Exchange, Correlation, and Spin Effects in Molecular and Solid-State Theory*†

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INTRODUCTION

IN the theory of the electronic structure of atoms, molecules, and solid state, the exchange and correlation phenomena play a fundamental role in studying cohesive and elastic properties or electric and magnetic behavior. Conventionally it seems as if the exchange effects would be of particular importance in ferromagnetic and antiferromagnetic materials and the correlation effects in conductors and semiconductors, but actually the two phenomena are closely coupled together in all electronic systems.

EXCHANGE IN TWO-ELECTRON SYSTEMS

The exchange integral J was introduced by Heisenberg,[1] but since this concept has been strongly criticized by several authors and particularly by Slater,[2] we start by a redefinition of this important quantity. Let us consider a two-electron system ($N=2$) having a spin-free basic Hamiltonian leading to two basic states having either singlet or triplet character corresponding to $S=0$ and $S=1$, respectively. For convenience we may fix our attention on the lowest state of each type. Denoting their energies by ^1E and ^3E, respectively, we define the "exchange integral" J by the relation

$$J = \tfrac{1}{2}(^1E - {}^3E). \tag{1}$$

This implies that for $J>0$, one has $^3E<{}^1E$ and a parallel spin alignment in the ground state, (↑↑, ferromagnetism); whereas for $J<0$, one has $^1E<{}^3E$ and an antiparallel spin alignment in the ground state (↑↓, antiferromagnetism). The definition allows us to derive the Dirac-van Vleck vector-model formula in an exact way. In the relation

$$E = \tfrac{1}{2}(^1E + {}^3E) - \tfrac{1}{2}\kappa(^1E - {}^3E), \tag{2}$$

[1] W. Heisenberg, Z. Physik 38, 411 (1926); 39, 499 (1926); 41, 239 (1927).
[2] J. C. Slater, Revs. Modern Phys. 25, 199 (1953).

$\kappa = -1$ gives $E = {}^1E$ and $\kappa = +1$ gives $E = {}^3E$. Measuring the spin in units of $\hbar$, one has $\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2$ and further

$$\mathbf{S}^2 = \tfrac{3}{2} + 2\mathbf{s}_1 \cdot \mathbf{s}_2,$$

which operator has the eigenvalues $S(S+1)$. This implies that the operator

$$\tfrac{1}{2} + 2\mathbf{s}_1 \cdot \mathbf{s}_2 \tag{3}$$

has the eigenvalues $S(S+1)-1$ or -1 for $S=0$ and $+1$ for $S=1$, i.e., the numbers defined above by the symbol κ. Substituting the operator (3) for the symbol κ in (2), one obtains an operator

$$E_{op} = E_0 - 2\mathbf{s}_1 \cdot \mathbf{s}_2 J, \tag{4}$$

which has the correct eigenfunctions with respect to the spin and the correct energy values. Here $E_0 = \tfrac{1}{4}(^1E + 3{}^3E)$ is the average energy of all possible spin states taken with their weights. This is an exact form of the vector-model formula, independent of any assumptions about correlation, nonorthogonality, polar states, relativistic effects, etc. It is true that the derivation has an almost trivial character, but this makes it particularly convenient as a basis for further research.

Let us now discuss the detailed form of the exchange integral J. Since the permutation P_{12} commutes with the basic Hamiltonian H_{op}, it is a constant of motion. Any trial function $\Phi = \Phi(1,2)$ of the space coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ consists of two components:

$$\Phi(1,2) = \tfrac{1}{2}[\Phi(1,2)+\Phi(2,1)] + \tfrac{1}{2}[\Phi(1,2)-\Phi(2,1)], \tag{5}$$

of which the first is symmetric and the second antisymmetric in the space coordinates. The two components are orthogonal and non-interacting with respect to H and, by considering the possible spin functions and the antisymmetry requirement for the total wave function, it is easily seen that the first corresponds to the singlet state and the second to the triplet state. After normalizing the components, one obtains easily the corresponding energies

$$^1E = \frac{\langle\Phi|H|\Phi\rangle + \langle\Phi|HP|\Phi\rangle}{1 + \langle\Phi|P|\Phi\rangle}, \tag{6}$$

$$^3E = \frac{\langle\Phi|H|\Phi\rangle - \langle\Phi|HP|\Phi\rangle}{1 - \langle\Phi|P|\Phi\rangle}, \tag{7}$$

where $P=P_{12}$ and $\langle\Phi|\Phi\rangle=1$. Substituting these expressions into the definition of J, we get finally the exchange integral

$$J=\frac{\langle\Phi|HP|\Phi\rangle-\langle\Phi|P|\Phi\rangle\langle\Phi|H|\Phi\rangle}{1-\langle\Phi|P|\Phi\rangle^2}. \tag{8}$$

This quantity is invariant under a change of zero-point of the energy, so that $J'=J$ for $H'=H+\alpha$. If Φ is a mixture of the two exact space eigenfunctions involved, the expression for J is exact also. The formula is also a convenient starting point for discussing approximate theories. Only if from the very beginning Φ is either symmetric or antisymmetric, there is not enough information available about the other state, and the formula for J breaks down.

Let us now consider the model in which the two electrons occupy two normalized orbitals a and b, so that

$$\Phi(1,2)=a(1)b(2).$$

Introducing the overlap integral $S_{ab}=\int a^*(1)b(1)dv_1$, one obtains $\langle\Phi|P|\Phi\rangle=|S_{ab}|^2$ and further

$$J=\frac{\langle ab|H|ba\rangle-|S_{ab}|^2\langle ab|H|ab\rangle}{1-|S_{ab}|^4}, \tag{9}$$

which is the corresponding approximation for the exchange integral. Since the overlap integral S_{ab} causes some mathematical difficulties, there has been an almost universal tendency in the literature to neglect this quantity and to consider $\langle ab|H|ba\rangle$ as a proper approximation of J. This is by no means justified.

For a two-electron system, the basic Hamiltonian may be written in the form

$$H_{op}=H_0+H_1+H_2+H_{12}, \tag{10}$$

where the constant H_0 represents the internuclear Coulomb repulsion or vanishes for a single atom, $H_i=T_i+V_i$ is the sum of the kinetic energy T_i and the potential energy V_i in the nuclear framework of electron i ($i=1$ or 2), and $H_{12}=e^2/r_{12}$. This leads to the exchange integral

$$J=[\langle a|H_1|b\rangle S_{ba}+\langle b|H_1|a\rangle S_{ab}+\langle ab|e^2/r_{12}|ba\rangle$$
$$-|S_{ab}|^2\{\langle a|H_1|a\rangle+\langle b|H_1|b\rangle$$
$$+\langle ab|e^2/r_{12}|ab\rangle\}]/[1-|S_{ab}|^4]. \tag{11}$$

If overlap is neglected ($S_{ab}=0$) one gets directly

$$J=\left\langle ab\left|\frac{e^2}{r_{12}}\right|ba\right\rangle=e^2\int\int\frac{a^*(1)b(1)\cdot a(2)b^*(2)}{r_{12}}dv_1dv_2,$$

and, since this is the "self-potential" of an electronic cloud having the density $ea^*(1)b(1)$ it is definitely positive:

$$J>0, \quad\text{when}\quad S_{ab}=0. \tag{12}$$
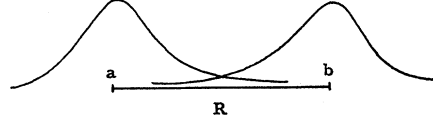
This implies that one cannot develop a theory of spin

FIG. 1. Diatomic molecule with two overlapping atomic orbitals a and b and internuclear distance R.

alignment and ferromagnetism on the basis of the Heitler-London-Heisenberg model, if overlap is neglected, since the exchange integral cannot change its sign. The use of strictly orthogonalized orbitals is convenient for many purposes,[3-5] but the use of the simple product form $\Phi=a(1)b(2)$ leads then to a situation where the triplet state always has a lower energy than the singlet state and, for a two-atomic system, the latter state can further never be bonding.[6] In order to use orthogonalized orbitals properly, one must therefore consider also contributions from "polar states" of the form $a(1)a(2)$ and $b(1)b(2)$ which will influence the energy of the singlet but not of the triplet.

The general expression for the exchange integral J associated with two overlapping orbitals a and b contains the operator $H_1=T_1+V_1$ and hence also the kinetic energy. Let us now consider a system consisting of two atoms having each *one valence electron* (Fig. 1). The internuclear distance is denoted by R, and the core potentials by V_a and V_b. Let us further assume that a and b are solutions of the approximate Schrödinger equations for the free atoms:

$$[T_1+V_{a1}]a(1)=\epsilon_a a(1), \quad [T_1+V_{b1}]b(1)=\epsilon_b b(1). \tag{13}$$

Noting that $V=V_a+V_b$ and using these relations, one obtains the expression:

$$J=\left[\langle a|V_{a1}|b\rangle S_{ba}+\langle b|V_{b1}|a\rangle S_{ab}\right.$$
$$+\left\langle ab\left|\frac{e^2}{r_{12}}\right|ba\right\rangle-|S_{ab}|^2\left\{\langle a|V_{b1}|a\rangle+\langle b|V_{a1}|b\rangle\right.$$
$$+\left.\left.\left\langle ab\left|\frac{e^2}{r_{12}}\right|ab\right\rangle\right\}\right]\Big/[1-|S_{ab}|^4] \tag{14}$$

$$=\left[\int\int a^*(1)b^*(2)\left\{V_{a1}+V_{b2}+\frac{e^2}{r_{12}}\right\}b(1)a(2)dv_1dv_2\right.$$
$$-|S_{ab}|^2\int\int a^*(1)b^*(2)\left\{V_{b1}+V_{a2}+\frac{e^2}{r_{12}}\right\}$$
$$\left.\times a(1)b(2)dv_1dv_2\right]\Big/[1-|S_{ab}|^4]. \tag{15}$$

[3] R. Landshoff, Z. Physik 102, 201 (1936).
[4] G. H. Wannier, Phys. Rev. 52, 191 (1937).
[5] P. O. Löwdin, Arkiv Mat. Astron. Fysik 35A, 9 (1947); J. Chem. Phys. 18, 365 (1950); Advances in Phys. 5, 1 (1956).
[6] J. C. Slater, J. Chem. Phys. 19, 220 (1951).

For hydrogen-like atoms, one has $V_{a1} = -e^2 Z_a/r_{1a}$ and $V_{b2} = -e^2 Z_b/r_{2b}$, where Z_a and Z_b are the atomic numbers or the "effective" nuclear charges, respectively. All terms in the numerator of J are actually of the same order as $|S_{ab}|^2$. It is therefore not justified to neglect any term in comparison to the other. Nevertheless, in the last expression, one has often in the literature neglected the second term because of the factor $|S_{ab}|^2$ and the expression

$$J = \int\int a^*(1)b^*(2)\left\{-e^2\frac{Z_a}{r_{1a}}-e^2\frac{Z_b}{r_{2b}}+\frac{e^2}{r_{12}}\right\}$$

$$\times b(1)a(2)dv_1 dv_2, \quad (16)$$

is known as the "Heisenberg exchange integral." Personally the author feels that the use of this formula is just as unjustified as the use of the expression $J = \langle ab|e^2/r_{12}|ba\rangle$. For a two-electron system, there are no difficulties whatsoever to include the overlap properly, and the exchange integral is then given correctly by formula (15). One should observe, however, that the two atoms involved are actually deformed in forming a molecule, and that one must scale the two valence orbitals a and b to satisfy the virial theorem.[7] Since one cannot use (13), the exchange integral is then given by the basic formulas (9) or (11). The author believes it would be worthwhile to reexamine the entire exchange problem from this point of view.

EXCHANGE IN MANY-ELECTRON SYSTEMS

For the two-electron case, we have proven that the vector-model formula (4) can be given an exact derivation which is valid even if correlation, non-orthogonality effects, relativistic corrections, etc. are included. Conventionally,[8,9] one has generalized the approach to many-electron systems by building the spin discussions on a Hamiltonian of the form

$$E_{op} = E_0 - 2\sum_{i<j} J_{ij}\mathbf{s}_i\cdot\mathbf{s}_j, \quad (17)$$

where there will be one more term if there is an outer magnetic field present. The formalism has been particularly utilized in Bethe's spin-wave model,[10] in which only exchange between nearest neighbors (nei) is considered under the assumption of a constant exchange integral J:

$$E_{op} = E_0 - 2J\sum_{i<j}^{nei}\mathbf{s}_i\cdot\mathbf{s}_j. \quad (18)$$

Following Kramers,[11] the method has to a large extent been used also to discuss superexchange.[12]

The weak point in these generalizations of the vector model to many-electron systems is undoubtedly that so far all derivations are based on the assumption of orthogonality between the basic orbitals. The simple case of $N=2$ shows that, in the case a and b were orthogonal, one could neither discuss ferromagnetism nor covalent bonding. The remedy is to use overlapping basic orbitals or to include polar states,[13,14] but the fundamental Hamiltonian (17) will then also contain terms related to higher exchange. The same result is obtained by generalizing our trivial derivation for $N=2$ to a many-electron system. This important problem is definitely worth a great deal of research in the future.[15]

CORRELATION PROBLEM

In addition to exchange, another phenomenon is of fundamental importance in many-electron theory, namely the interelectronic correlation. Because of their mutual coulomb repulsion, two electrons try always to avoid each other to keep the energy as low as possible which leads to a certain "correlation" between their motions. In this connection, there is actually an increase in the kinetic energy of the two electrons because of the more complicated motions they have to perform, but this is compensated by a still larger decrease in the coulomb repulsion energy; the balance is regulated by the virial theorem, $\langle T\rangle = -\frac{1}{2}\langle V\rangle$.

The mutual behavior of two electrons is conveniently described by the second-order density matrix[16]:

$$\Gamma(x_1'x_2'|x_1x_2) = \binom{N}{2}\int \Psi^*(x_1'x_2'x_3\cdots x_N)$$

$$\times \Psi(x_1 x_2 x_3 \cdots x_N)dx_3\cdots dx_N. \quad (19)$$

The diagonal element $\Gamma(x_1 x_2|x_1 x_2)$ gives the probability

[7] See e.g., P. O. Löwdin, J. Mol. Spectroscopy 3, 46 (1959).

[8] P. A. M. Dirac, Proc. Roy. Soc. (London) A123, 714 (1929); Quantum Mechanics (Oxford University Press, London, 1935), 2nd ed., Chap. X.

[9] J. H. Van Vleck, Theory of Electric and Magnetic Susceptibilities (Oxford University Press, London 1932); Phys. Rev. 45, 405 (1934).

[10] H. Bethe, Z. Physik 71, 205 (1931); L. Hulthén, Arkiv Mat. Astron. Fysik 26A, 11 (1938); P. W. Anderson, Phys. Rev. 86, 694 (1952); R. Kubo, ibid. 87, 568 (1952); F. J. Dyson, ibid. 102, 1217 (1956); J. van Kranendonk and J. H. Van Vleck, Revs. Modern Phys. 30, 1 (1958); F. Bopp and E. Werner, Z. Physik 151, 10 (1958); and others.

[11] H. A. Kramers, Physica 1, 182 (1934).

[12] P. W. Anderson, Phys. Rev. 79, 350 (1950); J. Yamashita, J. Phys. Soc. Japan 9, 339 (1954); S. V. Tyablikov, Fiz. Metal i Metalloved 4, 193 (1956); G. W. Pratt, Phys. Rev. 106, 53 (1957); J. Kondo, Progr. Theoret. Phys. (Kyoto) 18, 541 (1957); J. Yamashita and J. Kondo, Phys. Rev. 109, 730 (1958); P. W. Anderson, ibid. 115, 2 (1959); J. Kanamori, J. Phys. Chem. Solids 10, 87 (1959); F. Keffer and T. Oguchi, Phys. Rev. 115, 1428 (1959); J. Kondo, Progr. Theoret. Phys. (Kyoto) 22, 41, 819 (1959); S. Koide, K. P. Sinha, and Y. Tanabe, Progr. Theoret. Phys. (Kyoto) 22, 647 (1959); S. Rodriguez, Phys. Rev. 116, 1474 (1959); T. Oguchi, ibid. 117, 117 (1960); and others.

[13] R. Serber, J. Chem. Phys. 2, 697 (1934); Phys. Rev. 45, 461 (1934).

[14] W. J. Carr, Jr., Phys. Rev. 92, 28 (1953).

[15] For some recent developments, see R. K. Nesbet, Ann. Phys. 4, 87 (1958); J. S. Smart, J. Phys. Chem. Solids 11, 97 (1959).

[16] P. O. Löwdin, Phys. Rev. 97, 1474 (1955).

density to find an electron pair in the points $x_1 = (\mathbf{r}_1, \zeta_1)$ and $x_2 = (\mathbf{r}_2, \zeta_2)$ in configuration space; here ζ_1, and ζ_2 are the spin coordinates. Because of the Coulomb repulsion, each electron should be surrounded by a "Coulomb hole" with respect to all other electrons, i.e., $\Gamma(x_1 x_2 | x_1 x_2)$ should be small when $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ tends to zero.

In the independent-particle model based on a wave function in the form of a Hartree product, the Coulomb correlation is entirely neglected so the approximation is subject to a large correlation error. The situation is somewhat changed by the introduction of the Pauli principle and the antisymmetry requirement. The wave function is now approximated by a Slater determinant and since $\Gamma(x_1' x_2' | x_1 x_2)$ is antisymmetric in each set of its indices, the density $\Gamma(x_1 x_2 | x_1 x_2)$ vanishes to the second order when $x_1 = x_2$, i.e., when $r_{12} = 0$ and $\zeta_1 = \zeta_2$. For parallel spin coordinates, the antisymmetry requirement leads then to the occurrence of a "Fermi hole" which to a certain extent replaces the "Coulomb hole." In the Hartree-Fock scheme, the essential part of the correlation error is hence associated with electron pairs having antiparallel spins.

The *correlation energy* is not a physical quantity but the measure of the energy error due to the neglect of correlation in a certain approximation. One is particularly interested in the correlation error in the Hartree-Fock (HF) scheme corresponding to the band theory in solid-state physics, and it seems convenient to use the definition:

$$\text{Correlation energy} = E_{\text{exact}} - E_{\text{HF}}, \qquad (20)$$

where E_{exact} is the true eigenvalue for the Hamiltonian under consideration.[17]

For the H_2 molecule, the correlation energy is -1.06 ev corresponding to errors of $+1.06$ ev in the kinetic energy and -2.12 ev in the potential energy. Since 1 ev $= 23.07$ kcal/mole, these quantities are appreciable even from a chemical point of view. For the series of He-like ions, the correlation energy is approximately constant -1.2 ev, varying from -1.142 for He to -1.197 for C^{4+}. For Be, the correlation energy is -2.4 ev but, for the series of Be-like ions, it seems to vary linearly with Z depending on the degeneracy of the $2s$ and $2p$ orbitals.[18] For the Ne-like ions, it is probably fairly constant of the order of magnitude -11 ev.[19] For the alkali metals Li, Na, and K, Wigner

[19] A. Fröman, Phys. Rev. **112**, 870 (1958).

has given the values -1.89, -1.73, and -1.58 ev, respectively.

In forming energy differences, there is sometimes a balance between the correlation errors which leads to

TABLE I. Hartree scheme vs Hartree-Fock scheme

Scheme	↑↑	↑↓	Remark
Hartree	bad	bad	balance
Hartree-Fock	good	bad	out of balance

surprisingly good results. This happens e.g., in treating the cohesive energy and elastic constants of the alkali halides, but not for the alkali metals. Table I shows also that in the Hartree-Fock scheme there is a remarkable unbalance between the treatments of parallel and antiparallel spins, which is not favorable for a theory of magnetic behavior.[2,20] It has been remarked that it may therefore be easier to formulate a good semi-empirical theory of ferromagnetism in the Hartree scheme than in the Hartree-Fock approximation. In order to restore the balance, one has apparently to include the correlation effects for pairs having antiparallel spins.

The band theory or molecular-orbital method is not convenient for a treatment of magnetic properties from another point of view since the theory may give a good description of the system when the atoms are in their equilibrium positions, whereas it breaks down completely and has a wrong asymptotic behavior for separated atoms in the antiparallel case.[21,22] The situation may be illustrated by considering an H_2 molecule consisting of two hydrogen atoms a and b at the internuclear distance R. In the HF scheme, the wave function for the singlet has a space part of the form $\varphi(1)\varphi(2)$, where φ is a molecular orbital. Because of the symmetry of the molecule, one can write $\varphi = (u_a + u_b)(2 + 2S_{ab})^{-\frac{1}{2}}$, where $S_{ab} = \int u_a u_b dv$. In the conventional MO-LCAO theory, the function is approximated by a $1s$ orbital, but better results may be obtained by also including higher orbitals and varying the coefficients. The total wave function for the singlet is such that, for separated atoms, there is a 50% chance that the molecule will dissociate into H^- and H^+, and a 50% chance that it will dissociate into two H atoms, and the total energy is given by the expression

$$E_{\text{HF},\infty} = \tfrac{1}{2}(H^+ + H_{u^2}^-) + \tfrac{1}{2}(H_u + H_u), \qquad (21)$$

where $H_{u^2}^-$ is the expectation value of the H^- Hamiltonian with respect to $u(1)u(2)$. Actual calculations give $E_{\text{HF},\infty} = -0.715$ atomic units instead of -1, showing an enormous correlation error of -0.285 atomic units $= -7.74$ ev for $R = \infty$.

In this approach, the total wave function permits apparently electrons of different spins to accumulate on the same atom and give rise to negative and positive

[17] E. Wigner, Phys. Rev. **46**, 1002 (1934); Trans. Faraday Soc. **34**, 678 (1938); F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940) p. 698; J. C. Slater, Revs. Modern Phys. **25**, 199 (1953); E. P. Wohlfarth, *ibid.* 211 (1953); D. Pines, Solid State Phys. **1**, 368 (1955).
[18] J. Linderberg and H. Shull, J. Mol. Spectroscopy **4**, 30 (1960).

[20] D. Pines, *Les électrons dans les métaux* (Proceedings 10th Solvay Conference 1954, Brussels 1955), p. 9.
[21] J. C. Slater, Phys. Rev. **35**, 509 (1930); **82**, 538 (1951).
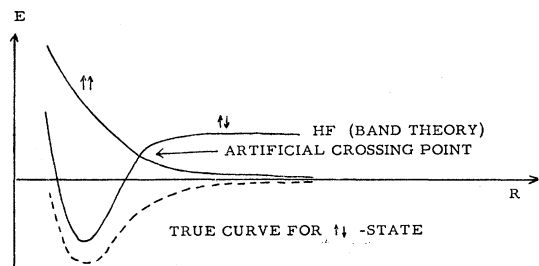[22] J. H. Van Vleck and A. Sherman, Revs. Modern Phys. **7**, 167 (1935).

Fig. 2. Comparison between energy curves for the states having parallel and antiparallel spins.

ions with higher energy than the ordinary dissociation products. This is a typical "correlation error" associated with the independent-particle model since, in nature, the strong Coulomb repulsion between the electrons prevents the formation of negative ions with too many electrons.

On the other hand, for the triplet state, the Pauli principle will prevent the formation of negative ions, and the energy will approach the correct value for $R = \infty$. The general shape of the energy curves is indicated in Fig. 2. Since the $\uparrow\downarrow$ curve has a wrong asymptotic behavior for $R = \infty$, there will always be an artificial crossing point with the $\uparrow\uparrow$ curve which may lead to wrong conclusions about the general magnetic properties of the system. This may prevent a theory of ferromagnetism from being developed within the framework of ordinary band theory.[2]

In discussing the influence of the correlation error, it is also illustrative to look at the curve (Fig. 3) for the correlation energy of the H_2 molecule as a function of R. This curve differs greatly in character from the one obtained in the plasma-model[17,20] in which the nuclear positive charge is smeared out to a uniform background. Since there are no discrete nuclei, there will be no excessive negative ions, and the correlation energy is simply considered as a function of the average electron density going to zero at the low density limit. This picture may be useful for discussing certain properties of a metal but, in general, it is an oversimplification of the actual problem.

BAND THEORY VERSUS VALENCE BOND METHOD

From our discussion, it is clear that neither band theory nor valence bond method will ultimately solve the difficulties in molecular and solid-state theory. The collective electron theory for ferromagnetism[23,24] has been successful from many points of view, but it is essentially based on band theory and is therefore subject to the difficulties connected with the wrong asymptotic behavior.[2] Band theory is particularly advantageous in connection with problems concerning conductivity, but even here there are difficulties in connection with crystals like NiO which are good

insulators having incompletely filled bands.[25] Since band theory is further subject to a large correlation error, one has to use a great deal of caution in practically all applications.

The valence-bond method or the Heitler-London-Heisenberg scheme has perhaps a more favorable starting point, since a great deal of correlation seems to be automatically included. Among other things, the method leads to a correct asymptotic behavior for separated atoms, which is essential for any theory of magnetic properties. Most theories for ferromagnetism and antiferromagnetism have so far been based on Dirac's vector model, where the basic Hamiltonian is derived under the assumption that all orbitals are strictly orthogonal. This assumption seems unfortunately to prevent a correct treatment of bonding or magnetism, unless polar states are included, which is seldom the case. Also in the theory of conductivity, the polar states are quite essential.[26] Even more thorough treatments of the cohesive properties of solids have been given along these lines.[27] The problem of including overlap or polar states is by no means fully solved.
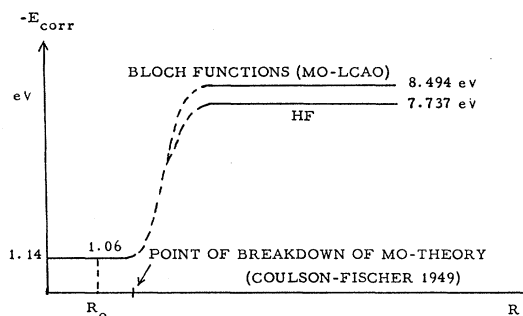

Fig. 3. Correlation energy of hydrogen molecule as a function of internuclear distance R.

In solid-state theory, the overlap problem is of particular importance, since the inclusion of the overlap integrals in the expectation values of the fundamental physical quantities leads to *diverging* numerators and denominators.[28] In the theory of ferromagnetism, this led also to a "nonorthogonality catastrophe,"[29] which has only been partly removed.[14,30] Today it is clear that there is no "catastrophe." All expectation values are definitely unique and finite, even if their explicit form is not yet fully known.[31] A great deal of research

[23] For a review, see E. C. Stoner, Repts. Progr. Phys. **11**, 43 (1948); J. phys. radium **12**, 372 (1951).
[24] E. P. Wohlfarth, Revs. Modern Phys. **25**, 211 (1953).
[25] N. F. Mott, Proc. Phys. Soc. (London) **A62**, 416 (1949).
[26] S. Schubin and S. Wonssowsky, Proc. Roy. Soc. (London) **A145**, 159 (1934); Phys. Z. Sowjetunion **7**, 292 (1935); **10**, 348 (1936); S. Wonssowsky, Fortschr. Physik **1**, 239 (1954).
[27] L. Pauling, Proc. Roy. Soc. (London) **A196**, 343 (1949); Physica **15**, 23 (1949); C. A. Coulson, Proc. Intern. Conf. Theoret. Phys., Kyoto and Tokyo, Japan **629**, (1953).
[28] J. C. Slater, Phys. Rev. **35**, 509 (1930).
[29] D. R. Inglis, Phys. Rev. **46**, 135 (1934).
[30] J. H. Van Vleck, Phys. Rev. **49**, 232 (1936).
[31] Y. Mizuno and T. Izuyama, Progr. Theoret. Phys. (Kyoto) **22**, 344 (1959).

remains hence to be done in connection with this problem.

COMBINATION OF BAND THEORY AND VALENCE BOND METHOD

From many points of view, it seems desirable to combine the obvious advantages of the band theory and the valence bond method, and this can be done by generalizing the former to include a certain amount of correlation.

The large correlation errors in the conventional Hartree-Fock approximation mentioned previously depends essentially on the fact that pairs of electrons of opposite spins are forced together in doubly filled orbitals. This pairing goes back partly to the classical formulation of the Pauli principle, partly to the fact that this procedure permits a simple construction of Slater determinants as pure spin states. One can therefore remove part of the defects coming from correlation by *letting electrons with different spins occupy different orbitals in space*, so that they can get a chance to avoid each other. For a detailed description of this idea, the author refers to some recent papers in reference 32.

It is clear that, if one permits "different orbitals for different spins," the corresponding Slater determinants will no longer be pure spin functions but mixtures of components associated with different spins. In the new scheme, *the total wave function will be approximated by the component of the Slater determinant which has the spin desired.* The component of multiplicity $(2S+1)$ is selected by a "projection operator" of the form

$$^{(2S+1)}O = \prod_{k}^{k \neq S} \frac{[S^2 - k(k+1)]}{[S(S+1) - k(k+1)]}, \quad (22)$$

which fulfills the relation $O^2 = O$. A detailed theory for such projection operators has been developed.[33] If the Slater determinant is denoted by D, the wave function $^{(2S+1)}\Psi$ in our generalized Hartree-Fock scheme is hence defined by the formula

$$^{(2S+1)}\Psi = {}^{(2S+1)}OD. \quad (23)$$

If the basic spin-orbitals ψ_1, ψ_2, $\cdots$, ψ_N in D are subject to a linear transformation, the wave function Ψ will be changed only by a constant. Since the projection will affect only the spin functions, it is clear that Ψ will depend only on the two space-density matrices $\rho_+(\mathbf{r}_1, \mathbf{r}_2)$ and $\rho_-(\mathbf{r}_1, \mathbf{r}_2)$ which are associated

with D. For the expectation value of the energy, one obtains

$$\langle H_{op} \rangle_{av} = \frac{\int \Psi^* H_{op} \Psi(dx)}{\int \Psi^* \Psi(dx)} = \frac{\int D^* H_{op} OD(dx)}{\int D^* OD(dx)}, \quad (24)$$

where one has used the turnover rule and the relation $O^2 = O$. The variation principle $\delta \langle H \rangle = 0$ leads to the best possible density matrices ρ_+ and ρ_- or to the corresponding best spin-orbitals.[34] The simple applications carried out so far show that about 85% of the total correlation error can be removed in this way.

For a solid-state system, the solution of the extended Hartree-Fock equations is a very complicated problem, and one has probably to be satisfied with approximate solutions for quite some time. The *alternant molecular-orbital method*[32] is an approximate device for evaluating ρ_+ and ρ_- or the corresponding orbitals in a molecular or solid-state system of alternant character. The method is based on the fact that, by using a single parameter θ, a suitable linear combination of a bonding orbital ψ_j', and a corresponding anti-bonding orbital ψ_j'' one can construct basic orbitals

$$\psi_{jI} = \cos\theta \cdot \psi_j' + \sin\theta \cdot \psi_j'',$$
$$\quad (25)$$
$$\psi_{jII} = \cos\theta \cdot \psi_j' - \sin\theta \cdot \psi_j'',$$

which are semilocalized so that electrons with opposite spins get a possibility to avoid each other. We note that the orbitals of type I and II are overlapping for the same j value, $\int \psi_{jI} \psi_{jII} dv = \cos 2\theta$, but otherwise orthogonal. As an example, we will consider the six orbitals connected with the benzene problem (See Fig. 4). Only a single parameter θ is involved, and one obtains the following special cases of orbitals:

$\theta = 0$,   bonding Bloch orbitals
           (ordinary band theory)
$\theta = 45°$, purely alternant orbitals
$\theta = 90°$, antibonding Bloch orbitals
           (upper half of the band).
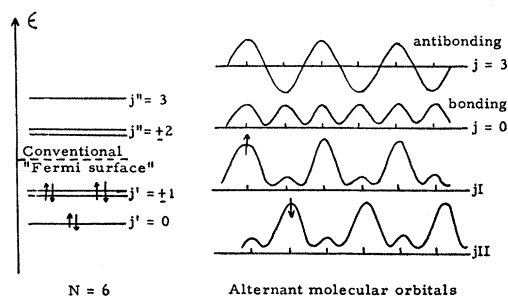
FIG. 4. Ordinary and alternant molecular orbitals for the benzene molecule.

[32] P. O. Löwdin, Nikko Symp. Mol. Phys. (Maruzen, Tokyo) 13 (1954); Phys. Rev. 97, 1509 (1955); Proc. 10th Solvay Conference, 71 (1955); Advances in Phys. 5, 1 (1956); Advances in Chem. Phys. 2, 207 (1959).

[33] P. O. Löwdin, Phys. Rev. 97, 1509 (1955); Proc. Paris Symposium Molecular Quantum Mechanics, 23 (1958); Technical Note 12, Uppsala Quantum Chemistry Group, Uppsala, Sweden (1958); H. McIntosh, Technical Note 19, Uppsala Quantum Chemistry Group (1958).

[34] P. O. Löwdin, Ann. Acad. Reg. Sci. Upsaliensis 2, 127 (1958).

TABLE II. Schematic survey of different approaches to solid-state theory.

Property	Band theory	Valence bond theory	Combined approach: "different bands for different spins"
Cohesive and elastic properties	Large energy correlation error; wrong asymptotic behavior of energy for separated atoms.	Large energy error at equilibrium, but correct asymptotic behavior for separated atoms.	Small energy error at equilibrium; correct asymptotic behavior for separated atoms.
Conductivity	Concept of conduction band simple and striking, but remarkable exceptions (NiO).	Complicated approach with polar states of main importance.	Seems to offer a favorable starting point for research.
Magnetic properties (ferromagnetism and antiferromagnetism).	Basis for collective electron theory; unbalanced treatment of parallel and antiparallel spins; artificial crossing point of energy curves.	Most treatment based of Dirac vector model oversimplified, since nonorthogonality neglected. Necessity to take overlap or polar state into account.	Balanced treatment of parallel and antiparallel spins; no artificial crossing point of energy curves. Seems to offer a good starting point for future research.
Main advantage	Offers a simple and visual physical picture of electronic structure of a solid. No nonorthogonality problem involved.	Offers a simple chemical picture of a solid connected with valence concept. Includes automatically certain correlation effects.	Offers a simple and visual physical picture of a solid. Includes still a large amount of correlation effects.
Main disadvantage	Insufficient as basic theory, because of neglect of correlation effects.	"Nonorthogonality catastrophe"-necessity to include overlap or polar states. Approximate linear dependencies between basic orbitals.	Nonorthogonality of "orbital pairs" requires a careful mathematical study.

The electrons are permitted to avoid each other by assigning α spin to orbitals of type I and β spin to orbitals of type II. The best value of θ is then determined by minimizing the energy given by formula (24). In the benzene case, Itoh and Yoshizumi[35] obtained $\theta = 23°$ and a removal of 85% of the previously known correlation error.

Of particular importance is the asymptotic behavior for separated atoms, in which case θ approaches 45° and one obtains purely alternant orbitals which give a description of the system closely analogous to the valence bond method. For $\theta = 45°$, orbitals of type I and II are strictly orthogonal, and formula (24) takes the simple form

$$\langle H_{op} \rangle_{av} = \int D^* H D (dx)$$

$$- \frac{2S(S+1) - N}{N^2} \sum_{j,k} \left\langle j\mathrm{I}, k\mathrm{II} \left| \frac{e^2}{r_{12}} \right| k\mathrm{II}, j\mathrm{I} \right\rangle, \quad (27)$$

where the latter term goes to zero for separated atoms. Since there is no accumulation of negative ions, the energy curve gets a correct asymptotic behavior. Hence the approach gives a generalization of band theory, "different bands for different spins," which has taken over one of the main advantages of valence bond theory of particular importance for treating magnetic properties. Applications to the linear chain and conjugated systems are in progress in Uppsala (Pauncz, de Heer, and Löwdin), and after a treatment of free electrons in a box, applications to the alkali metals are planned. In connection with the explanation of the alternating spin densities in odd alternant hydrocarbon radicals, the approach has recently proven to be quite successful.[36] Apparently the idea has also influenced Anderson's new theory of superexchange.[37]

The concept itself will influence the theory of conductors and semiconductors and the treatment of cohesive, elastic, and magnetic properties. It provides a simple one-parameter method for dealing with at least the main part of the correlation effects. It seems hence to be a very promising starting point for intensified research on the basic problems of solid-state

[35] T. Itoh and H. Yoshizumi, J. Phys. Soc. Japan 10, 201 (1955); J. Chem. Phys. 23, 412 (1955); Busseiron Kenkyu No. 83, 13 (1955).

[36] R. Lefebvre, H. H. Dearman, and H. M. McConnell, J. Chem. Phys. 32, 176 (1960).
[37] P. W. Anderson, Phys. Rev. 115, 2 (1959).

theory, particularly since the general idea of using "different orbitals for different spins" is by no means limited to alternant systems.

Note added in proof: A numerical investigation of the direct exchange of $3d$ electrons based on the Heisenberg exchange integral has been reported by R. Stuart and W. Marshall, Phys. Rev. **120**, 353 (1960). A similar investigation based on the more exact definition of the exchange integral presented here has been carried out by A. J. Freeman and R. E. Watson *Theory of Direct Exchange in Ferromagnetism* (available in preprint; to be published).

The two papers on the application of the alternant molecular orbital method to the linear chain by Pauncz, de Heer, and Löwdin has now been accepted for publication in J. Chem. Phys.

Theory of Magnetic Properties of Molecules with Particular Emphasis on the Hydrogen Molecule*

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I. INTRODUCTION

DURING the last decade a considerable amount of work has been reported on the calculation of molecular diamagnetic susceptibilities and of proton shielding constants. Although there is not much resemblance between these two quantities from an experimental point of view, their calculations show many points of similarity and it is therefore profitable to consider the theories of both phenomena simultaneously. The theoretical value of a molecular diamagnetic susceptibility χ may be derived from a study of the interaction between the electronic motion in the molecule and a homogeneous magnetic field $\mathbf{H}$, whereas a theoretical determination of a proton shielding constant σ involves a calculation of the interaction between the electronic motion, a homogeneous magnetic field $\mathbf{H}$, and an infinitesimally small magnetic dipole $\mathbf{\mu}$ at the position of the proton. Widely different methods for calculating these interaction terms have been suggested. The present paper gives a critical evaluation of the various approaches and investigates whether there are any connections between them. In particular we wish to discuss a few questions that are connected with calculations of χ and σ from gauge invariant atomic orbitals that were either overlooked or not satisfactorily answered in previous work.

A necessary condition that has to be imposed on calculations of molecular magnetic properties is that they lead to correct, or at least reliable, numerical results. Therefore it is necessary to study not only the general theory but also the numerical applications. However, we do not wish to obscure the main points of the argument by many tedious numerical calculations,

so that we will take the hydrogen molecule as a basis of our discussion. This follows the customary trend in the calculations where each method is usually tested by applying it to the hydrogen molecule and extended to more complicated systems only after a satisfactory result has been obtained for the simple case. At least a qualitative discussion of the question as to whether each calculation for hydrogen can easily be extended to larger molecules is included in this paper.

We discuss the theory of diamagnetic susceptibilities first. This has the same basic problems as are encountered in calculations of σ but lacks some additional complications.

The various theories on diamagnetic susceptibilities and magnetic shielding constants are often subdivided into three sets, namely (1) those that are derived by means of perturbation theory, (2) those that are based on applications of Ritz' variational principle, and (3) those that make use of additional experimental information connected with the rotational magnetism of the molecule. It is shown that a distinction between the first two sets is artificial because all results may be derived from variational methods.

First we give a general survey of the various variational methods, next we investigate some questions that are connected with calculations from gauge invariant atomic orbitals, and after that we discuss the connection between diamagnetic susceptibilities and rotational magnetism.

II. VARIATIONAL METHODS

We are interested in finding the lowest eigenvalue E_0' of the equation

$$\mathcal{H}_{op}\Phi = E\Phi, \qquad (1)$$