Non-Orthogonal Wave Functions and Ferromagnetism

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Close consideration of the influence of non-orthogonality of the electronic wave functions in a crystal shows that because of the large number of terms arising from the possible permutations of electrons, the usual procedure involving the neglect of most of the terms arising from this lack of orthogonality may be seriously in error. The dependence of the relative energies of the states of low and high multiplicity on this factor is discussed and exemplified in the cases of some simple molecular models.

INTRODUCTION

A LL treatments¹ of the problem of the existence of ferromagnetism from the atomic point of view have been guilty of the convenient but otherwise unjustified neglect of the lack of orthogonality of the electronic wave functions of two neighboring atoms in a crystal. The terms in question are negligible in the limit of extreme dilation. Though suggestive, it is not entirely satisfactory to explain only the weak ferromagnetism of an ideally distended crystal (and no more has been done), because ferromagnetism does not exist in the opposite extreme of high concentration,² due to the electrons' zero-point energy.

It is here suggested that the neglected terms have probably much more influence on the result of the first-order calculation than do the terms which have been given as a "criterion for ferromagnetism." The influence of the neglected terms is expected to appear not only in the existence of ferromagnetism and the magnitude of the "exchange coupling," but perhaps also in saturation and paramagnetic magneton numbers. It is further suggested that a consistent manner of neglecting non-orthogonality does not lead to the usual exchange integral as the criterion, but rather shows, as one should expect, that the inter-nuclear terms would have no influence on the orientation of the electron spins.

In calculating the first-order energies, the terms due to non-orthogonality may not be tacitly neglected because of their enormous number, arising from the large number of permutations of the electron coordinates in even a small crystal.

Ι

This may be seen by examining the elements of the secular determinant. It is derived from the Hamiltonian

$$H = -\sum_{a} \Delta^{a} + \sum_{\alpha < \beta} V_{\alpha\beta} + \sum_{\alpha b} V_{\alpha}^{b} + \sum_{a < b} V^{ab},$$

 $\Delta^a = (h^2/8\pi^2 m)(\partial^2/\partial x_a^2 + \partial^2/\partial y_a^2 + \partial^2/\partial z_a^2),$

where

Greek letters refer to the atomic cores, Roman letters to electrons and the V's to mutual electrostatic energies of two particles. This in the wave equation

$$(H-NE_0-\epsilon)\sum_{m_{\alpha}m_{\beta}\cdots}c_{m_{\alpha}m_{\beta}\cdots m_{\nu}}\sum_{P}(-)^{P}P\psi_{m_{\alpha}}{}^{a}\psi_{m_{\beta}}{}^{b}\cdots\psi_{m_{\nu}}{}^{n}=0,$$

where permutation operator P acts on the atomic coordinates α , $\beta \cdots \nu$ and P in the exponent is the order of P, and where $\psi_{m_{\alpha}}{}^{a} = \psi_{\alpha}{}^{a}\delta(m_{s_{\alpha}}/\sigma_{a}) = \psi(x_{\alpha}{}^{a}y_{\alpha}{}^{a}z_{\alpha}{}^{a})\delta(m_{s_{\alpha}}/\sigma_{a})$ satisfies the atomic wave equation $(\Delta^{a} - V_{\alpha}{}^{a} + E_{0})\psi_{m_{\alpha}}{}^{a} = 0$, gives for the first order energies ϵ of the states having the spin

Bethe, Zeits. f. Physik 71, 205 (1931); D. R. Inglis, Phys. Rev. 45, 128 (1934) (Abstract—further details to appear soon).

² F. Bloch, Zeits. f. Physik 57, 545 (1930).

^{*}From Mexico City, as a Letter to the Editor. ¹W. Heisenberg, Zeits. f. Physik **49**, 619 (1928); *Sommerfeld Festschrift* 114; D. R. Inglis, Phys. Rev. **42**, **442** (1932); J. C. Slater, Phys. Rev. **35**, 509 (1930); F. Bloch, Zeits. f. Physik **61**, 206 (1930); **74**, 295 (1932); H.

projection $M = \Sigma m_{\theta}$ the crystalline secular determinant:

$$\left| \left\{ \sum_{P} (-)^{P} \sum_{\sigma_{a} \cdots} \int \bar{\psi}^{a}{}_{m_{\alpha}'} \cdots \bar{\psi}^{n}{}_{m_{\nu}'} (\sum_{\alpha < \beta} V_{\alpha\beta} - \epsilon + \sum_{\alpha, \beta} V_{\alpha}{}^{b} - \sum_{\alpha} V_{P\alpha}{}^{a} + \sum_{a < b} V^{ab}) P \psi_{m_{\alpha}}{}^{a} \cdots \psi_{m_{\nu}}{}^{n} \right\} \right| = 0.$$
 (1)

The determinant is here written with only one sample element. The rows are characterized by choices of $m_{\alpha} \cdots m_{\nu}$ and the columns by choices of $m_{\alpha}' \cdots m_{\nu}'$ each m_{θ} being $\pm \frac{1}{2}$ and subject to the condition $\Sigma m_{\theta} = M$. (Volume elements $dx^k dy^k dz^k$ are unwritten.)

Here, as in molecules but contrary to the case in many atomic problems, the electronic wave functions are not orthogonal. The integral

$$S = \int \bar{\psi}_{\kappa}{}^{k} \psi_{\lambda}{}^{k}$$

is less than one but distinctly greater than zero. (Here and hereafter, λ is a neighbor of κ .)

A term of (1) is in general large if the set $m_{\alpha} \cdots m_{\nu}$ differs from $m_{\alpha}' \cdots m_{\nu}'$ not at all (diagonal term), or by the interchange of the sign of $m_{\gamma}m_{\delta}$ of a pair of neighbors $\gamma\delta$, whereas a term is small if the sets differ by interchanges of many pairs of neighbors, or of a distant pair. Excepting the case M = n/2, even the largest non-diagonal terms of the determinant are of the order of nz times as numerous as the diagonal terms.

Even if we neglect that complication, and examine only a diagonal term, we see that we are not justified in tacitly neglecting non-orthogonality. In a diagonal term of (1), with $m_{\alpha}' \cdots m_{\nu}' = m_{\alpha} \cdots m_{\nu}$ we find in making the summation over P that the multiplier of $(\Sigma V_{\alpha\beta} - \epsilon)$ has as first term 1 due to the identical permutation P=1. Added to this are nZ/2 terms due to permutations which differ from P=1 only by exchange of two neighbors $\gamma\delta$ (Z=number of neighbors of each atom). For such a permutation, the integration (and the accompanying summation over spins σ) gives $-S^2$ if $m_{\gamma}=m_{\delta}$, or 0 if $m_{\gamma}=-m_{\delta}$. The fraction of pairs of m's which are equal to each other is

$$f(n_{+}) = [n_{+}(n_{+}-1) + n_{-}(n_{-}-1)]/n(n-1),$$

where n_+ is the number of $m_{\theta} = +\frac{1}{2}$ and n_- is the number of $m_{\theta} = -\frac{1}{2}$ so that $\frac{1}{2}n_+ -\frac{1}{2}n_- = M$. Hence we get as the term in S^2 : $-\frac{1}{2}nZf(n_+)S^2$. By a similar process, neglecting overlapping except that of wave functions of nearest neighbors, we get the approximate expression for a diagonal term of (1):

$$\left(\sum_{\alpha<\beta} V_{\alpha\beta}-\epsilon\right)\left\{1-(n/2)f(n_+)zS^2+\frac{1}{4}n(n-2)\left[f(n_+)z\right]^2S^4-\cdots\right\}$$
(2.1)

$$+\sum_{\alpha\neq k} n\left\{\int \bar{\psi}_{\kappa}^{k} V_{\alpha}^{k} \psi_{\kappa}^{k} - f(n_{+})zS\int \bar{\psi}_{\kappa}^{k} V_{\alpha}^{k} \psi_{\lambda}^{k}\right\} \left\{1 - \frac{1}{2}(n-2)f(n_{+})zS^{2} + \cdots\right\}$$
(2.2)

$$+\frac{1}{2}nz\left\{\int \bar{\psi}_{\kappa}^{k}\bar{\psi}_{\lambda}^{l}V^{kl}\psi_{\kappa}^{k}\psi_{\lambda}^{l}-f(n_{+})\int \bar{\psi}_{\kappa}^{k}\bar{\psi}_{\lambda}^{l}V^{kl}\psi_{\lambda}^{k}\psi_{\kappa}^{l}\right\}\left\{1-\left(\frac{1}{2}(n-4)z+1\right)f(n_{+})zS^{2}+\cdots\right\}.$$
(2.3)

The calculations which have as yet been made¹ tacitly neglect terms in S^2 , considering them small in comparison with the terms without S. In actual crystals, S is of the order of magnitude of 1/10. Taking $n = 10^5$, z = 10, we see that the S^2 term, the second term in the first line of (2), amounts to over 10³ times as much as the first term, and the terms in S^4 , 10⁷ times as much as the first term. Even if S were only 10^{-3} (probably making the Curie point below 10° K), the higher terms would hardly be negligible compared to the first. The ratios of the three series in (2) demands investigation, ere we may claim to have explained the order of magnitude of the Weiss "internal field" from the atomic viewpoint. The alternation of signs leaves the possibility that the higher powers of S may prove to be negligible. In our problem, it is important to know how the energies ϵ (or their centers of gravity) vary with n_+ and n_- (that is, with M). Thus, in the usual "approximation," the nature of the multiplier of $f(n_+)$ in (2) [and in the non-diagonal terms] appears as the "criterion for ferromagnetism." This multiplier is

$$\frac{1}{2}nzS^{2}(\sum V_{\alpha\beta}-\epsilon)+nzS\int \bar{\psi}_{\kappa}^{k}\sum_{\alpha\neq k}V_{\alpha}^{k}\psi_{\lambda}^{k}+\sum_{k>l}\int \bar{\psi}_{\kappa}^{k}\bar{\psi}_{\lambda}^{l}V^{kl}\psi_{\lambda}^{k}\psi_{\kappa}^{l},\qquad(3.1)$$

which takes a form similar to an "exchange integral":

$$\frac{1}{2}nz\int \bar{\psi}_{\kappa}^{k}\bar{\psi}_{\lambda}^{l}\{(\sum V_{\alpha\beta}-\epsilon)+2V_{\lambda k}+V^{kl}\}\psi_{\lambda}^{k}\psi_{\kappa}^{l}$$
(3.2)

if we neglect integrals of electronic potentials involving more than two neighboring atoms.

It has been customary to carry along, rather inconsistently, only one term in S^2 , namely, the term $V_{\kappa\lambda}$ in (3.2), neglecting $(\frac{1}{2}nz-1)$ equal terms $V_{\alpha\beta}$ and ϵ . This has given the "exchange integral" familiar from the problem of the hydrogen molecule:

$$\int \bar{\psi}_{\kappa}^{k} \bar{\psi}_{\lambda}^{l} (V_{\kappa\lambda} + 2V_{\lambda}^{k} + V^{kl}) \psi_{\lambda}^{k} \psi_{\kappa}^{l}.$$
(3.3)

It is more consistent to neglect $V_{\kappa\lambda}$ as well. We thus have the revised "exchange integral":

$$\int \bar{\psi}_{\kappa}^{\ k} \bar{\psi}_{\lambda}^{\ l} (2 V_{\lambda}^{\ k} + e^2/r_{kl}) \psi_{\lambda}^{\ k} \psi_{\kappa}^{\ l}, \qquad (3.4)$$

of which only a positive value may lead to a ferromagnetic result in this convenient "approximation." Here ferromagnetism should arise from the tendency of the Pauli exclusion principle to rarefy the charge distribution of states of high multiplicity in the space between adjacent nuclei. If this detracts less from the integrated negative energy $2V_{\lambda}^{k}$ than from the positive energy e^{2}/r_{kl} , the states of high multiplicity should have low energy and there should be ferromagnetism. It is thus more satisfactory that the mutual energy $V_{\kappa\lambda}$ of the fixed nuclei does not enter (3.4).

\mathbf{III}

Pending a satisfactory solution of the secular problem for the crystal, we may get some indication of the nature of the effects of non-orthogonality by the study of the effects in molecules, and their tendencies as we increase the number of atoms. We shall confine our comparison to three molecules composed of equidistant and similar atoms and one outer *s*-electron per atom: a diatomic molecule, a triatomic molecule forming an equilateral triangle, and a tetratomic molecule which forms an equilateral tetrahedron. In these cases, the possible permutations of the electrons are few enough that we may neglect higher powers of S in comparison with low powers.

In molecules, the analog of ferromagnetism is a state of high multiplicity with lower energy than has each state of low multiplicity. The familiar solution³ for the singlet and triplet energies, ${}^{1}\epsilon = \epsilon_{+}$ and ${}^{3}\epsilon = \epsilon_{-}$, of the hydrogenic molecule

$$\epsilon_{\pm} = \int \bar{\psi}_{\alpha}{}^{a}\bar{\psi}_{\beta}{}^{b}(V_{\alpha\beta} + V_{\beta}{}^{a} + V_{\alpha}{}^{b} + V^{ab})(\psi_{\alpha}{}^{a}\psi_{\beta}{}^{b} \pm \psi_{\beta}{}^{a}\psi_{\alpha}{}^{b})/(1\pm S^{2})$$

$$\tag{4}$$

gives, to the degree of accuracy S^2 , the triplet-singlet separation:

$${}^{3}\epsilon^{-1}\epsilon = -2\left\{\int \bar{\psi}_{\alpha}{}^{a}\bar{\psi}_{\beta}{}^{b}(2V_{\beta}{}^{a}+V^{a}{}^{b})\psi_{\beta}{}^{a}\psi_{\alpha}{}^{b}-S^{2}\int \bar{\psi}_{\alpha}{}^{a}\bar{\psi}_{\beta}{}^{b}(2V_{\beta}{}^{a}+V^{a}{}^{b})\psi_{\alpha}{}^{a}\psi_{\beta}{}^{b}\right\}.$$
(5)

⁸ Heitler and London, Zeits. f. Physik 44, 455 (1927).

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Neglecting S^2 in the denominator of (4), the singlet-triplet separation is measured by the exchange integral (3.3). Taking into account the S^2 terms, the separation is measured by (5), which lacks $V_{\alpha\beta}$, but contains instead a correction term $-2S^2 \int \overline{\psi}_{\alpha}{}^a \psi_{\alpha}{}^a V_{\beta}{}^a - S^2 \int \overline{\psi}_{\alpha}{}^a \psi_{\alpha}{}^a V^{ab} \overline{\psi}_{\beta}{}^b \psi_{\beta}{}^b$ which is essentially positive (favoring ferromagnetism), and for H₂ approximately equal to the lacking $V_{\alpha\beta}$ term. In the equilateral triatomic molecule, the energy difference between the quartet and the coincident doublets is

$${}^{4}\epsilon - {}^{2}\epsilon = -3\left\{\int \bar{\psi}_{\alpha}{}^{a}\bar{\psi}_{\beta}{}^{b}(2V_{\beta}{}^{a} + V^{ab})\psi_{\beta}{}^{a}\psi_{\alpha}{}^{b} - 3S^{2}\int \bar{\psi}_{\alpha}{}^{a}\bar{\psi}_{\beta}{}^{b}(2V_{\beta}{}^{a} + V^{ab})\psi_{\alpha}{}^{a}\psi_{\beta}{}^{b} + 2S\int \bar{\psi}_{\alpha}{}^{a}\bar{\psi}_{\beta}{}^{b}(V_{\alpha}{}^{b} + V_{\beta}{}^{a} + V^{ab})\psi_{\alpha}{}^{a}\psi_{\gamma}{}^{b}\right\}.$$

$$(6)$$

Here we have neglected terms in the third power of the overlapping. In the regular tetratomic molecule, the corresponding energy differences are

There are three triplet states with equal energy, and likewise two singlets.

[Note: Suffice it merely to outline the derivation of these results. The calculation has been organized for more general cases by Slater.⁴ For the three-electron case he gives expressions for the energies which simplify immediately for our equilateral molecule to

$${}^{4}\epsilon = \{(abc|H|abc) - 3(abc|H|bac)\}(1+3S^{2}),$$

$${}^{2}\epsilon = (abc|H|abc).$$

In the four-electron case, the quintet is had as the diagonal element for his state I (reference 4, page 1125). The singlets fall together because the symmetry in our tetratomic molecule makes P = Q = R. Among the states D, E, and F, the non-diagonal elements are zero and the diagonal elements are equal, so the triplets coincide and are ${}^{3}\epsilon = (D | H | D)$. It happens also that the energy sum rule for the states with $M_{S} = 0$, 1, and 2, holds to the degree of approximation S^{3} , and determines the energies, once the degeneracy has been established.

 ${}^{5}\epsilon = \{(abcd | H | abcd) - 6(abcd | H | abdc)\}(1+6S^{2}),$ ${}^{3}\epsilon = \{(abcd | H | abcd) - 2(abcd | H | abcd)\}(1+2S^{2}),$ ${}^{1}\epsilon = (abcd | H | abcd).]$

The low-multiplicity energies are of interest in the question of saturated valence. The degeneracy of like multiplicities is the analog of a sharp distribution replacing Heisenberg's "Gaussian distribution" or the Bloch-Bethe spreading.

Comparison of (5), (6), and (7) shows that the "criterion for ferromagnetism" depends increasingly on the terms in S^2 as the number of atoms in the molecule increases. This fact, as well as the above examination of Eq. (2), makes it seem very probable that the lack of orthogonality is very important in so large a molecule as a crystal. The integrals arising from the lack of orthogonality are such as to decrease the energy of the states of high multiplicity, so this seems in the molecular analog to be a tendency toward "ferromagnetism."

⁴ J. C. Slater, Phys. Rev. 38, 1109 (1931).