

for this model neutral structures extend to infinity. But in this case we can consider an atomic ion with a low value of Z and exceedingly low difference between positive and negative charges. Such a structure will have a high polarizability. If we now bring up a

bare nucleus of very great charge Z' the effect of polarizability will again outweigh the effect of the electrostatic repulsion. Indeed, the former is proportional to $(Z')^2$, whereas the latter increases only as the first power of Z' .

Critique of the Heitler-London Method of Calculating Spin Couplings at Large Distances

CONYERS HERRING

Bell Telephone Laboratories, Murray Hill, New Jersey

1. INTRODUCTION

A. Scope of the Present Paper

FOR a third of a century the concept of exchange coupling of two or more non-singlet atoms has occupied a prominent place in theories of molecular binding and of magnetism. This concept, born in the Heitler-London theory¹ of the chemical bond, was applied by Heisenberg² in his celebrated theory of ferromagnetism, and soon received a very appealing formulation in terms of spin vectors at the hands of Van Vleck³ and Møller.⁴ Although the "spin Hamiltonian" resulting from this formulation has continued to be used in much—even most—theoretical work on magnetism, grave doubts as to its validity have been expressed,^{5,6} and various papers have attempted to disprove it, justify it, or test it.⁷ The object of the present paper is to clarify the status of the spin Hamiltonian and of the Heitler-London method of calculating the constants entering into it for the limiting case to which the original derivations were intended to apply, namely, the case of well-separated atoms. We shall give a rigorous justification of the concept of a spin Hamiltonian, a physical picture of the virtues and limitations of the Heitler-London

approach, and a prescription, which may even be practical in simple cases, for exact *a priori* calculation of the limiting exchange coupling.

It should be emphasized at once, however, that the arguments to be presented here are of more value to the world of pure thought than to the world of magnetic phenomena. For they are based, as we have implied, on the assumption that the wave functions of neighboring atoms overlap only slightly, and this is almost never true in molecules and solids. It has, of course, sometimes been supposed that the coupling of the atomic spins of unfilled $3d$ or $4f$ shells can be calculated by applying the Heitler-London method to the wave functions of these shells alone, ignoring the valence electrons responsible for chemical or metallic binding. If this were so, the assumption of weak overlap of neighbors would indeed be justified in many, though not all, cases. But in recent years it has become clear that the valence electrons just mentioned usually play a vital role in the coupling of the spins of neighboring atoms, via the indirect exchange⁸ and superexchange⁹ mechanisms. In metals, moreover, it may often happen that even the electrons responsible for ferro- or antiferromagnetism must be treated as itinerant, rather than tightly bound to their atoms.¹⁰

¹ W. Heitler and F. London, *Z. Physik* **44**, 455 (1927).

² W. Heisenberg, *Z. Physik* **49**, 619 (1928).

³ J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities* (Clarendon Press, Oxford, 1932).

⁴ C. Møller, *Z. Physik* **82**, 559 (1933).

⁵ J. C. Slater, *Revs. Modern Phys.* **25**, 199 (1953).

⁶ G. Heber, *Fortschr. Physik* **1**, 707 (1954).

⁷ For a general review of this and other topics in the theory of direct exchange see C. Herring, "Theory of Direct Exchange" in *Magnetism* edited by G. Rado and H. Suhl (Academic Press Inc., New York, to be published).

⁸ See the review by T. Kasuya in *Magnetism* edited by G. Rado and H. Suhl (Academic Press Inc., New York, to be published).

⁹ See the review by P. W. Anderson, "Exchange in Insulators: Superexchange, Direct Exchange and Double Exchange," in *Magnetism* edited by G. Rado and H. Suhl (Academic Press Inc., New York, to be published).

¹⁰ See the review by C. Herring, "Exchange Interactions Among Itinerant Electrons," in *Magnetism* edited by G. Rado and H. Suhl (Academic Press Inc., New York, to be published).

B. Formulation of the Problem

Consider a system of N atoms, without orbital degeneracy, and possessing spins S_1, \dots, S_N . At infinite separations, the ground state of this system has degeneracy

$$\nu = \prod_i (2S_i + 1). \quad (1)$$

As the interatomic separations R_{ij} are decreased, this degeneracy will split up, but if the R_{ij} are not too small, there will still be a group of ν lowest levels, well separated (if N is not too large) from more highly excited states. If, as we shall assume, there are no spin-orbit terms in the Hamiltonian, these ν states can be chosen to be eigenstates of the total spin variables S^2, S_z . Moreover, each such state can be placed in a one-to-one correspondence—not quite free of arbitrariness, of course—with a state of the system of completely separated atoms having the same S, S_z , and having a similar distribution of spin density on the various atoms. In other words, the subspace spanned by the ν lowest eigenstates is isomorphic to the spin space of N atomic spins. The first of the statements whose validity we wish to examine is that the Hamiltonian in the former subspace is equivalent to a constant plus a certain “spin Hamiltonian”

$$H_{\text{eff}} = -2 \sum_{i>j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \quad (2)$$

in the spin space, to within an error which becomes negligible in comparison with the range of eigenvalues of (2) as the $R_{ij} \rightarrow \infty$.

It is well known⁷ that (2) can be derived on the basis of the Heitler-London approximation. In this approximation one assumes that, in the subspace we are considering, a complete (though not orthonormal) basis is provided by the antisymmetrized products of single-atom functions, usually though not necessarily assumed to be eigenfunctions of the corresponding one-atom problems. In other words, one tries to make eigenfunctions out of linear combinations of the ν functions

$$\begin{aligned} \Psi_k \equiv \Psi_{k_1, \dots, k_N} = & A [\psi_{k_1}(\mathbf{r}_1, \dots, \mathbf{r}_{n_1}; s_1, \dots, s_{n_1}) \\ & \times \psi_{k_2}(\mathbf{r}_{n_1+1}, \dots, \mathbf{r}_{n_1+n_2}; s_{n_1+1}, \dots, s_{n_1+n_2}) \dots], \quad (3) \end{aligned}$$

where the subscripts k_i identify different spin states of atom i , and where

$$A = (N!)^{-1} \sum_P \delta_P P \quad (4)$$

is the antisymmetrizer, P being a permutation applied both to coordinates and spins, and δ_P being

+1 for even, -1 for odd permutations. If the atomic wave functions have the property

$$\psi_{k_i}(\mathbf{r}_1, \dots, \mathbf{r}_{n_i}) \sim e^{-\alpha_i r_i} \text{ as } r_i \rightarrow \infty, \quad (5)$$

then it is not hard to show that the matrix element of the Hamiltonian H between any pair of states of the form (3) is dominated, at large interatomic distances, by terms of the form

$$\left(\prod_i \psi_{k_i} | H | \prod_i \psi_{k'_i} \right) \text{ or } \left(\prod_i \psi_{k_i} | H | P_{ij} \prod_i \psi_{k'_i} \right), \quad (6)$$

where P_{ij} is a permutation of a single pair of electrons which appear in $\prod_i \psi_{k'_i}$ on two atoms i, j , which are close neighbors. The second type of term in (6) is of order

$$ij \text{ pair term} \sim \max [e^{-2\alpha_i R_{ij}}, e^{-2\alpha_j R_{ij}}], \quad (7)$$

while contributions to matrix elements of H involving higher-order permutations turn out to contain negative exponentials of three or more αR terms. With neglect of terms of the latter order, the Heitler-London approximation leads to a secular equation equivalent to that obtained from the spin Hamiltonian (2), with the coefficients J_{ij} given explicitly as two-atom exchange integrals.

Unfortunately, it is far from obvious that the Heitler-London approximation should become asymptotically correct at large separations; as we shall see below, it is, in fact, not asymptotically correct. It is true, of course, that functions of the form (3) approach the exact eigenfunctions as the separations are increased, but it is not obvious that the subspace spanned by them approaches the correct one rapidly enough for the *fractional* error in the energy splittings computed from them to go to zero. Consider the hydrogen molecule, for example. One might use as a basis the Heitler-London set (3) formed from the free-atom eigenfunctions $\varphi_a\alpha, \varphi_a\beta, \varphi_b\alpha, \varphi_b\beta$ around the two nuclei a, b , where φ_a, φ_b are coordinate wave functions and α, β are spin functions. This choice leads, as is well known, to a negative J , i.e., a ground-state singlet lying below the triplet (at reasonable values of R_{ab} , see below). Alternatively, one might construct a set of the form (3) from functions whose coordinate parts $\bar{\varphi}_a, \bar{\varphi}_b$ are related to φ_a, φ_b by

$$\begin{aligned} \bar{\varphi}_a &= \mu\varphi_a - \lambda\varphi_b \\ \bar{\varphi}_b &= \mu\varphi_b - \lambda\varphi_a \end{aligned} \quad (8)$$

with $\mu \approx 1, \lambda \approx \frac{1}{2}$, (ψ_a, ψ_b), chosen to make the set φ_a, φ_b orthonormal. Since $\bar{\varphi}_a \rightarrow \varphi_a, \bar{\varphi}_b \rightarrow \varphi_b$ as $R_{ab} \rightarrow \infty$, this choice might seem as plausible, superficially, as the first. But substitution of the wave

functions (8) in the Heitler-London expression for the exchange constant J , which to the lowest order ($e^{-2\alpha R_{ab}}$) in exponentials is

$$J = e^2 \iint d^3\mathbf{r}_1 d^3\mathbf{r}_2 \left[\frac{1}{R_{ab}} + \frac{1}{r_{12}} - \frac{1}{r_{1b}} - \frac{1}{r_{2a}} \right] \times |\varphi_a(1)\varphi_b(2)|^2, \quad (9)$$

always gives $J > 0$, i.e., triplet below singlet, since the orthogonality makes the negative terms vanish. Why should the one choice be more plausible than the other? May not the true singlet-triplet splitting differ from either of these computed values?

Closer inspection of the Heitler-London calculation for the hydrogen molecule shows that at very large interatomic separations ($R_{ab} \sim 50a_H$) it becomes physically unreasonable and its predictions impossible.^{7,11} For at large R_{ab} , the positive $1/r_{12}$ term in (9) becomes dominant,¹² being larger than the other terms by a factor containing $\ln R_{ab}$. This term represents the self-energy of the exchange charge distribution $\varphi_a\varphi_b$, and as $R_{ab} \rightarrow \infty$ this charge distribution approaches a cylindrical distribution about the internuclear line, the radius of the cylinder being of order $(R_{ab}a_H)^{1/2}$; the logarithm arises from the potential of this cylinder. Thus, at large R_{ab} , J becomes positive (triplet below singlet). But this is impossible, by virtue of the theorem that the lowest eigenfunction of a Sturm-Lionville equation must be nodeless,¹³ a theorem cited in this connection by Heisenberg² himself, and recently extended by Lieb and Mattis.¹⁴ What is wrong, clearly, is that the Heitler-London approximation greatly overestimates $\langle 1/r_{12} \rangle_{av}$. The true eigenfunctions of the hydrogen molecule will contain correlations in the positions of the two electrons, so that they avoid each other.

These considerations show that we must reject the Heitler-London approximation as lacking even an asymptotic validity at large separations. While one intuitively expects that a spin Hamiltonian of the form (2) should be asymptotically a valid approximation, the proof has yet to be given. It also remains to be shown that the J_{ij} for an N -atom problem can be computed as a two-atom problem, i.e., that exchange forces are pairwise additive, and if so, how an explicit *a priori* calculation can be carried out. We shall address ourselves to these questions, and to keep the discussion tractable, we shall consider only quantities

of the dominant order as the interatomic spacings become infinite, i.e., (as we shall see) quantities of the order of (7). All quantities with negative exponentials of four or more αR terms will be discarded. This means that we shall not enter into the complex of questions which arise when the number N of atoms is allowed to become very large as in a crystal, so that quantities of the form $Ne^{-2\alpha R}$ cease to be $\ll 1$. These questions, mathematically quite difficult, but not provoking one's physical intuition to any grave doubts, have been extensively discussed elsewhere.^{7,15}

C. Some Unsatisfactory Approaches to the Problem

It is worthwhile to mention here some of the difficulties, and even misleading conclusions, which one can encounter in pursuing what at first sight seem to be appealing ways of improving upon the Heitler-London approximation. As these are treated in some detail elsewhere,⁷ we shall discuss them only very briefly.

The several approaches we shall mention are all based on the idea of configuration interaction, i.e., on solving a secular equation in a subspace containing not only the Heitler-London basis (3), but also a finite or infinite set of other functions. One might, for example, augment the set (3) by functions constructed in a similar manner from ψ_{k_i} functions pertaining to excited atomic states. However, it turns out that if only a finite set of such excited functions is used, the splittings between the various spin states will contain factors of the form (7) with α_i^* , α_j^* , the quantities describing the radial decay of wave functions of excited states. At large R_{ij} such terms will dominate over terms of the form (7). It is physically clear, however, that the splittings must be of the order (7). For the physical meaning of an exchange constant J_{ij} is that if we were to make a particular assignment of electrons $1, \dots, n_i$ to atom i , $n_i + 1, \dots, n_i + n_j$ to atom j , then we should have to wait a time of order \hbar/J_{ij} before finding an appreciable probability to have one of the first n_i electrons on atom j and one of the second n_j on atom i . This exchange process is a tunneling through a region of configuration space in which the potential energy exceeds the total energy by the ground-state ionization energy of one or both of the atoms. It must therefore contain the factor (7), with α_i and α_j determined from the respective ground-state ionization energies.

The difficulty just mentioned can be avoided by including in the configuration-interaction calculation

¹¹ W. A. Bingel, H. Preuss, and H. H. Schmidtke, *Z. Naturforsch.* **16a**, 434 (1961).

¹² Y. Sugiura, *Z. Physik* **45**, 484 (1927).

¹³ R. Courant and D. Hilbert, *Methoden der Mathematischen Physik* (Springer-Verlag, Berlin, 1931), 2nd ed., Chap. VI, No. 6.

¹⁴ E. Lieb and D. Mattis, *Phys. Rev.* **125**, 164 (1962).

¹⁵ T. Arai, *Phys. Rev.* **126**, 471 (1962).

all the possible excited states of the atoms, including the continuous spectrum. Terms from the latter, having imaginary α^* 's, can, by proper combination of phases, cancel the undesirable terms with small real α^* 's. But formulations which have been attempted¹⁶ in terms of infinite summations over excited states turn out to involve logical as well as practical difficulties,⁷ and have not yet led to a satisfactory derivation of (2).

The approach¹⁷⁻²¹ which has received most attention in recent years is one which is admittedly only a rough approximation, but which at least avoids conflict with (7). This is to augment the Heitler-London basis (3) by wave functions representing ionized states, the electrons on the negative ions being placed in orbits with the same α 's as the neutral atoms. While this approach gives some insight into the way in which the Heitler-London approximation gives way to the molecular-orbital approximation at small interatomic separations, it can be shown⁷ that at large separations it gives results which differ negligibly from those of the Heitler-London method; thus it does not remedy the defects of the latter with which we are concerned. Similar remarks apply to other methods based on a limited configuration interaction.²²

2. A MODIFIED HEITLER-LONDON METHOD

A. Existence of an Analogous Method which Is Exact

As we have just demonstrated, the Heitler-London method with its use of products of isolated-atom eigenfunctions is not even asymptotically exact at large interatomic separations. However, it is not hard to see that there must be a closely analogous method which is exact. We know that at large separations the subspace spanned by the exact eigenfunctions Φ_s ($s = 1$ to ν) of the exchange degeneracy problem must nearly coincide with the subspace spanned by the Heitler-London functions ψ_k of (3). We could make a similar statement, in fact, relating the subspace spanned by all the permutations of the wave function in square brackets in (3) to the subspace spanned by the $m!/\prod n_i!$ corresponding eigenfunctions of the Hamiltonian in the full (not just the antisymmetric) coordinate-spin space. There must therefore be some linear combination $\Phi_k = \sum C_s \Phi_s$ of

true eigenfunctions which closely approximates the particular function $\prod \psi_{k_i}$ occurring in square brackets in (3). Since at large separations any permutation P of $\prod \psi_{k_i}$ which assigns the electrons differently to the various atoms is almost orthogonal to $\prod \psi_{k_i}$, $P \Phi_k$ must be almost orthogonal to Φ_k . Therefore the functions Φ_k have two important properties:

- (i) Like $\prod \psi_{k_i}$, Φ_k has a strong degree of localization of electrons 1 to n_1 on atom 1, $n_1 + 1$ to $n_1 + n_2$ on atom 2, etc.
- (ii) The exact eigenfunctions can be constructed from the Φ_k and their permutations.

Of course, finding functions Φ_k of the sort just described is no easier than finding the eigenfunctions Φ_s themselves. But the fact that such functions exist spurs us to search for a better approximation to them than the Heitler-London products. This improved approximation will have to take account of the mutual polarization of different atoms, since the van der Waals term which this polarization introduces into the energy is large compared with the exchange splittings we are trying to calculate. This suggests that we should try to construct functions which will obey the complete wave equation exactly in that part of configuration space which makes the main contribution to the van der Waals energy, i.e., the region where each electron is fairly definitely associated with "its own" atom, but which are so defined as to be small outside of this region. We shall define such wave functions χ_k presently, and show that for large separations they adequately approximate the Φ_k in terms of which the exact eigenfunctions can be expressed. It may be objected that finding an exact solution of the wave equation, even in a limited region of configuration space, is of a difficulty comparable with that of solving the entire problem and getting the Φ_s directly. But this is not true: Whereas grave difficulties beset the direct calculation of the eigenstates of the many-atom system from the free-atom eigenfunctions by perturbation methods, the difference between the wave equation obeyed by a product of free-atom functions and that obeyed by the χ_k , which we shall define below, is of a sort which can readily be treated as a small perturbation.

B. Illustration of the Method for H_2^+

Although our ultimate objective is to carry through the program just outlined for the general problem of spin exchange among N many-electron atoms, the essential features of the method can be seen by considering an analogous problem involving only one electron, capable of exchanging positions between two potential minima. The H_2^+ molecule is a

¹⁶ R. Eisenschitz and F. London, *Z. Physik* **60**, 491 (1930).

¹⁷ J. C. Slater, *Phys. Rev.* **52**, 198 (1937).

¹⁸ J. C. Slater, *J. Chem. Phys.* **19**, 220 (1951).

¹⁹ D. I. Paul, *Phys. Rev.* **118**, 92 (1960).

²⁰ L. F. Mattheiss, *Phys. Rev.* **123**, 1219 (1961).

²¹ L. F. Mattheiss, *Phys. Rev.* **123**, 1209 (1961).

²² R. K. Nesbet, *Ann. Phys. (N. Y.)* **4**, 87 (1958).

case of this type, for which the exact Σ_o and Σ_u energies are known.²³ These energies can be calculated approximately from the assumption that the corresponding wave functions are, respectively, the normalized sum and difference of the 1s free-atom wave functions centered on nuclei a and b .²⁴ The resulting energy difference $E(\Sigma_u) - E(\Sigma_o)$ is, for large separations R , less than the correct value in the ratio 1:1.1. This means that even for $R \rightarrow \infty$ the free-atom eigenfunction $\psi_a(\mathbf{r})$ is not an adequate approximation to the function Φ_a defined in Sec. 2A above, i.e., to

$$\Phi_a(\mathbf{r}) \equiv 2^{-1/2} [\Phi_o(\mathbf{r}) + \Phi_u(\mathbf{r})], \quad (10)$$

where Φ_o , Φ_u are the exact eigenfunctions of Σ_o , Σ_u states.

Figure 1 shows, as the full curve, the potential acting on the electron along the internuclear line. The dashed curve is the one-atom potential due to nucleus a alone. Let an artificial potential V' be constructed as shown by the beaded curve in Fig. 1. This V' is chosen to coincide with the two-proton potential everywhere on the a side of some surface Σ_p (e.g., a plane as shown in Fig. 2) lying well to the right of the median plane M but still far enough away from nucleus b for the potential on Σ_p to be small (compared to a Rydberg unit). On the b side of Σ_p , we define V' to be zero (actually, it does not matter how V' is defined here, as long as it has no deep potential trough). Let $\chi_a(\mathbf{r})$ be defined as the ground-state eigenfunction in the potential V' . It clearly differs very little from $\psi_a(\mathbf{r})$, and we shall

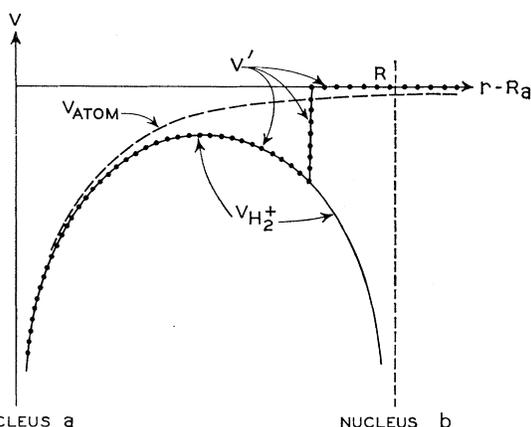


FIG. 1. Potentials for the H_2^+ ion, as functions of distance along the internuclear line. Full curve: true potential. Dashed curve: one-atom potential. Beaded curve: potential V' .

²³ D. Bates, K. Ledsham, and A. L. Stewart, *Phil. Trans. Roy. Soc. London* **246**, 215 (1953).

²⁴ H. Bethe, "Quantenmechanik der Ein- und Zwei-Elektronenprobleme," in *Handbuch der Physik* (Springer-Verlag, Berlin, 1933), 24/2, No. 58.

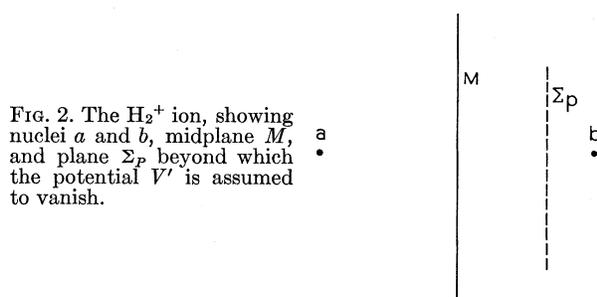


FIG. 2. The H_2^+ ion, showing nuclei a and b , midplane M , and plane Σ_p beyond which the potential V' is assumed to vanish.

now show that it differs from $\psi_a(\mathbf{r})$ in just such a way as to be a good approximation to the $\Phi_a(\mathbf{r})$ defined by (10). We do this by showing that the sum and difference of χ_a and its mirror image χ_b in the plane M have energies which as $R \rightarrow \infty$ adequately approach the $E(\Sigma_o)$ and $E(\Sigma_u)$ which we seek.

For the proof we use the well-known theorem^{25,26} that the error δE in the energy of a normalized approximation Ψ to any eigenstate obeys

$$|\delta E| \leq (\Psi | (H - \bar{E})^2 | \Psi) / |\Delta E_{\min}| \quad (11)$$

where \bar{E} is the mean energy of the state Ψ and ΔE_{\min} is the energy interval from \bar{E} to the nearest neighboring eigenvalue of the same symmetry as Ψ . Let us apply (11) to the functions

$$\Psi_{\pm} \equiv F_{\pm}(\chi_a \pm \chi_b), \quad (12)$$

where $F_{\pm} \approx 2^{-1/2}$ is a normalizing factor. The numerator of (11) can be written

$$|F_{\pm}|^2 \int d^3\mathbf{r} |(H - \bar{E})(\chi_a \pm \chi_b)|^2, \quad (13)$$

and if \bar{E} were the eigenvalue E_x of χ_a in the potential V' , $(H - E_x)\chi_a$ would vanish on the a side of the surface Σ_p , and $(H - E_x)\chi_b$ would vanish on the b side of the mirror-image surface. Since insertion of any number other than \bar{E} into (11) only increases the value of the right-hand side, we have for the difference δE_{\pm} between the mean energy of either of the functions (12) and the corresponding exact eigenvalue

$$|\delta E_{\pm}| \leq 2|F_{\pm}|^2 \int_{b \text{ side } \Sigma_p} d^3\mathbf{r} |(H - E_x)\chi_a|^2 / \Delta E_{\min}. \quad (14)$$

Now since V' differs only slightly from a free-atom potential, its eigenfunction χ_a and the corresponding energy E_x will differ only slightly from those of a hydrogenic 1s function. In particular, when R is large, $V' - E$ will be positive and of the order of a

²⁵ G. Temple, *Proc. Roy. Soc. (London)* **A119**, 276 (1928); W. Kohn, *Phys. Rev.* **71**, 902 (1947).

²⁶ T. Kato, *J. Phys. Soc. Japan* **4**, 334 (1949).

Rydberg unit not only on the b side of the surface Σ_P but also over most of the region between nucleus a and Σ_P . Therefore, on the b side of Σ_P ,

$$|\chi_a| \lesssim \exp \{ [- (1 + \xi)R - \Delta Z] / 2a_H \}, \quad (15)$$

where $\Delta Z \geq 0$ measures distance to the right of Σ_P and where $0 < \xi < 1$, $\xi R/2$ measuring how far the closest point of Σ_P lies to the right of the midpoint. Thus, the right of (14) must contain a factor $\exp [- (1 + \xi) R/a_H]$ times quantities which are finite and at most algebraic in R (actually they involve R^0), so

$$|\delta E_{\pm}| = O \{ \exp [- (1 + \xi)R/a_H] \}. \quad (16)$$

Since the splitting $E(\Sigma_a) - E(\Sigma_o)$ is of order $R e^{-R/a_H}$, (16) shows that our errors δE_{\pm} are asymptotically \ll the splitting.

C. Explicit Calculation for H_2^+

The explicit expression for the energy splitting in terms of χ_a can be given in various forms. Particularly convenient for our purposes is a formulation in terms of a surface integral over the median plane, the plane M of Fig. 2. This formulation is especially appealing because it reminds us of the physical meaning of the energy splitting as a tunneling probability between the two potential minima. We write, from (12)

$$\begin{aligned} E(\Sigma_a) - E(\Sigma_o) &= 2(\chi_a, H\chi_a) (|F_-|^2 - |F_+|^2) \\ &\quad - 2\Re(\chi_a, H\chi_b) (|F_-|^2 + |F_+|^2). \end{aligned} \quad (17)$$

Since this is an energy difference, it is unchanged by adding any constant to H in the expressions on the right. If we replace H by $H - E_x$, the quantity $(H - E_x)\chi_a$ will vanish to the left of the surface Σ_P in Fig. 2, and will be $\lesssim \exp [- (1 + \xi) R/2a_H]$ to the right of it. Since $|F_-|^2 - |F_+|^2$ contains the factor e^{-R/a_H} , the first term of (17) is negligible, being of the same order as (16). To this order of accuracy we can replace $|F_-|^2 + |F_+|^2$ by 1 in the second term. If we choose the phase of χ_a and χ_b so that these quantities are real, and note that $(H - E_x)\chi_b$ vanishes in the region to the right of M , we have

$$\begin{aligned} E(\Sigma_a) - E(\Sigma_o) &\approx -2 \int_{\text{left}} d^3 \mathbf{r} \chi_a (H - E_x) \chi_b \\ &= -2 \int_{\text{left}} d^3 \mathbf{r} \chi_b (H - E_x) \chi_a \\ &\quad + \frac{\hbar^2}{m} \int_M d\mathbf{S} \cdot (\chi_a \nabla \chi_b - \chi_b \nabla \chi_a) \\ &= -\frac{2\hbar^2}{m} \int_M d\mathbf{S} \cdot \chi_a \nabla \chi_a, \end{aligned} \quad (18)$$

since χ_a equals its mirror image χ_b on the plane M and $(H - E_x)\chi_a = 0$ to the left of M . The error in (18) is of the order of (16).

Having shown that the eigenfunction χ_a of the potential V' of Fig. 1 can be used, via the LCAO expressions (12), to get asymptotically accurate energies, let us now see if we can obtain an adequate explicit approximation to χ_a by perturbation of the single-atom eigenfunction ψ_a . This has been done by Holstein²⁷ in a study of the charge-exchange problem in gases, a study which, though entirely independent of the present work, very closely resembles the method described in the present section. As our main interest, unlike Holstein's, is in the spin-exchange problem to be discussed in the next section, we shall not attempt, as Holstein does, a systematic development of χ_a/ψ_a in powers of $1/R$, but shall only sketch, without rigor, how the leading term can be obtained. We set

$$\chi_a = \psi_a g \quad (19)$$

and choose atomic units $\hbar = m = e = 1$, so that $\psi_a = \pi^{-1/2} e^{-r}$ and

$$-\frac{1}{2} \nabla^2 g + \frac{\partial g}{\partial r} - \left(\frac{1}{|r - R_b|} + E_x - E_\psi \right) g = 0. \quad (20)$$

Now we expect g to vary smoothly over distances of the order of R , so that $\nabla^2 g$ is of order g/R^2 , $\partial g/\partial r$ of order g/R . For the same reason we expect the ratio of the surface integral (18) to its value with χ_a replaced by ψ_a to be simply the square of g at the midpoint, plus quantities of order $1/R$ or smaller. Using the fact that the leading term in $E_x - E_\psi$ is just the potential $-1/R$ of nucleus b at the position of a , we therefore approximate the differential equation (20) along the internuclear line (Z direction) by

$$\partial g/\partial Z + [1/R - 1/(R - Z)]g = 0, \quad (21)$$

the solution of which is

$$g = cR(R - Z)^{-1} e^{-Z/R}. \quad (22)$$

Normalization requires that $g \approx 1$ for small Z , hence that $c \approx 1$, so the value of g at the midpoint is, to the leading order in $1/R$,

$$g(R/2) = 2e^{-1/2}. \quad (23)$$

The value of the surface integral (18), when $\psi_a = \pi^{-1/2} e^{-r}$ is substituted for χ_a , is easily found to

²⁷ T. Holstein, Westinghouse Research Report 60-94698-3-R9 (1955). I am indebted to Dr. Holstein for informing me of the existence of this work, and of subsequent corrections, and for some illuminating discussions of it.

be Re^{-R} atomic units (1 a. u. = 27.2 eV). Note that this does not correspond to the LCAO energy splitting calculated with ψ_a, ψ_b , which is²⁴

$$[E(\Sigma_u) - E(\Sigma_g)]_{\text{LCAO}} = (4/3) Re^{-R} + O(R^{-1}e^{-R}) \text{ a.u.}; \quad (24)$$

the reason is that the reduction of (17) to (18) is not valid for ψ_a, ψ_b . Multiplying Re^{-R} by the square of (23), we get

$$E(\Sigma_u) - E(\Sigma_g) = (4/e) Re^{-R} + O(e^{-R}) \text{ a.u.} \quad (25)$$

which differs from the asymptotic LCAO value by the factor $3/e = 1.104$. Comparison with the supposedly exact numerical calculations of Bates, Ledsham, and Stewart²³ that the ratio of the splitting to the LCAO value appears to pass through a maximum of about 1.14 at $R = 9$ or 10 a.u., the curvature of the plot being such that extrapolation to 1.104 at $R = \infty$ would be reasonable. The reasonableness of such an extrapolation is supported by the fact that it requires a $1/R$ term in the ratio, of approximately the magnitude predicted by Holstein.²⁷

D. Definitions of Concepts to be Used for the Spin-Exchange Problem

After this illustrative digression, let us return to the problem of the coupling of the spins of weakly interacting atoms. We shall try to construct an asymptotically exact formalism for this case which will be related to the Heitler-London formalism in much the same way that our calculation in the two preceding sections was related to the LCAO method. For H_2^+ we constructed a function χ_a which resembled, in its localization, the free-atom function ψ_a , but which at the same time approximated as closely as possible the sum of the exact Σ_g and Σ_u eigenfunctions of the molecule. Here we wish to construct a set of functions χ_k , one for each set of spin quantum numbers k , which will have two analogous properties: First, they should resemble the products $\prod_i \psi_{k_i}$ of atomic functions in (3) in having analogous spin quantum numbers and in having each electron associated with a definite atom; second, the χ_k should approximate as closely as possible to the Φ_k defined in Sec. 2A above, in terms of which the exact eigenfunctions can be expressed.

As before, we shall define χ_k to be an eigenfunction in a synthetic potential V' . Consider the $3n$ -dimensional configuration space of all the electrons. Let the term "original center" be applied to that point for which the positions of electrons 1 to n_1 coincide with the position of nucleus 1, electrons $n_1 + 1$ to $n_1 + n_2$ with nucleus 2, etc. Designate as the " P th

center" the point obtained from the original center by applying the permutation P to the electronic coordinates. Of course, any permutation of the subgroup G_0 which permutes the first n_1 electrons among themselves, the next n_2 among themselves, etc., leaves the original center invariant. Therefore only $n!/\prod n_i!$ of the P th centers are distinct. Let r_λ be the position of electron λ , R_λ^P the position of the nucleus at which this electron is localized in the P th center. Define Σ_P to be the $(3n - 1)$ -dimensional hypersurface

$$\max_\lambda |r_\lambda - R_\lambda^P| = L, \quad (26)$$

where L is to be chosen as small as possible, consistent with the requirement that the lowest eigenvalue of the Schrödinger equation for $n - 1$ electrons with the remaining electron fixed at a distance $\geq L$ from any nucleus is

$$(n - 1)\text{-el. energy} \geq E_0 + \eta\epsilon_I, \quad (27)$$

where E_0 is the ground-state energy of separated atoms, η is a number nearly unity, and ϵ_I is the least of the atomic ionization energies. Thus, L is moderately greater than an "atomic radius," and Σ_P is a surface outside which it is appropriate to say that the P th configuration is ionized. We can now define V' by

$$\begin{aligned} V' &= V && \text{inside } \Sigma_1 \\ &= V && \text{outside all } \Sigma_P \\ &= E_0 + \epsilon_I && \text{inside any } \Sigma_P, P \neq 1, \end{aligned} \quad (28)$$

where V is the true potential energy function, and E_0 is the ground-state energy of separated atoms. Thus, V' coincides with V in and somewhat beyond the potential well neighboring the original center, but differs from V in having no comparable potential wells around the P th centers, $P \neq 1$.

The eigenfunctions χ_k in the potential V' will, of course, have a spin degeneracy. Since V' is invariant under the subgroup G_0 of permutations which in the original assignment permute electrons of each atom among themselves only, the χ_k can be classified according to the irreducible representations of G_0 to which they belong. We wish to limit our consideration to those χ_k whose energies are close to E_0 . These χ_k will be antisymmetric under G_0 , and it is easy to show (see Appendix I) that the χ_k can be so chosen as to be eigenfunctions of the operators $S_i^2, S_{i_2}(i = 1, \dots, N)$, where S_1 is the sum of the spins of electrons 1 to n_1 , etc. Thus, the set of ν possible spin indices k for the χ_k is isomorphic to the set $\{k_1, \dots, k_N\}$ of spin indices for N separate atoms.

E. Asymptotic Accuracy of the Modified Heitler-London Method

We are interested in the ν roots \bar{E} of the secular equation

$$\det (\chi_{k'} | H - \bar{E} | A \chi_k) = 0, \quad (29)$$

where A is the antisymmetrizer (4). These roots, as we shall now show, approximate the corresponding exact eigenvalues to within errors which, for large interatomic separations, are exponentially small compared with the spacings of the eigenvalues. For the demonstration we need a generalization of the energy-bounding inequality (11). As (11) is written, the energy interval in the denominator could, in some cases, be of the order of the level splitting we are seeking, which goes to zero at large separations. However, Kato²⁶ has given a generalization of (11) for sets of eigenvalues, which contains in the denominator only an interval to the nearest eigenvalue not of the set being approximated. Specifically, if the functions ψ_s ($s = 1$ to ν) are the orthonormal linear combinations of any ν approximating functions which diagonalize the Hamiltonian in the subspace spanned by them, then the error δE_s in the s th eigenvalue obeys²⁸

$$|\delta E_s| \equiv |E_s - \bar{E}_s| \leq \max_t (\Psi_t | (H - \bar{E}_t)^2 | \Psi_t) / |\Delta E_{\min}|, \quad (30)$$

where \bar{E}_s is the mean energy of ψ_s and $|\Delta E_{\min}|$ is the minimum energy interval from any of the \bar{E}_s to any eigenvalue other than the set being approximated.

In the application of (30) to our problem it is convenient to write

$$\bar{E}_t = E_\chi + (\bar{E}_t - E_\chi), \quad (31)$$

where E_χ is the eigenvalue of the χ_k in the potential V' . Since $(H - E_\chi) \chi_k$ vanishes outside the Σ_P for $P \neq 1$, the evaluation of the numerator of (30) reduces to the evaluation of the following types of terms, in which $\sum_{\text{all } s}$ means a spin scalar product and the integration is over all electronic coordinates inside Σ_P :

$$\sum_{\text{all } s} \int_{\Sigma_P \neq 1} \prod dr | (H - E_\chi) \chi_k |^2 \quad (32)$$

$$(\bar{E}_t - E_\chi) \sum_{\text{all } s} \int_{\Sigma_P \neq 1} \prod dr \chi_k^* (H - E_\chi) \chi_k \quad (33)$$

$$(\bar{E}_t - E_\chi)^2, \quad (34)$$

²⁸ The relation (30) differs slightly from the form given by Kato (reference 26), which has a summation on t instead of a maximum. However, (30) is easily derived from Kato's Eq. (22). Either form of the inequality will suffice for our purposes, but (30) makes the analogy with the nondegenerate case closer.

plus terms differing from (32) or (33) by replacement of one of the χ_k 's in the integrand by a permuted function $Q\chi_k$ ($Q \neq P$), and terms differing from (34) by multiplication by an overlap integral of χ_k and $Q\chi_k$. Terms with $k' \neq k$ do not enter because of the spin orthogonality of χ_k and $\chi_{k'}$.

To establish the smallness of (32) and (33) we need only the intuitively obvious fact that χ_k decays exponentially with increasing distance from the original center, once one is outside the surface Σ_1 . Inside Σ_P , for $P \neq 1$, at least two electrons have to be within a distance L of some nucleus other than the ones with which they were associated in the original center. We therefore expect that inside any such Σ_P ,

$$|\chi_k| \leq \Lambda \exp [- 2\alpha(R_{\min} - L)], \quad (35)$$

where the coefficient Λ is, at most, algebraic in the separations R_{ij} . Here R_{\min} is the least of the interatomic distances, L is the length defined in (26), which remains finite as the interatomic spacings become infinite, and

$$\alpha = (2m\eta\epsilon_t/\hbar^2)^{1/2} \quad (36)$$

is related to (27) and approximates one of the α_t defined in (5). For the case of H_2^+ the analogous inequality (15), though stated in Sec. 2B without proof, can be proved easily,²⁹ from the fact that V' is well in excess of E_χ once one is well away from nucleus a . A rigorous proof of (35) is, in general, more difficult, since for the many-electron case there are paths in configuration space from Σ_1 to Σ_P along which V' is $-\infty$, i.e., for which one or more of the electrons not being exchanged remains very close to its nucleus. However, this should not vitiate (35) because in the neighborhood of such paths one expects χ_k to approximate a ground-state eigenfunction for the electrons not being exchanged, times a coefficient which is an exponentially decreasing function of the coordinates of the exchanging electrons. Appendix II gives a rigorous argument which, if combined with reasonable assumptions about the boundedness of certain momentum distributions, implies (35).

Accepting (35), then, we see that (32), (33), and their modifications involving a $Q\chi_k$ obey

$$(32), (33), \text{ and their } Q \text{ modifications} \leq \Lambda' \exp (-4\alpha R_{\min}), \quad (37)$$

²⁹ I am indebted to Dr. J. McKenna for the details of a rigorous proof, which will not be given here for lack of space and because of its similarity to the more general (though less satisfactory) arguments of Appendix II.

where Λ' , like the Λ of (35) is, at most, algebraic in the separations R_{ij} . As for the quantities (34), it is easy to show that

$$|\bar{E}_i - E_x| \leq \Lambda'' \exp(-2\alpha R_{\min}), \quad (38)$$

where Λ'' is again, at most, algebraic in the R_{ij} , hence that (34) and its Q modification also obey (37). For, as we shall see explicitly in Sec. 2F below, the solutions \bar{E} of the secular equation (29) must differ from the dominant term $(\chi_k|H|\chi_k)$ of the diagonal elements by quantities of the order of the $(\chi'_k|H|P\chi_k)$, where P is some permutation exchanging at least two electrons on different atoms. The latter quantities involve the small overlap of χ'_k and $P\chi_k$, which contain factors $\lesssim \exp(-2\alpha R_{\min})$. Thus we conclude, finally, that the upper limits (30) to the departures of the roots of (29) from the corresponding true eigenvalues are bounded by quantities of the order (37). Since (37) is asymptotically \ll (38), we have proved the asymptotic exactness of the solutions of (29) at large separations.

F. The Spin Hamiltonian

Having thus described a method for the construction of an asymptotically exact solution to the coupled-atom problem, we shall now undertake to show that this method is equivalent to the use of a spin Hamiltonian of the form (2), to within the accuracy of the original approximation. The argument is really identical with that for the ordinary Heitler-London approximation (3). However, despite the extensive literature using the latter approximation, no completely general derivation of (2) from (3) seems to have been given; all papers make special assumptions, e.g., one electron per atom, no doubly filled orbitals, determinantal wave functions with nearest-neighbor exchange integrals the same for all pairs of orbits, etc. We shall therefore give a general argument *ab initio*, assuming only that H does not contain spin variables and that the separated atoms have no orbital degeneracy. (The latter assumption can be dispensed with,⁷ but the complications which this entails will not be discussed here.)

Consider the matrix elements in the secular equation (29), after inserting the explicit expression (4) for the antisymmetrizer A . The general term is

$$(\chi_{k'}|H - \bar{E}|P\chi_k). \quad (39)$$

Now the functions χ_k are localized near the original center in the $3n$ -dimensional configuration space, while the $P\chi_k$ are localized near the P th center. If P belongs to the subgroup G_0 of permutations which never mix electrons associated with different nuclei

in the original center of configuration space, the P th center and the original center will be the same, and (39) can be large. For all other cases (39) will be small, approaching zero as the interatomic separations become large. As in (35), it is intuitively obvious (and proved mathematically in Appendix II under the momentum-boundedness proviso described there) that the overlap of $\chi_{k'}$ and $P\chi_k$ contains a factor at least as small as

$$\exp[-\alpha \sum_{\lambda} |R_{\lambda}^1 - R_{\lambda}^2|], \quad (40)$$

where α is given by (36), or roughly by (5), the summation is over all electrons, and, as in (26), R_{λ}^p is the position of the nucleus with which electron λ is associated in the P th center. The other factors in the overlap are at most algebraic in the separations. If R_{λ}^p differs from R_{λ}^1 for only two electrons λ , i.e., if P transfers only one pair of electrons to new atoms, (40) has the value $\exp(-2\alpha R_{ij})$, where i and j are the two nuclei in question. The maximum value of this, for near neighbors, is

$$\text{max pair-transfer term} \sim \exp(-2\alpha R_{\min}). \quad (41)$$

[This maximum will be attained for off-diagonal matrix elements of the form (39) if there exists a pair of non-singlet atoms with separation R_{\min} , at least one of which possesses the minimum ionization energy ϵ_i used in the definition (36) of α . While there are important cases for which this condition is not met,⁷ we shall not complicate the present discussion by considering them.] If P is a higher-order permutation, i.e., transfers more than two electrons to new atoms, then the contribution to (39) is of order

$$\text{higher-order terms} \lesssim \exp(-3\alpha R_{\min}), \quad (42)$$

hence negligible, at large separations, compared with (41). [Actually, it can be shown^{7,30} that all terms of this order can still be described by a spin Hamiltonian of the form (2).]

Having thus shown that for large separations we need consider only those terms (39) which correspond to transfer of at most one pair of electrons between closely neighboring atoms, let us now consider how these terms can be simplified. The no-transfer terms are of course very simple: If Q is an element of the group G_0 which permutes only electrons associated with the same nucleus in the original center, then, because of the antisymmetry and spinorthogonality of the χ_k ,

$$\begin{aligned} \text{no-transfer terms} &= (n!)^{-1} \sum_{Q \in G_0} (\chi_{k'}|H - \bar{E}|\delta_Q Q\chi_k) \\ &= [\prod_i (n_i!)/n!] (\bar{E}_x - \bar{E}) \delta_{kk'}, \end{aligned} \quad (43)$$

³⁰ H. A. Kramers, *Physica* 1, 182 (1934).

where \bar{E}_χ is the mean energy of any of the χ_k . For the pair-transfer terms, we note that the most general P which transfers just one pair of electrons between atoms i and j can be written in the form

$$P = QP_{ij}Q', \quad (44)$$

where Q and Q' are elements of G_0 , and P_{ij} is the simple interchange of the first electron of atom i with the first electron of atom j . The number of distinct P 's obtained by letting Q and Q' run independently over G_0 is

$$\text{No. } (ij) \text{ transfer permutations} = n_i n_j \prod_k (n_k!) . \quad (45)$$

Thus, the pair-transfer terms of the general element of (29) are

$$\begin{aligned} & \text{pair-transfer terms} \\ &= - \sum_{i>j} \frac{n_i n_j \prod_i (n_i!)}{n!} (\chi_k | H - \bar{E} | P_{ij} \chi_k) . \end{aligned} \quad (46)$$

The next step is to express P_{ij} in terms of spin operators. If we designate the two electrons which P_{ij} interchanges as 1, 2, we have the familiar relation³¹

$$P_{ij} \equiv P(1,2) = P_{ij}^{(\tau)} \left(\frac{1}{2} + 2\mathbf{s}_1 \cdot \mathbf{s}_2 \right), \quad (47)$$

where $P_{ij}^{(\tau)} \equiv P^{(\tau)}(1,2)$ interchanges coordinates only. But (47) contains only the spins of individual electrons, and to derive (2) we must get into the picture the total spin vectors \mathbf{S}_i of the atoms, i.e., of the sets of electrons associated with nucleus i and nucleus j in the original center. If the atoms have no doubly filled orbits, so that their wave functions are spin symmetric, replacement of $\mathbf{s}_1, \mathbf{s}_2$, in (47) in terms of $\mathbf{S}_i, \mathbf{S}_j$, is quite easy. For the general case a slightly longer argument is necessary, which we shall now sketch.

We have noted at the end of Sec. 2D, and proved in Appendix I, that the χ_k have the same permuta-

tional and spin-rotation symmetries as products of single-atom wave functions. Therefore, χ_k has the form³²

$$\begin{aligned} \chi_k = & (M_i M_j)^{-1/2} \sum_{\xi=1}^{M_i} \sum_{\zeta=1}^{M_j} \varphi_{\xi\zeta}(\mathbf{r}'\mathbf{s}, \text{ other spins and } k_i'\mathbf{s}) \\ & \times \Theta_{k_i\xi}(s_1, \dots) \Theta_{k_j\zeta}(s_2, \dots), \end{aligned} \quad (48)$$

where s_1, \dots are the n_i spin variables of the electrons associated in the original center with nucleus i , and the orthonormal spin functions $\Theta_{k_i\xi}$ are transformed irreducibly into combinations of the $\Theta_{k_i\xi'}$ by spin permutations and into combinations of the $\Theta_{k_i\xi}$ by spin rotations; similar statements hold for the n_j spin variables s_2, \dots and the $\Theta_{k_j\zeta}$. If D_i is the M_i -dimensional irreducible representation of the spin permutation group of i to which the $\Theta_{k_i\xi}$ belong, the $\varphi_{\xi\zeta}$ for different ξ will be transformed irreducibly among themselves by the corresponding coordinate permutations, according to the associated representation \bar{D}^* ; \bar{D} differs from D in having the signs of the matrices of odd permutations reversed.

The major step in our argument is now to use the Wigner-Eckart theorem³³ that the matrix of a vector operator connecting two subspaces each irreducible under spin rotations equals the matrix of the total spin vector times a constant, dependent on the subspaces in question; the constant is nonzero only if the representations of the spin-rotation group in the two subspaces are equivalent. Thus, in the space of the spin functions $\Theta_{k_i\xi}$, we have, using angular brackets to designate spin scalar products,

$$\langle k_i'\xi' | \mathbf{S}_i | k_i\xi \rangle = f_{\xi'\xi}^{(i)} \langle k_i'\xi' | \mathbf{S}_i | k_i\xi \rangle, \quad (49)$$

where the coefficients $f_{\xi'\xi}^{(i)}$ are determined by the symmetry properties of the atomic spin functions $\Theta_{k_i\xi}$. The last factor in (49) is independent of ξ , and will be written henceforth simply $\langle k_i' | \mathbf{S}_i | k_i \rangle$. The $f_{\xi'\xi}^{(i)}$ obey

$$f_{\xi\xi}^{(i)} = f_{\xi\xi}^{(i)*}, \quad \sum_{\xi} f_{\xi\xi}^{(i)} = M_i/n_i. \quad (50)$$

Using (49) and (50) and the corresponding equations for atom j in (46) and (47), we get for the pair-transfer contribution to the general element of the secular equation (29)

$$\begin{aligned} & \text{pair-transfer terms} = -n_i n_j \frac{\prod_i (n_i!)}{n!} \\ & \times \sum_{i>j} \left[\frac{1}{2} (\chi_k | H - \bar{E} | P_{ij}^{(\tau)} \chi_k) \delta_{kk'} + 2(M_i M_j)^{-1} \sum_{\xi, \xi'=1}^{M_i} \sum_{\zeta, \zeta'=1}^{M_j} f_{\xi'\xi}^{(i)} f_{\zeta'\zeta}^{(j)} \int \prod dr \varphi_{\xi\zeta}^{(ij)*} (H - \bar{E}) P_{ij}^{(\tau)} \varphi_{\xi'\zeta'}^{(ij)} \langle k_i' | \mathbf{S}_i \cdot \mathbf{S}_j | k_i \rangle \right] \end{aligned} \quad (51)$$

³¹ P. A. M. Dirac, *The Principles of Quantum Mechanics* (Clarendon Press, Oxford, 1930); Proc. Roy. Soc. (London), **A123**, 714 (1929).

³² E. Wigner, *Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atom spektren* (Friedrich Vieweg & Sohn, Braunschweig, 1931); *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra*, translated by J. J. Griffin (Academic Press Inc., New York, 1959), Chap. 22.

³³ Reference 32, Chap. 21. For a very concise proof see, B. L. Van der Waerden, *Die gruppentheoretische Methode in der Quantenmechanik*, (Springer-Verlag, Berlin, 1932), Sec. 19. For a proof not presupposing a familiarity with group theory see, E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (The Macmillan Company, New York, 1935), Chap. 3, Sec. 8.

where $\varphi_{\xi\xi}^{ij}$ is the $\varphi_{\xi\xi}$ of (48), considered as a function of coordinates only, for any arbitrary k_i and any single set of spin variables of the atoms other than i, j , for which it does not vanish, and renormalized to unity. The first term of (51) can be neglected, to the order to which we are working, since it is $(\bar{E}_x - E_x)$ times an overlap integral, and each factor is of the order of (38) or (41). Thus, combining (51) with (43), we can write the secular equation (29) in terms of matrix elements in spin space only:

$$\det \left[-2 \sum_{i>j} J_{ij} \langle k' | \mathbf{S}_i \cdot \mathbf{S}_j | k \rangle + (\bar{E}_x - \bar{E}) \delta_{kk'} + \text{higher-order terms} \right] = 0, \quad (52)$$

where the "higher-order terms" contain factors at least as small as (42). Here the exchange constant J_{ij} is given by

$$J_{ij} = n_i n_j (M_i M_j)^{-1} \sum_{\xi', \xi=1}^{M_i} \sum_{\zeta', \zeta=1}^{M_j} f_{\xi'\xi}^{(i)} f_{\zeta'\zeta}^{(j)} \int \prod dr \varphi_{\xi'\zeta'}^{(ij)*} \times (H - \bar{E}_x) P_{ij}^{(r)} \varphi_{\xi\xi}^{(ij)}. \quad (53)$$

This completes the justification of (2).

3. ADVANTAGES OF EXPRESSING J_{ij} AS A SURFACE INTEGRAL

A. The Surface-Integral Transformation

In Sec. 2C we found that the $\Sigma_u - \Sigma_g$ separation for H_2^+ could be conveniently expressed by a surface integral (18), an expression which was especially appealing because it embodied the notion that this energy splitting represents a tunneling frequency from the one atom to the other. We shall show here that an exactly similar formulation is possible for the spin coupling problem.

Define Σ_{ij}^* to be the $(3n - 1)$ -dimensional hyperplane in coordinate space consisting of all points equidistant from the original center and the P_{ij} th center. In the expression (53) for J_{ij} , we may replace \bar{E}_x by the eigenvalue E_x of the χ_k in the potential V' defined in Sec. 2D; this alters J_{ij} only by an amount comparable with the neglected "higher-order terms" of (52). Since the $\varphi_{\xi\xi}^{(ij)}$, like the χ_k , are eigenfunctions in the potential V' with eigenvalue E_x , the integrand in (53) vanishes on the side of Σ_{ij}^* on which the P_{ij} th center lies. The integral may therefore be extended only over the half-space on the side of the original center. Integrating by parts as in the derivation of (18), we obtain a vanishing volume integral

and a surface integral whose two terms turn out to be equal. Thus, finally,

$$J_{ij} = \frac{\hbar^2}{m} n_i n_j (M_i M_j)^{-1} \mathcal{R} \times \sum_{\xi', \xi=1}^{M_i} \sum_{\zeta', \zeta=1}^{M_j} f_{\xi'\xi}^{(i)} f_{\zeta'\zeta}^{(j)} \int_{\Sigma_{ij}^*} d\mathbf{S} \cdot (P_{ij}^{(r)} \varphi_{\xi\xi}^{(ij)}) \nabla_n \varphi_{\xi'\zeta'}^{(ij)*}, \quad (54)$$

where the n vector $d\mathbf{S}$ is the normal to the hyperplane Σ_{ij}^* , directed away from the original center.

Since $\varphi_{\xi\xi}^{(ij)}$ decreases exponentially as we go away from the original center, it is clear that the predominant contribution to (54) comes from regions of Σ_{ij}^* close to that point of Σ_{ij}^* , often near the midpoint between the original and P_{ij} th centers, at which $\varphi_{\xi\xi}^{(ij)}$ is largest. (It may happen that $\varphi_{\xi\xi}^{(ij)}$ is small or zero exactly at this midpoint, but we cannot go very far away from it without the integrand becoming exponentially small.) Thus, (54) accords nicely with the physical picture of tunneling via the easiest path in configuration space.

Note that, in perfect analogy to our finding in connection with (24), it is not possible to express the J_{ij} given by the Heitler-London approximation in the form of a surface integral like (54).

B. The Question of Additivity

The Heitler-London model possesses a property which it would be nice to verify for the present, asymptotically exact, model. This is the property that, for large separations, the exchange coupling constant J_{ij} between any two atoms of the array is a function of the relative positions of these two atoms, independent of the presence of the other atoms.

In the Heitler-London approximation this follows from the expression of J_{ij} as an overlap matrix element similar to (53). Coordinates of electrons located on atoms other than i and j can be integrated out, the result being merely to replace H , the N atom Hamiltonian, by \bar{H}_{ij} , a two-atom Hamiltonian formed by averaging over the wave functions of the other atoms. If the other atoms are neutral, \bar{H}_{ij} will differ only by exponentially small quantities from the Hamiltonian of the two atoms i, j . If some of the other atoms are ionized, however, the reasoning breaks down.

For the present model the elimination of the coordinates of electrons belonging to atoms other than i and j is less automatic, since the $\varphi_{\xi\xi}^{(ij)}$ are not product functions. However, we can make good use of the fact, already noted, that the surface integral (54) is dominated by the contribution from points of

Σ_{ij}^* not too far from one or more "peaking points." Since on Σ_{ij}^* one or both of the electrons 1, 2 being exchanged is far from its nucleus, all the electrons of other atoms must be close to their respective nuclei as long as we stay close enough to the peaking point for the integrand to be appreciable. Thus, the functions $\varphi_{\xi\xi}^{(ij)}$ can be well approximated, near the peaking point, by products of two-atom $\varphi_{\xi\xi}^{(ij)}$'s and isolated-atom functions for the remaining atoms. However, we may expect the departures from this approximate form, due to van der Waals type interactions with the other atoms, to decrease only algebraically with increasing interatomic separations.

Thus, we conclude that, for neutral atoms, the asymptotically exact J_{ij} for an N -atom array, computed from (53) or (54), coincides with the corresponding value for a two-atom problem to within a fractional error which is only algebraically small as the R_{ij} increase, not exponentially small as in the Heitler-London approximation.

C. Sign of the Exchange Constant

A particularly useful application of the surface-integral expression (54) is to the problem of the sign of the exchange constant J_{ij} . Common sense, augmented by the mathematical analysis of Appendix II, tells us that the functions $\varphi_{\xi\xi}^{(ij)}$, which are eigenfunctions of the potential V' described in Sec. 2D, must be decreasing exponentially as we cross the surface Σ_{ij}^* going away from the original center. Therefore $d\mathbf{S} \cdot \nabla_n \varphi_{\xi\xi}^{(ij)}$ must, at each point of Σ_{ij}^* , have a sign opposite to $\varphi_{\xi\xi}^{(ij)}$. Therefore, if $M_i = M_j = 1$ (all spins of each atom parallel), and if $\varphi_{\xi\xi}^{(ij)}$ has the same sign at all points of Σ_{ij}^* reasonably close to the peaking point, J_{ij} must be negative, i.e., antiferromagnetic.

A negative J_{ij} must also occur if $M_i = M_j = 1$ and if P_{ij} takes each point of Σ_{ij}^* into itself, as is the case for a pair of atoms (with any number of electrons) in one dimension. This conclusion supplements that of Lieb and Mattis.¹⁴ These authors proved that for any one-dimensional n -electron system the lowest state of total spin S lies below the lowest state of total spin $S + 1$, etc. Their result is more general than ours, in not being restricted to almost-separated atoms, while ours goes beyond theirs in applying to levels derived from maximum-multiplicity excited states of the atoms.

Our result is also more general than that of Lieb and Mattis in being applicable to systems in three dimensions with nonseparable potentials. Our conclusion for such real atomic systems is that for atoms with all spins aligned a positive (ferromagnetic) J_i ,

is possible, in the limit of large separations, only if $\varphi_{\xi\xi}^{(ij)}$ can assume opposite signs at points \mathbf{r} and $P_r^{(ij)} \mathbf{r}$ both in close proximity to peaking points of Σ_{ij}^* . This requires that there be angular nodes in the wave functions; more specifically, there must be angular nodes in the tail of at least one of the atomic wave functions considered as a function of the coordinates of one electron, when this electron is far from the nucleus. Although the presence of filled inner shells spoils the vigor of the foregoing argument by making $M_i > 1$ and allowing some of the eigenvalues of $f_{\xi\xi}^{(i)}$ to be < 0 , it is probable that the conclusion holds for Hund's-rule atoms in general. Thus, antiferromagnetic J_{ij} 's should be the rule, ferromagnetic J_{ij} 's the exception.

4. DISCUSSION AND CONCLUSIONS

In this section we recapitulate what has been assumed and what has been proved so far, and then add a few remarks about possible extensions and applications.

We have assumed an array of N atoms, without orbital degeneracy and with no spin-dependent terms in the Hamiltonian. Nothing has been assumed about the internal wave functions of the atoms, which are, in general, of a many-electron type with correlations. Nor have we assumed the atoms to be spherically symmetrical: The word "atom" could everywhere be interpreted to mean "molecule." We have assumed that some, at least, of the atoms have nonzero spins, and have undertaken to find an effective Hamiltonian which will suffice to calculate the energy splittings arising from the coupling of these spins, to within errors which will be exponentially small compared with the splittings as the interatomic separations are allowed to become infinite. Our procedure has involved neglecting quantities of the order of (37), where R_{\min} is the minimum interatomic separation and α is related to the minimum ionization potential of the atoms by (36). Since the lowest-order terms in the energy splittings being sought are of the order of (41) with R_{\min} interpreted as a minimum distance between non-singlet atoms and α related to the lesser of the ionization potentials of these atoms, the terms we neglect are negligible only if the latter type of αR_{\min} is not too large compared with the former. If this condition fails to be fulfilled, something like the theory of superexchange must be used.^{7,9} Implicit, too, in our neglect of quantities of the order of (37), is that the interatomic separations be large enough to make these negligible even when multiplied by numbers like N , the number of atoms. While it is not to be expected that the

coupling in large arrays will be physically different from that in small arrays, the mathematical rigor of our approach would be spoiled if N were allowed to become infinite. The mathematical difficulties in applying the Heitler-London method to very large systems have, in fact, been the object of considerable discussion in the literature.^{7,15}

Having made these assumptions, we have shown: (i) To within neglect of terms of the order of (37) [or (42), unless supplemental arguments are used to show that these vanish], the term structure of the system is the same as that of the eigenvalues of a spin Hamiltonian of the form (2). In this spin Hamiltonian only those neighboring pairs i, j , of atoms need be included whose exchange constants J_{ij} [of the order of (41) with α and R appropriate to the pair, i, j] contain exponential factors of larger order than that occurring in the neglected quantities (37).

(ii) If all atoms are neutral, the exchange constants J_{ij} appropriate to a given array of atoms differ from those for corresponding isolated pairs i, j , by fractional amounts which go to zero at infinite interatomic separations as an inverse power of the latter. This behavior differs from that of the Heitler-London approximation, where the fractional departure from additivity is exponentially small.

(iii) The exchange constants J_{ij} can be expressed as surface integrals, of the form (54), over a hyperplane in configuration space separating the original assignment of electrons to atoms from the exchanged assignment. The wave functions $\varphi_{\xi\xi}^{(ij)}$ entering into this expression are solutions of the wave equation in the fictitious potential V' defined by (28), which reduce the group of coordinate permutations on each atom. The principal contribution to the surface integral comes from regions not too far from a "peaking point," and corresponds to the physical notion of barrier penetration by tunneling.

(iv) For atoms with all spins parallel, and probably for all Hund's-rule atoms, the exchange constant J_{ij} can be positive (ferromagnetic) only if the tail of at least one of the atomic wave functions has angular nodes.

The analysis leading to these conclusions was based on the properties of the χ_k or $\varphi_{\xi\xi}^{(ij)}$, which are eigenfunctions of the potential V' defined by (28). These were shown in Sec. 3E to be adequate approximations to the functions Φ_k defined in Sec. 3A, in terms of which the true eigenfunctions can be exactly expressed. Actually, all the analysis of Secs. 3F and 3G could have been carried through with Φ_k replacing χ_k , provided one were willing to assume that the Φ_k possess exponentially decaying tails leading to prop-

erties like (35), (40), etc. If one were willing to make such an assumption, one could formally evaluate successively higher-order approximations to an effective Hamiltonian, leading to terms in four, six, etc. atomic \mathbf{S}_i vectors. However, a rigorous proof that such terms have successively smaller orders of magnitude seems hard to construct by our approach.

The assumption of no orbital degeneracy can easily be dispensed with, at the cost of a little complication of the formalism, provided the assumption that H contains no spin variables is retained.⁷ In practice, of course, spin-orbit coupling will always exceed the interatomic spin couplings at large enough separations.

It does not seem beyond the range of possibility to compute an asymptotically exact exchange-coupling constant J for, say, the hydrogen molecule; perhaps by an extension of Holstein's method for H_2^+ . This remains a problem for the future.

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APPENDIX I

Rotational and Permutational Symmetry of χ_k

We have defined the χ_k in Sec. 2D as eigenfunctions in the potential V' defined by (28). This potential is invariant under the subgroup G_0 of the permutation group, consisting of all permutations of the first n_1 electrons among themselves, of the next n_2 among themselves, etc. Accordingly, it must be possible to express any χ_k in terms of coordinate functions which reduce the corresponding group $G_0^{(i)}$ of coordinate permutations. Let such functions be designated $\varphi(\xi_1, \dots, \xi_N; \mathbf{r}'s)$, where for any $P_i^{(r)}$ permuting the i th group of coordinates only (i.e., permuting "electrons of the i th atom"),

$$P_i^{(r)} \varphi(\dots \xi_i \dots; \mathbf{r}'s) = \sum_{\xi'_i} D_{\xi'_i \xi_i}^{(i)}(P_i) \varphi(\dots \xi'_i \dots; \mathbf{r}'s), \quad (\text{A1})$$

the coefficients $D_{\xi'_i \xi_i}^{(i)}(P_i)$ being matrices of an irreducible representation of the permutation group of n_i objects. Thus,

$$\chi_k = \sum_{\xi' s} \Theta_k(\xi_1, \dots, \xi_N; s_1, \dots, s_N) \varphi(\xi_1, \dots, \xi_N; \mathbf{r}'s). \quad (\text{A2})$$

Now we have required each χ_k to be antisymmetric when the operations of G_0 are applied to coordinates and spins together. Therefore, the functions Θ_k in

(A2) must transform under the group $G_0^{(s)}$ of spin permutations, according to the complex conjugate of a representation differing from that to which the $\varphi(\xi$'s; \mathbf{r} 's) belong simply in having signs of the matrices of odd permutations reversed.³² Since the group G_0 is the direct product of the "single-atom" groups G_i (consisting of the P_i defined above), the matrices of its irreducible representations are simply products of the $D_{\xi_i \xi_i}^{(s)}(P_i)$. Therefore, permutations $P_i^{(s)}$ of the i th group of spins must transform the Θ_k according to

$$P_i^{(s)} \Theta_k(\dots \xi_i \dots; s_1, \dots s_n) = \sum_{\xi'_i} \delta_{P_i} \overline{D_{\xi'_i \xi_i}^{(s)}}^*(P_i) \Theta_k(\dots \xi'_i \dots, s_1, \dots s_n). \quad (A3)$$

Out of all the 2^n possible spin functions for n electrons, all those, and only those, can occur in the Θ_k which belong to the irreducible representations $\overline{D}^{(s)}$ of the subgroup G_i , where $\overline{D}^{(s)}$ is defined by the matrix occurring in (A3). Continuity requires that for the set of ν states of interest to us, the $\overline{D}^{(s)}$ be the same as for isolated atoms. It is known³⁴ that among all possible functions of the i th group of spins the representation $\overline{D}^{(s)}$ occurs $(2S_i + 1)$ times, and that corresponding basis functions of these different equivalent representations are transformed into one another by rotations of the i th group of spins according to the irreducible representation $\Delta^{(s)}$ going with total spin quantum number S_i . Therefore, the set of allowable functions Θ_k must transform according to $\Delta^{(s)}$ under rotations of the i th group of spins; they can thus be chosen as eigenfunctions of S_i^2, S_{iz} , where

$$\mathbf{S}_1 = \sum_{\lambda=1}^{n_1} \mathbf{s}_\lambda, \quad \mathbf{S}_2 = \sum_{\lambda=n_1+1}^{n_1+n_2} \mathbf{s}_\lambda, \text{ etc.} \quad (A4)$$

It is obvious, and not hard to demonstrate explicitly, that identical statements hold for the functions Φ_k defined in Sec. 2A.

APPENDIX II

Exponential Decay of χ_k at Large Distances from the Original Center

Consider any function $\chi(x, y)$ of two sets of variables $x_1, \dots x_p$ and $y_1, \dots y_q$, obeying a wave equation

$$[-\nabla_x^2 - \nabla_y^2 + V'(x, y) - E]\chi = 0, \quad (A5)$$

where ∇_x^2, ∇_y^2 are the p - and q -dimensional Laplacian operators in x - and y -space, respectively, and where the boundary condition is to be the usual one of vanishing at infinity, E being thus an eigenvalue of a bound state. Suppose that for each y outside of some

surface Σ_y in y -space the lowest eigenvalue of the operator

$$H_x(y) \equiv -\nabla_x^2 + V' \quad (A6)$$

is $\epsilon(y)$, so that

$$\int \chi^* H_x(y) \chi d^p x \geq \epsilon(y) \int |\chi|^2 d^p x. \quad (A7)$$

Define

$$I(y) = \int |\chi|^2 d^p x. \quad (A8)$$

Then

$$\begin{aligned} \nabla_y^2 I &= \int \chi^* \nabla_y^2 \chi d^p x + \text{c.c.} + 2 \int |\nabla_y \chi|^2 d^p x \\ &\geq 2[\epsilon(y) - E]I + 2 \int |\nabla_y \chi|^2 d^p x. \end{aligned} \quad (A9)$$

Also,

$$\nabla_y I = \int \chi^* \nabla_y \chi d^p x + \text{c.c.}$$

$$|\nabla_y I|^2 \leq 4 \left| \int \chi^* \nabla_y \chi d^p x \right|^2 \leq 4I \int |\nabla_y \chi|^2 d^p x \quad (A10)$$

by Schwarz's inequality. From (A9) and (A10),

$$\nabla_y^2 I - (1/2I)|\nabla_y I|^2 \geq 2[\epsilon(y) - E]I^{1/2}$$

or

$$\nabla_y^2 I^{1/2} \geq [\epsilon(y) - E]I^{1/2} \quad (A11)$$

Now suppose that for all points of y -space outside the surface Σ_y we have

$$\epsilon(y) - E > \beta^2. \quad (A12)$$

Let $g_\beta(y, y')$ be the q -dimensional Green's function obeying

$$-\nabla_y^2 g_\beta + \beta^2 g_\beta = \delta(y - y') \quad (A13)$$

with the boundary condition of vanishing at infinity. It is a Hankel function with the properties³⁵

$$g_\beta > 0 \text{ everywhere,} \quad (A14)$$

$$g_\beta = \Omega(|y - y'|)e^{-\beta|y - y'|}, \quad (A15)$$

where Ω is a rational algebraic function. We have

$$\begin{aligned} I^{1/2}(y') &= \int_{\text{outside } \Sigma_y} g_\beta(y - y') [-\nabla_y^2 I^{1/2}(y) \\ &\quad + \beta^2 I^{1/2}(y)] dy \\ &\quad + \int_{\Sigma_y} d\mathbf{S} \cdot [g_\beta(y - y') \nabla_y I^{1/2}(y) \\ &\quad - I^{1/2}(y) \nabla_y g_\beta(y - y')], \end{aligned} \quad (A16)$$

³⁵ G. N. Watson, *Treatise on the Theory of Bessel Functions* (The Macmillan Company, New York, 1948), 2nd ed., Secs. 3.4, 3.6, and 3.71.

³⁴ Reference 32, Chap. 13.

where $d\mathbf{S}$ is along the outward normal to Σ_ν . By (A11) and (A12), the volume integral in (A16) is < 0 , so finally

$$I^{1/2}(y) < \Omega' e^{-\beta|y-y_0|}, \tag{A17}$$

where Ω' is algebraic and y_0 is the nearest point of Σ_ν to the point y .

We wish to apply this theorem to the bounding of the χ_k of Sec. 2D inside the surfaces $\Sigma_P, P \neq 1$. Draw a straight line in configuration space from a point of Σ_1 to a point of Σ_P , and let these points be so chosen as to minimize the distance between them. Let y be the coordinate in the direction of this line, x_1, \dots, x_{n-1} the coordinates in all orthogonal directions. For most values of y , the hyperplane $y = \text{constant}$ will not pass near any point corresponding to a negative-ion configuration, and (A12) will be valid with [cf. (36)]

$$\beta^2 = (2m/\hbar^2)\eta\epsilon_I, \tag{A18}$$

where ϵ_I is the least of the atomic ionization energies and $\eta \approx 1$ is a factor by which ϵ_I must be reduced if the electron being removed is removed only to a distance L from its atom. For y values for which the hyperplane $y = \text{constant}$ passes close to a negative-ion configuration, ϵ_I in (18) should be replaced by ϵ_I

minus an electron affinity. However, there will be only finite ranges of y for which this occurs, and since the right of (A17) must contain $I^{1/2}(y_0)$ as a factor, we can apply (A17) consecutively to the large ranges of y values for which (A18) holds as written and the small ranges for which it must be modified. The result will be that (A17) holds everywhere outside Σ_1 , the only effect of the negative-ion configurations being to increase the coefficient Ω' .

Unfortunately, the bounding of I , defined by (A8), is not enough for our needs, since in our use of (35) and (40) we have to multiply values of χ_k inside Σ_P by a potential-energy perturbation which may become locally infinite. We expect, of course, that the maximum of χ_k on the x variables will obey a relation of the form (A17). This will be the case unless this maximum becomes more and more sharply peaked in x as y increases. This would mean that the x -momentum distribution would have to spread to ever larger momentum values. In mathematical terms, if $f(p,y)$ is the Fourier transform of χ_k on the x variables,

$$\int f(p,y) d^{3n-1}p / \left[\int |f(p,y)|^2 d^{3n-1}p \right]^{1/2}$$

would have to increase without limit. This seems physically unlikely.

Dynamics of Band Electrons in Electric and Magnetic Fields

GREGORY H. WANNIER
*University of Oregon, Eugene, Oregon**

INTRODUCTION

THE following lines are a tribute to my teacher, Eugene Wigner, who introduced me to the subject of solid state physics.

The present communication reaches rather directly across a quarter century into the time when I was the Benjamin among his solid-state physics students at Princeton University. He first suggested to me that there ought to be a way to reconcile the local and the band concept for electrons, and that such a reconciliation would probably be useful in

understanding the spectra of insulators. The result of this suggestion was a paper on the electronic excitation levels in insulators.¹

When I did that work I felt that it had rather wide implications. Unfortunately, the trend of the times, and perhaps also my own negligence in clarifying the ideas sketched in the article (I had been taught in Switzerland that the cardinal sin of a physicist is to restate the obvious, a tenet to which I now no longer subscribe) left the duality of energy band and lattice cell in a haze from which it was not to emerge for some time.

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¹ Gregory H. Wannier, Phys. Rev. 52, 153 (1937).