of molecular binding and interatomic exchange.

Assume nuclei fixed at  $R_a$  and  $R_b$ , with interatomic spacing  $R_{ab}$  = several atomic radii. (We set the mass of the proton =  $\infty$  so as to be able to localize it. Taking the finite mass into account does not change the results much, but leads to an interesting exchange effect: the existence of two species of  $H_2$ , ortho- and parahydrogen. The energy splitting is related to the overlap between protons rotating about a common axis, the overlap due to vibrational motion being negligible. So when the molecule is hindered in its rotation, e.g., by a crystal field, the splitting between ortho- and parahydrogen must disappear.) To a first approximation each neutral atom exerts no force on the other, and each electron "sees" only the central force field of its own proton. According to this hypothesis, we simplify the two-particle Schrödinger equation,

$$\mathcal{H}\Psi_1 = E\Psi_1$$

with

$$\mathcal{H} = \left( \frac{p_1^2}{2m} - \frac{e^2}{r_{1a}} + \frac{p_2^2}{2m} - \frac{e^2}{r_{2b}} \right) + \left( \frac{e^2}{R_{ab}} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{1b}} - \frac{e^2}{r_{2a}} \right) \quad (2.8)$$

<sup>2</sup> See [2.7] or any good text on molecular physics or chemistry.

by choosing  $\Psi_1(\mathbf{r}_1, \mathbf{r}_2)$  to be a product function  $\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2)$ , where each factor obeys the one-particle Schrödinger equation, (there should be no confusion between the ground state eigenvalue  $e_0$  and the charge of the electron)

$$\left( \frac{p_1^2}{2m} - \frac{e^2}{r_{1a}} \right) \varphi_a(\mathbf{r}_1) = e_0 \varphi_a(\mathbf{r}_1)$$

and

$$\left( \frac{p_2^2}{2m} - \frac{e^2}{r_{2b}} \right) \varphi_b(\mathbf{r}_2) = e_0 \varphi_b(\mathbf{r}_2). \quad (2.9)$$

At the total Hamiltonian is invariant under the interchange of the two coordinates  $\mathbf{r}_1$  and  $\mathbf{r}_2$ , an equally good choice must be  $\Psi_{II} = \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)$ . Therefore, let us diagonalize the Hamiltonian of (2.8) within the subspace of these two simple functions. Assume the atomic orbitals  $\varphi(\mathbf{r})$  to be normalized, and define various overlap integrals  $I, V, U$  as follows:

$$I = \int d^3r |\varphi_a(\mathbf{r})|^2 = \int d^3r |\varphi_b(\mathbf{r})|^2 \quad I \equiv \int d^3r \varphi_a^*(\mathbf{r})\varphi_b(\mathbf{r})$$

$$V \equiv \int d^3r_1 d^3r_2 |\Psi_I|^2 \left( \frac{e^2}{R_{ab}} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{1b}} - \frac{e^2}{r_{2a}} \right) \\ = \int d^3r_1 d^3r_2 |\Psi_{II}|^2 \left( \frac{e^2}{R_{ab}} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{1a}} - \frac{e^2}{r_{2b}} \right)$$

and an "exchange integral":

$$U \equiv \int d^3r_1 d^3r_2 \Psi_I^* \Psi_{II} \left( \frac{e^2}{R_{ab}} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{1b}} - \frac{e^2}{r_{2a}} \right). \quad (2.10)$$

Let us take a variational wavefunction

$$\Psi = c_I \Psi_I + c_{II} \Psi_{II} \quad (2.11)$$

and determine the coefficients  $c_I$  and  $c_{II}$  so as to make the variational energy stationary

$$E_{\text{var}} = \frac{\int d^3r_1 d^3r_2 \Psi^* \mathcal{H} \Psi}{\int d^3r_1 d^3r_2 \Psi^* \Psi}, \quad \frac{\partial E_{\text{var}}}{\partial c_{I,II}} = 0. \quad (2.12)$$

The solutions to this are best expressed in matrix notation. Let  $\Psi_I$  correspond to the vector (1, 0) and  $\Psi_{II}$  to the vector (0, 1). In this notation, the variational wavefunction  $\Psi$  is merely  $(c_I, c_{II})$ , and the variational equations can be expressed in compact matrix form as an eigenvalue problem:

$$\begin{bmatrix} V & U \\ U^* & V \end{bmatrix} \begin{bmatrix} c_I \\ c_{II} \end{bmatrix} = (E - 2e_0) \begin{bmatrix} 1 & I \\ I^* & 1 \end{bmatrix} \begin{bmatrix} c_I \\ c_{II} \end{bmatrix}. \quad (2.13)$$

As in fact all functions under consideration are (or can be made) real, we shall henceforth omit the asterisk. It is not difficult to guess that the solutions to this equation are the symmetric and antisymmetric functions corresponding to

$$c_I = \pm c_{II} \quad (2.14)$$

and that the respective eigenvalues are

$$E_{\pm} = 2e_0 + \frac{V \pm U}{1 \pm I^2} \quad (2.15)$$

The space symmetric (+) solution calls for the spin antisymmetric "singlet" function, and the space antisymmetric function (-) for any of the three symmetric "spin-triplet" functions. The triple-singlet separation is

$$\Delta E = E_- - E_+ = 2 \frac{VI^2 - U}{1 - I^4} \quad (2.16)$$

and can be used to define an effective exchange force in the Heisenberg Hamiltonian. For the energy levels of

$$\mathcal{H}_{\text{Heis}} = -J_{12} \mathbf{S}_1 \cdot \mathbf{S}_2 = -J_{12} \left[ \frac{(\mathbf{S}_1 + \mathbf{S}_2)^2}{2} - \frac{3}{4} \right] \quad (2.17)$$

are  $-\frac{3}{4}J_{12}$  in the triplet states, and  $+\frac{3}{4}J_{12}$  in the singlet state. (See Chap. 3). By comparison with (2.16), the exchange constant is deduced to be

$$J_{12} = -2 \frac{VI^2 - U}{1 - I^4} \quad (2.18)$$

Ferromagnetism, of an embryonic molecular sort, would occur if the exchange constant  $J_{12}$  turned out positive. Antiferromagnetism would be the consequence of an antiferromagnetic bond  $J_{12} < 0$ . What the actual sign turns out to be depends on the relative magnitudes of the "Coulomb integral"  $V$ , the "overlap integral"  $I$ , and the "exchange integral"  $U$ . In the primitive calculation of Heitler and London unperturbed hydrogen  $1s$  orbitals were used in these various integrals—yielding results in satisfactory agreement both with experiment and more accurate modern calculations (see Problem 1, below). The exchange constant turned out *negative*, corresponding to a singlet (i.e. embryonic antiferromagnetic) ground state, and varied with internuclear distance  $R_{ab}$  as shown in Fig. 2.3. The triplet state was found, correctly, to be *unbound*, to have energy greater than the energy of two separate atoms,  $2e_0$ .

A second method for treating the  $\text{H}_2$  molecule owes its origin to the work of

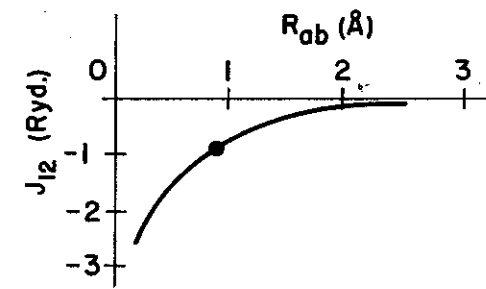


Fig. 2.3. Exchange parameter  $J_{12}$  as function of internuclear distance  $R_{ab}$  in hydrogen molecule ( $\text{H}_2$ ). Dot shows equilibrium value

F. Hund and R. S. Mulliken,<sup>3</sup> and is known as the method of molecular orbitals (M-O). The one-electron functions are chosen, in this method, to be eigenfunctions of some of the symmetry operations which leave an appropriately defined zeroth order Hamiltonian invariant. In this case, the eigenstates of the ion  $\text{H}_2^+$  could be chosen as the molecular orbitals. These fall into two classes, the even ones and odd ones. A further refinement would be to take for the one-electron functions the solutions of a Hamiltonian in which the ionic potentials are screened in a self-consistent way. But even the following crude choice gives reasonable agreement with the exact solution, at the equilibrium value of  $R_{ab}$ . Let

$$\varphi_g = \frac{\varphi_a(\mathbf{r}) + \varphi_b(\mathbf{r})}{\sqrt{2(1+I)}} \quad (2.19)$$

and

$$\varphi_u = \frac{\varphi_a(\mathbf{r}) - \varphi_b(\mathbf{r})}{\sqrt{2(1-I)}} \quad (2.19a)$$

approximating the even and odd (*gerade*, *ungerade*, in the time-honored notation *g*, *u*) eigenfunctions of  $\text{H}_2^+$  by linear combinations of the atomic orbitals. This generates four functions with which to diagonalize the Hamiltonian,

$$\varphi_g(\mathbf{r}_1) \cdot \varphi_g(\mathbf{r}_2), \quad \varphi_g(\mathbf{r}_1) \cdot \varphi_u(\mathbf{r}_2), \quad \varphi_u(\mathbf{r}_1) \cdot \varphi_g(\mathbf{r}_2), \quad \varphi_u(\mathbf{r}_1) \cdot \varphi_u(\mathbf{r}_2). \quad (2.19b)$$

The M-O method generates four states from two atomic orbitals, twice as many as either the H-L scheme or the Heisenberg Hamiltonian. Molecular orbitals are related to the Bloch functions of solid state theory, discussed elsewhere in the text. There also exists another set of states, more perspicuous than the previous, being mutually orthogonal functions that properly reduce to atomic orbitals in the limit of large separation,  $I \rightarrow 0$ . They are:

<sup>3</sup> See, for example, [2.8.9].



$$\psi_a = \frac{\varphi_a - g\varphi_b}{\sqrt{1 + g^2 - 2gl}} \quad (2.20)$$

and

$$\psi_b = \frac{\varphi_b - g\varphi_a}{\sqrt{1 + g^2 - 2gl}} \quad (2.20a)$$

with

$$g = \frac{1}{l}(1 - \sqrt{1 - l^2})$$

to ensure orthogonality. (These functions are prototypes of Wannier functions, treated elsewhere in this book). The eigenvalues of the two-body Hamiltonian can be found with the aid of the four orthonormal functions,

$$\begin{aligned} F_1 &= \psi_a(\mathbf{r}_1) \cdot \psi_a(\mathbf{r}_2) & F_2 &= \psi_a(\mathbf{r}_1) \cdot \psi_b(\mathbf{r}_2) \\ F_3 &= \psi_b(\mathbf{r}_1) \cdot \psi_b(\mathbf{r}_2) & F_4 &= \psi_b(\mathbf{r}_1) \cdot \psi_a(\mathbf{r}_2) \end{aligned} \quad (2.20b)$$

As these functions span the same "function space" as the four M-O functions (2.19b), the four eigenvalues will be the same as if we worked with molecular orbitals.  $F_2$  and  $F_4$  correspond approximately to  $\Psi_I$  and  $\Psi_{II}$  for the nonorthogonal orbitals,  $F_1$  and  $F_3$  to "ionized configurations." The two lowest eigenvalues will correspond to  $E_{\pm}$  of (2.15); see Problem 2.1.

**Problem 2.1.** Find the eigenvectors and eigenvalues of the  $4 \times 4$  matrix

$$\mathcal{H}_{ij} = \int F_i \mathcal{H} F_j d^3r_1 d^3r_2.$$

In addition to the definitions in (2.10), this requires the definition of additional integrals  $W$  and  $X$ , etc. Define them.

(a) Show that there is one triplet (space antisymmetric) eigenfunction, with energy  $E_- = \mathcal{H}_{22} - \mathcal{H}_{24} =$  identically as given in (2.15). Find the lowest of the three space symmetric, singlet, solutions. Prove that it has energy *lower* than  $E_+$ , the H-L ground state.

(b) Second-order perturbation theory can also be used to calculate the singlet ground state energy,

$$E_+ \sim \mathcal{H}_{22} + \mathcal{H}_{24} - \frac{(\mathcal{H}_{12} + \mathcal{H}_{14})^2}{\mathcal{H}_{11} - \mathcal{H}_{22} - \mathcal{H}_{24}}.$$

Express this formula in terms of  $U$ ,  $V$ ,  $W$ ,  $X$ , and  $l$ , and by comparison with the exact result found in part (a) determine the physical region of approximate validity of the perturbation theory.

The importance of this calculation is that it shows that the Heisenberg Hamiltonian can be derived qualitatively on the basis of first- and second-order pertur-

bation theory, using orthogonalized orbitals; and therefore many of the results of the theory (exchange constant, spin waves, existence of Curie temperature, etc.) are valid even when H-L theory is not.

### 2.3 Three Hydrogen Atoms

The total Hamiltonian is separated into terms appropriate to individual hydrogen atoms  $\mathcal{H}_0$  + the interaction terms  $\mathcal{H}'$ :

$$\begin{aligned} \mathcal{H} &= \left[ \left( \frac{p_1^2}{2m} - \frac{e^2}{r_{1a}} \right) + \left( \frac{p_2^2}{2m} - \frac{e^2}{r_{2b}} \right) + \left( \frac{p_3^2}{2m} - \frac{e^2}{r_{3c}} \right) \right] \\ &\quad + e^2 \left[ \left( \frac{1}{R_{ab}} + \frac{1}{R_{bc}} + \frac{1}{R_{ac}} \right) + \left( \frac{1}{r_{12}} + \frac{1}{r_{23}} + \frac{1}{r_{13}} \right) - \left( \frac{1}{r_{1b}} + \frac{1}{r_{1c}} \right) \right] \\ &\quad - \left( \frac{1}{r_{2a}} + \frac{1}{r_{2c}} \right) - \left( \frac{1}{r_{3a}} + \frac{1}{r_{3b}} \right) \\ &= \{\mathcal{H}_0\} + \{\mathcal{H}'\} \end{aligned} \quad (2.21)$$

and as before, we use products of the nonorthogonal atomic functions of (2.9) of which there are  $3! = 6$  in total. Let us label them according to the following table:

$$\begin{aligned} \psi_1 &= \varphi_a(1)\varphi_b(2)\varphi_c(3) \\ \psi_2 &= \varphi_a(2)\varphi_b(1)\varphi_c(3) \\ \psi_3 &= \varphi_a(3)\varphi_b(2)\varphi_c(1) \\ \psi_4 &= \varphi_a(1)\varphi_b(3)\varphi_c(2) \\ \psi_5 &= \varphi_a(2)\varphi_b(3)\varphi_c(1) \\ \psi_6 &= \varphi_a(3)\varphi_b(1)\varphi_c(2). \end{aligned} \quad (2.22)$$

How are these related to each other under the permutations of various particles? For typographical simplicity, let us omit the Greek symbols, and write  $\psi_1$  as 1,  $\psi_2$  as 2, etc. Then we can draw up simple tables (showing into which functions any of the six transform) under transpositions (permutations of two particles):

$$\begin{aligned} 1 &\rightarrow 2,3, \text{ or } 4 \\ 2 &\rightarrow 1,5, \text{ or } 6 \\ 3 &\rightarrow 1,5, \text{ or } 6 \\ 4 &\rightarrow 1,5, \text{ or } 6 \\ 5 &\rightarrow 2,3, \text{ or } 4 \end{aligned} \quad (2.23)$$

$$6 \rightarrow 2,3, \text{ or } 4$$

and under nontrivial permutations of all *three* particles:

$$\begin{aligned} 1 &\rightarrow 5,6 \\ 2 &\rightarrow 3,4 \\ 3 &\rightarrow 2,4 \\ 4 &\rightarrow 2,3 \\ 5 &\rightarrow 1,6 \\ 6 &\rightarrow 1,5 \end{aligned} \quad (2.24)$$

Thus, for equidistant atoms at the vertices of an equilateral triangle (Fig. 2.4)

$$\int \psi_1^* \psi_2 d\tau = \int \psi_1^* \psi_3 d\tau = \int \psi_1^* \psi_4 d\tau = I^2 = \int \psi_2^* \psi_5 d\tau, \text{ etc.} \quad (2.25)$$

and

$$\int \psi_1^* \psi_5 d\tau = \int \psi_1^* \psi_6 d\tau = I^3 = \int \psi_2^* \psi_3 d\tau, \quad (2.26)$$

etc. Or in general if we use these integrals to define an overlap matrix  $\Omega$

$$\Omega_{ij} = \int \psi_i^* \psi_j d\tau \quad (2.27)$$

then we have simply,

$$\Omega = \begin{pmatrix} 1 & I^2 & I^2 & I^2 & I^3 & I^3 \\ I^2 & 1 & I^3 & I^3 & I^2 & I^2 \\ I^2 & I^3 & 1 & I^3 & I^2 & I^2 \\ I^2 & I^3 & I^3 & 1 & I^2 & I^2 \\ I^3 & I^2 & I^2 & I^2 & 1 & I^3 \\ I^3 & I^2 & I^2 & I^2 & I^3 & 1 \end{pmatrix} \quad (2.28)$$

a real symmetric matrix. And as for the matrix elements of the Hamiltonian, we do not have to examine all 36 possibilities, but in fact just 6:

$$\int \psi_i^* \mathcal{H} \psi_i d\tau = H_{1,i}, \quad i = 1, 2, \dots, 6 \quad (2.29)$$

for we can obtain all the others by appropriate permutations. And of these only three are independent. They are,

$$H_{1,1} = 3e_0 + H'_{1,1} \quad (2.30a)$$

$$H_{1,2} = H_{1,3} = H_{1,4} = 3e_0 I^2 + H'_{1,2} \quad (2.30b)$$

$$H_{1,5} = H_{1,6} = 3e_0 I^3 + H'_{1,5}. \quad (2.30c)$$

From (2.30a) we also get  $H_{2,2} = H_{3,3} = \dots = H_{1,1}$ . From (2.30b) we get the matrix elements of  $\mathcal{H}$  between any function in (2.23) and its transform, for example,  $H_{2,5} = H_{1,2}$ , etc.; and (2.30c) gives the archetype matrix element between functions of (2.24) and their transform. A slight change of notation will greatly simplify the appearance of the interaction matrix. We define  $A$ ,  $b$ , and  $c$  by

$$A = H'_{1,1}, \quad bI^2 \cdot A = H'_{1,2} \quad \text{and} \quad cI^3 \cdot A = H'_{1,5}. \quad (2.31)$$

This replaces the matrix elements as parameters by  $A$ ,  $b$ ,  $c$ , and the previously defined overlap integral  $I$  [cf. (2.10)]. The Hamiltonian matrix is then particularly convenient to derive:  $3e_0$  times the overlap matrix, plus  $A$  times an interaction matrix (which can be derived from the overlap matrix merely by replacing  $I^2$  by  $bI^2$  and  $I^3$  by  $cI^3$  in the latter), so that the eigenvalue equation now reads:

$$A \begin{pmatrix} 1 & bI^2 & bI^2 & bI^2 & cI^3 & cI^3 \\ bI^2 & 1 & cI^3 & cI^3 & bI^2 & bI^2 \\ bI^2 & cI^3 & 1 & cI^3 & bI^2 & bI^2 \\ bI^2 & cI^3 & cI^3 & 1 & bI^2 & bI^2 \\ cI^3 & bI^2 & bI^2 & bI^2 & 1 & cI^3 \\ cI^3 & bI^2 & bI^2 & bI^2 & cI^3 & 1 \end{pmatrix} \cdot \mathbf{v} = (E - 3e_0) \begin{pmatrix} 1 & I^2 & I^2 & I^2 & I^3 & I^3 \\ I^2 & 1 & I^3 & I^3 & I^2 & I^2 \\ I^2 & I^3 & 1 & I^3 & I^2 & I^2 \\ I^2 & I^3 & I^3 & 1 & I^2 & I^2 \\ I^3 & I^2 & I^2 & I^2 & 1 & I^3 \\ I^3 & I^2 & I^2 & I^2 & I^3 & 1 \end{pmatrix} \cdot \mathbf{v} \quad (2.32)$$

We denote eigenvectors by  $\mathbf{v}$ . We construct the six distinct eigenvectors by use of the permutation tables given just previously. One starts with  $\psi_1$ , or

$$\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad (2.33)$$

in the vector notation. A totally symmetric un-normalized function is constructed by adding to this vector all the vectors obtained by permutations of the particles; for example,

$$\mathbf{v}_{\text{sym}} = (1, 1, 1, 1, 1, 1). \quad (2.34)$$



(For typographical reasons, we now write the vectors as row vectors. Technically, therefore, they are *left* eigenvectors.) For a totally antisymmetric but unnormalized function, we again start with  $\psi_1$ , subtract all the odd permutations, which are given in (2.23), and add the even permutations, given in (2.24)

$$v_{a-s} = (1, -1, -1, -1, +1, +1). \quad (2.35)$$

We next seek vectors antisymmetric in particles 2 and 3, but not *totally* antisymmetric, that is, orthogonal to  $v_{a-s}$ . We find

$$v_{23} = \left(1, \frac{1}{2}, \frac{1}{2}, -1, -\frac{1}{2}, -\frac{1}{2}\right) \text{ and } v'_{23} = (0, 1, -1, 0, +1, -1). \quad (2.36)$$

Next, we look for vectors symmetric in particles 2 and 3, but orthogonal to  $v_{sym}$

$$v_{23sym} = \left(1, -\frac{1}{2}, -\frac{1}{2}, 1, -\frac{1}{2}, -\frac{1}{2}\right) \text{ and } v'_{23sym} = (0, 1, -1, 0, -1, +1) \quad (2.37)$$

These choices are not unique. However, because of the invariance of the Hamiltonian under permutations, functions of different symmetries do not mix. The totally symmetric and the totally antisymmetric function both stand alone in their own symmetry class and therefore must be eigenvectors. The remaining four eigenvalues are obtained by diagonalizing the matrices of the eigenvalue equation (2.32), in the  $2 \times 2$  subspaces of the functions of (2.36, 37), respectively. This use of symmetry saves us from the tedium of diagonalizing  $6 \times 6$  matrices: the importance of the permutation operators should be already abundantly clear.

In the present problem, hidden symmetries simplify the eigenvalue equation further. For it happens that each of the last four vectors is simultaneously an eigenvector of both the overlap and the interaction matrices, and all are degenerate. The eigenvalues can be found almost by inspection now.

$$E_{sym} = 3e_0 + A \frac{1 + 3bl^2 + 2cl^3}{1 + 3l^2 + 2l^3} \quad (2.28)$$

$$E_{a-s} = 3e_0 + A \frac{1 - 3bl^2 + 2cl^3}{1 - 3l^2 + 2l^3} \quad (2.39)$$

and the four-fold degenerate eigenvalue,

$$E_{23} = 3e_0 + A \frac{1 - cl^3}{1 - l^3}. \quad (2.40)$$

Elsewhere we discuss how to combine space with spin to obtain wavefunctions of space and spin, obeying the Pauli principle. At present we need only the

following which the reader must accept on faith:  $v_{sym}$  is not an allowable eigenfunction for electrons;  $v_{a-s}$  will be used to construct the function of spin three-halves and  $v_{23}$  the function of spin one-half, known as quartet and doublet states, respectively. No other values of total spin angular momentum can be obtained with three electrons.

How do these results compare with the solutions of the Heisenberg Hamiltonian? To the two-spin Hamiltonian of (2.17) which corresponded to the hydrogen molecule,  $-J_{12}\mathbf{S}_1 \cdot \mathbf{S}_2$ , we now must add two more equal bonds to connect all sides of the equilateral triangle, as shown in Fig. 2.4. That is,

$$\mathcal{H}_{\text{Heis}} = -J_{12}^*(\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_2 \cdot \mathbf{S}_3 + \mathbf{S}_3 \cdot \mathbf{S}_1). \quad (2.41)$$

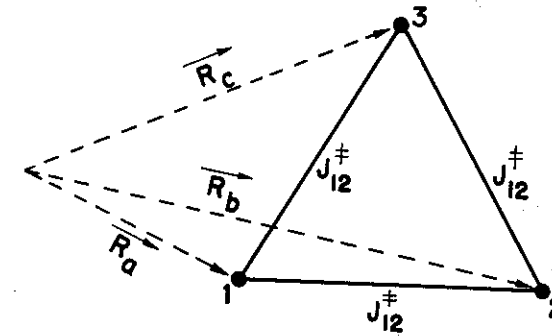


Fig. 2.4. Three-atom molecule, or three equivalent Heisenberg spins, with solid lines indicating bonds

We use a superscript ( $\neq$ ), however, to warn that the exchange “constant” might be rather more variable than its name suggests, and that the value we shall find in the present calculation may not agree with the result previously obtained for two atoms.

The distinct eigenvalues of the above Heisenberg Hamiltonian can be calculated by diagonalizing  $\mathcal{H}_{\text{Heis}}$  in the subspace of the three functions belonging to  $M = +\frac{1}{2}$ . Because of the rotational symmetry, it is found moreover that the two solutions belonging to  $M = S = \frac{1}{2}$  are degenerate. The quartet solution is of course unique and, therefore, automatically an eigenfunction of the Hamiltonian. The reader is encouraged to construct these states, starting with a basis

$$\chi_1 \equiv \uparrow\downarrow\downarrow \quad \chi_2 \equiv \downarrow\uparrow\downarrow \quad \chi_3 \equiv \downarrow\downarrow\uparrow \quad (2.42)$$

in an obvious notation. One can also obtain the eigenvalues more simply by completing the square in (2.41). Either way, he finds for the solutions of (2.41)

$$E_{\text{quart}} - E_{\text{doubt}} = -\frac{3}{2}J_{12}^*. \quad (2.43)$$

Now this must be set equal to

$$E_{a-s} - E_{23} = A \left( \frac{1 - 3bl^2 + 2cl^3}{1 - 3l^2 + 2l^3} - \frac{1 - cl^3}{1 - l^3} \right) = -\frac{3}{2} J_{12}^* \quad (2.44)$$

the calculated level separation, so as to obtain finally a value for the exchange parameter

$$J_{12}^* = -2Al^2 \frac{(1-b) + (l+l^2)(c-b)}{(1-l^3)(1+l-2l^2)} \quad (2.45)$$

Unless the overlap is very small, this expression has terms in  $l^3$ , etc., and is in no way comparable to the formula of (2.18) which we obtained previously. However, there is no reason to take the H-L scheme seriously if the overlap is that great. [Note that if the atoms are exceedingly close, then the eigenfunctions of atomic lithium are a better zeroth-order set than the three hydrogen atomic functions, whereas those of helium best approximate the solution of the  $H_2$  molecule. In vain can we expect the H-L picture to describe these physical systems when  $l \sim 1$ . In solids, the H-L picture breaks down completely once  $l$  approaches or exceeds  $1/z$  in magnitude, where  $z$  = number of nearest neighbors of each atom ( $z = 6$  for simple cubic structure, etc.) because  $\Omega$  becomes a singular matrix. That is, the wavefunctions cannot be normalized unless  $l < 1/z$ ; see ahead].

For the reasons above, in a microscopic derivation of the Heisenberg Hamiltonian and of the exchange constant, we must assume that  $R_{ab}$  = many atomic units, and calculate only to lowest order in the overlap,  $l$ . One is powerless to define interatomic exchange more accurately (although once again in the atom, for *intra*-atomic exchange, the situation is more favorable, as we shall see subsequently).

In accordance with these arguments, we now calculate the exchange parameters to lowest order in the overlap: From (2.18),

$$\begin{aligned} \frac{1}{2} J_{12} \doteq -Vl^2 + J = -l^2 \int d^3r_1 d^3r_2 \varphi_a^2(\mathbf{r}_1) \varphi_b^2(\mathbf{r}_2) \left( \frac{e^2}{R_{ab}} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{1b}} - \frac{e^2}{r_{2a}} \right) \\ + \int d^3r_1 d^3r_2 \varphi_a(\mathbf{r}_1) \varphi_b(\mathbf{r}_1) \varphi_a(\mathbf{r}_2) \varphi_b(\mathbf{r}_2) \left( \frac{e^2}{R_{ab}} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{1b}} - \frac{e^2}{r_{2a}} \right) \end{aligned} \quad (2.46)$$

and the calculation of (2.45) giving

$$\begin{aligned} \frac{1}{2} J_{12}^* &= -Al^2 + Al^2b = -H'_{1,1}l^2 + H'_{1,2} \\ &= -l^2 \int d^3r_1 d^3r_2 d^3r_3 \varphi_a^2(\mathbf{r}_1) \varphi_b^2(\mathbf{r}_2) \varphi_c^2(\mathbf{r}_3) \left[ \left( \frac{e^2}{R_{ab}} + \frac{e^2}{R_{ac}} + \frac{e^2}{R_{bc}} \right) \right. \\ &\quad \left. + \left( \frac{e^2}{r_{12}} + \frac{e^2}{r_{13}} + \frac{e^2}{r_{23}} \right) - \left( \frac{e^2}{r_{1b}} + \frac{e^2}{r_{1c}} + \frac{e^2}{r_{2a}} + \frac{e^2}{r_{2c}} + \frac{e^2}{r_{3a}} + \frac{e^2}{r_{3b}} \right) \right] \end{aligned}$$

$$\begin{aligned} &+ \int d^3r_1 d^3r_2 d^3r_3 \varphi_a(\mathbf{r}_1) \varphi_b(\mathbf{r}_1) \varphi_a(\mathbf{r}_2) \varphi_b(\mathbf{r}_2) \varphi_c^2(\mathbf{r}_3) \left[ \left( \frac{e^2}{R_{ab}} + \frac{e^2}{R_{ac}} + \frac{e^2}{R_{bc}} \right) \right. \\ &\quad \left. + \left( \frac{e^2}{r_{12}} + \frac{e^2}{r_{13}} + \frac{e^2}{r_{23}} \right) - \left( \frac{e^2}{r_{1b}} + \frac{e^2}{r_{1c}} + \frac{e^2}{r_{2a}} + \frac{e^2}{r_{2c}} + \frac{e^2}{r_{3a}} + \frac{e^2}{r_{3b}} \right) \right] \end{aligned} \quad (2.47)$$

recalling the definition of the various parameters in (2.31), and assuming also for simplicity that all the atomic functions are real, and normalized.

Let us try to reduce the second calculation to some of the integrals in the first, so that we may effect a comparison. First, (2.46): The terms in  $R_{ab}$  cancel exactly, and the remainder can be put in the form

$$\frac{1}{2} J_{12} = \int d^3r_1 d^3r_2 \left( \frac{2e^2}{r_{1b}} - \frac{e^2}{r_{12}} \right) (\rho_{12} l^2 - \rho_{12ex}) \quad (2.48)$$

defining  $\rho_{12}$  to be the ordinary electron density  $\varphi_a^2(\mathbf{r}_1) \varphi_b^2(\mathbf{r}_2)$  and  $\rho_{12ex}$  to be the "exchange density"  $\varphi_a(\mathbf{r}_1) \varphi_b(\mathbf{r}_1) \varphi_a(\mathbf{r}_2) \varphi_b(\mathbf{r}_2)$ , in an obvious notation.

Some simple manipulations of the terms in the integrals for  $J_{12}^*$  enable us finally to reach the desired result

$$J_{12}^* = J_{12} + 4le^2 \int d^3r_1 d^3r_2 \varphi_b^2(\mathbf{r}_2) \cdot [\varphi_a(\mathbf{r}_1) \varphi_c(\mathbf{r}_1) - l\varphi_a^2(\mathbf{r}_1)] \left( \frac{1}{r_{12}} - \frac{1}{r_{1b}} \right) \quad (2.49)$$

The correction term is not necessarily negligible compared to the exchange parameter itself (see Problem 2.2).

**Problem 2.2.**  $\varphi_a(\mathbf{r})$  is the unperturbed  $1s$  atomic ground-state wavefunction of an electron belonging to a hydrogen atom at  $\mathbf{R}_a$ , and  $\varphi_b$  is defined correspondingly. Calculate  $l(R_{ab})$  and  $J_{12}(l)$ ,  $J_{12}^*(l)$ . Is the exchange parameter increased or decreased by the presence of the third atom? (Assume  $R_{ab}$  to be large). See also [Ref. 2.12, Eq. (6)].

The presence of the third atom at  $\mathbf{R}_c$  modifies the exchange bond, as we have defined it, between spins at  $\mathbf{R}_a$  and  $\mathbf{R}_b$ . If atoms  $a$  and  $b$  were imbedded in a solid, the exchange interaction between them would be further modified, and the molecular exchange constant  $J_{12}$  or  $J_{12}^*$  would be of little quantitative use. Those who would calculate exchange parameters must heed the following warning: It is futile to imagine that exchange, even between similar atoms, can be characterized by a universal parameter  $J_{12}(R_{12})$  which one might calculate on a molecular model, no matter how refined. It should be regarded as a parameter which depends on all the other enviroing atoms as well, even to lowest order. When the Heisenberg Hamiltonian (2.1) is not applicable, the exchange parameter loses, of course, even this meaning, and exchange vanishes into the limbo of ill-defined concepts and ideas.

Herring [2.10] points out that the H-L scheme per se is in fact asymptotically wrong for  $R_{ab} >$  some 50 atomic distances, where it predicts a ferromagnetic exchange parameter, albeit an exponentially small one. Thus even if the Heisen-