THE RELATIVISTIC THEORY OF CHEMICAL BINDING

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Abstract

Starting from Breit's relativistic equation for a system of two electrons, it is shown that for a hydrogen molecule (or for a system of two electrons moving in a field of cylindrical symmetry) the component of the total angular momentum (J_z) along the axis of the molecule (axis of symmetry) is a constant of motion. Thus every eigenstate of the system is simultaneously an eigenstate of J_z also, and a state of the system will specify, besides its energy, only the eigenvalue of the component of the angular momentum parallel to the axis of symmetry. The form of the four large components of the wave function relating to their dependence on the azimuthal co-ordinates has been given.

The case of Russel-Saunders approximation has been considered in detail and the nature of the components of the wave function for the singlet and triplet states has been discussed. It is shown that the wave function for the ground state of the hydrogen molecule could be expressed as a sum of a set of symmetric functions of which the first term is the Heitler-London function, and that the wave function for a triplet state should be a superposition of anti-symmetric molecular orbitals. It is shown that relativistic theory brings about in a natural manner the facts relating to the ground state of the molecules C_2 and O_2. Finally, some remarks are made concerning the case of molecules for which the spin-orbit and the spin-spin couplings are strong.

I. Introduction

The theoretical solution of problems of molecular chemistry are based usually on one or the other of two methods, known as the Molecular Orbital Theory and the Valence Bond Theory.[1] In the former method, the binding electron is supposed to belong to the entire molecule and is assumed to be moving in the average potential field of the other electrons and the nuclei. The latter is the well-known theory of hydrogen molecule given by Heitler and London. An important consequence of this theory is that the ground state of the hydrogen molecule is the singlet state in which the spins of the two electrons are

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opposite to each other and that the states with the spins parallel to each other are unstable. In both the above-mentioned methods, the spin of the electron is introduced as an independent extraneous factor in such a way as to comply with the requirements of the Pauli Exclusion Principle, but is not brought out as an integral part of the theory itself. In view of the very important role that the spin of the electron plays in the chemical binding in molecules, it is desirable to develop a theory based on a relativistic equation which will bring out the spin as an essential part of the mathematical formalism itself, and to analyse the consequences of such a theory. This, precisely, is the object of the present paper.

II. The Hamiltonian of a System of Two Electrons

Let us consider a system of two electrons interacting with each other. Let ϕ^{I}, A^{I} and ϕ^{II}, A^{II} denote respectively the scalar and vector potentials of electrons I and II disregarding their interaction. A relativistic wave equation for a system of two electrons interacting with each other and with an external electromagnetic field was given by Breit[2] in the year 1929.

The equation is

$$\left\{ \begin{array}{l} p_0 + \sum_{k=1,\,2,\,3} (a_k{}^{\mathrm{I}} p_k{}^{\mathrm{I}} + a_k{}^{\mathrm{II}} p_k{}^{\mathrm{II}}) + (a_4{}^{\mathrm{I}} + a_4{}^{\mathrm{II}})\,mc \\[2mm] \qquad + \dfrac{e^2}{2cr} \left[\sum_k a_k{}^{\mathrm{I}} a_k{}^{\mathrm{II}} + \dfrac{(a^{\mathrm{I}} \cdot \mathbf{r})\,(a^{\mathrm{II}} \cdot \mathbf{r})}{r^2} \right] \end{array} \right\} \psi = 0 \qquad (1)$$

where

$$p_k{}^{\mathrm{I}} =]- i\hbar \frac{\partial}{\partial x_k{}^{\mathrm{I}}} + \left(\frac{e}{c}\right) A_k{}^{\mathrm{I}};$$

$$p_k{}^{\mathrm{II}} = - i\hbar \frac{\partial}{\partial x_k{}^{\mathrm{II}}} + \left(\frac{e}{c}\right) A_k{}^{\mathrm{II}}$$

and

$$p_0 = \frac{i\hbar}{c} \frac{\partial}{\partial t} + \frac{e}{c} (\phi^{\mathrm{I}} + \phi^{\mathrm{II}}) - \frac{e^2}{cr} \qquad (2)$$

The matrices $a_k{}^{\mathrm{I}}$ and $a_k{}^{\mathrm{II}}$ are the usual Dirac matrices, but now they operate on the first and second suffixes respectively. The representations that we choose for these are given in Appendix I. The wave function ψ has sixteen components which will be designated by ψ_{mn} ($m, n = 1, 2, 3, 4$), the first

suffix m referring to electron I and the second suffix n referring to electron II. If a^I and b^{II} be any of the above-mentioned matrices, then

$$(a^I b^{II} \psi)_{m,n} = \sum_{k,l} a_{mk}{}^I b_{nl}{}^{II} \psi_{kl} \tag{3}$$

Equation (1) is thus equivalent to sixteen differential equations in the sixteen functions ψ_{mn}.

By writing in (1)

$$a_1 = \rho_1 \sigma_1; \qquad a_2 = \rho_1 \sigma_2; \qquad a_3 = \rho_1 \sigma_3 \tag{4}$$

where ρ_1, σ_1, σ_2, σ_3 are the matrices (4) of Appendix I, we see that the Hamiltonian of the system is given by

$$H = e\,(\phi^I + \phi^{II}) + \frac{e^2}{r} - \rho_1{}^I c\,(\sigma^I \cdot \mathbf{p}^I)$$

$$- \rho_1{}^{II} c\,(\sigma^{II} \cdot \mathbf{p}^{II}) - mc^2\,(a_4{}^I + a_4{}^{II})$$

$$- \frac{e^2}{2r}\left[(\rho_1{}^I \sigma^I \cdot \rho_1{}^{II} \sigma^{II}) + \frac{(\rho_1{}^I \sigma^I \cdot \mathbf{r})(\rho_1{}^{II} \sigma^{II} \cdot \mathbf{r})}{r^2} \right] \tag{5}$$

III. THE x-COMPONENT OF THE TOTAL ANGULAR MOMENTUM

We shall consider the case of the hydrogen molecule which is the simplest example of a two-electron molecular system. Let the origin be chosen at one of the nuclei and let the line of action of the molecule coincide with the positive direction of the x-axis. If the nuclei are denoted by the suffixes A and B, the potentials ϕ^I and ϕ^{II} are given by

$$\phi^I = e\left(\frac{1}{r_{a_1}} + \frac{1}{r_{b_1}} \right)$$

and

$$\phi^{II} = e\left(\frac{1}{r_{a_2}} + \frac{1}{r_{b_2}} \right)$$

where $r_a = \sqrt{x^2 + y^2 + z^2}$ and $r_b = \sqrt{(x - R)^2 + y^2 + z^2}$, R being the internuclear distance.

Let $m_x{}^I$ and $m_x{}^{II}$ denote the x-component of the orbital angular momenta of electrons I and II respectively. Then the dynamical variable

$M_x = (m_x{}^I + m_x{}^{II})$ represents the x-component of the total orbital angular momentum of the system. In the same way, the quantity

$$S_x = \frac{\hbar}{2}(\sigma_x{}^I + \sigma_x{}^{II})$$

gives the component of the total spin angular momentum parallel to the axis of the molecule. The sum J_x of these two (*i.e.*)

$$J_x = m_x{}^I + m_x{}^{II} + \frac{\hbar}{2}(\sigma_x{}^I + \sigma_x{}^{II}) \tag{6}$$

represents therefore the x-component of the *total* angular momentum of the system parallel to the axis of the molecule.

It has been proved in Appendix II that

$$J_x H - H J_x = 0 \tag{7}$$

One can see from the Appendix that neither S_x nor M_x commutes with the Hamiltonian but only their sum has the property of commuting with H.

Thus the component of the total angular momentum parallel to the axis of the molecule is a constant of motion.

Since J_x commutes with H, every eigenfunction of H will be simultaneously an eigenfunction of J_x also. An eigenstate, thus, is specified by two parameters, namely, the energy of the state and the eigenvalue of the component of the total angular momentum parallel to the axis of the molecule.

IV. THE EIGEN ψ'S OF J_x

Let us denote the eigenvalues of J_x by $M\hbar$ where M is yet undetermined. The equation

$$J_x \psi = M\hbar\psi \tag{8 a}$$

or

$$\left[m_x{}^I + m_x{}^{II} + \frac{\hbar}{2}(\sigma_x{}^{II} + \sigma_x{}^{II}) \right] \psi = M\hbar\psi \tag{8 b}$$

will then be equivalent to sixteen equations in the sixteen components of ψ. We write here only four of these equations, namely, those involving the four large components ψ_{33}, ψ_{34}, ψ_{43} and ψ_{44} of ψ. From (3), it follows that the (3, 3), (3, 4), (4, 3) and (4, 4)th components of the equation (8) are given by

$$- i \left(\frac{\partial}{\partial \phi_1} + \frac{\partial}{\partial \phi_2} \right) \psi_{33} = (M - 1) \psi_{33}$$

$$- i \left(\frac{\partial}{\partial \phi_1} + \frac{\partial}{\partial \phi_2} \right) \psi_{34} = M \psi_{34}$$

$$- i \left(\frac{\partial}{\partial \phi_1} + \frac{\partial}{\partial \phi_2} \right) \psi_{43} = M \psi_{43}$$

$$- i \left(\frac{\partial}{\partial \phi_1} + \frac{\partial}{\partial \phi_2} \right) \psi_{44} = (M + 1) \psi_{44} \tag{9}$$

Hence

$$\psi_{33} = f_{33} (r_1, r_2, \theta_1, \theta_2) e^{i (\overline{m_1 - 1} \phi_1 + m_2 \phi_2)}$$

$$\psi_{34} = f_{34} (r_1, r_2, \theta_1, \theta_2) e^{i (m_1 \phi_1 + m_2 \phi_2)}$$

$$\psi_{43} = f_{43} (r_1, r_2, \theta_1, \theta_2) e^{i (m_1 \phi_1 + m_2 \phi_2)}$$

$$\psi_{44} = f_{44} (r_1, r_2, \theta_1, \theta_2) e^{i (m_1 \phi_1 + \overline{m_2 + 1} \phi_2)} \tag{10}$$

where $m_1 + m_2 = M$.

Since the ψ's should be single-valued, the numbers m_1 and m_2 are integers.

One can verify that the other twelve small components satisfy differential equations of the type (9) and their form is therefore similar to the expressions given by (10).

Now it has been shown by Breit[2, 3] that equation (1) involving sixteen components can be reduced to an approximate equation with four components expressed in terms of Pauli's spin matrices. This reduced equation is given by (6) of Appendix I and is equivalent to a set of four equations in the four large components of ψ which, following Breit, we denote by ψ_{33}, ψ_{34}, ψ_{43} and ψ_{44} respectively. Since the equation (6) of Appendix I is sufficient for all physical purposes and gives quantitative results correct to the order of $(v/c)^2$, we shall in the following sections be discussing the consequences following from this only.

The matrices σ^I and σ^{II} in (6) of Appendix I are the Pauli matrices and they operate on the suffixes 3 and 4. The operation rule for the product of any two matrices on ψ is still governed by (3), but now the summation for k or l extends over the numbers 3 and 4 only. One can verify that the equation $J_x \psi = M \hbar \psi$ is identical with the four equations given by (9), and the form of the four large components is therefore still given by the equations (10).

By solving the simultaneous differential equations (7), Appendix I, one can determine the functions ψ_{33}, ψ_{34}, ψ_{43} and ψ_{44} respectively. Thus a state ψ which we denote by the column vector $[\psi_{33}, \psi_{34}, \psi_{43}, \psi_{44}]$ consists in general of four non-zero components.

V. THE RUSSEL-SAUNDERS COUPLING

When the spin-orbit interaction is small compared to the electrostatic interaction of the two electrons, the terms involving B^I, B^{II}, C_{xy} as well as the last four terms in the expression for A in equation (6, Appendix I) could be ignored in the first approximation. This is the assumption underlying the case of the well-known Russel-Saunders coupling. The equations (7, Appendix I) now reduce to

$$(H - W)\, \psi_{33} = 0; \qquad\qquad (H - W)\, \psi_{34} = 0$$
$$(H - W)\, \psi_{43} = 0; \qquad\qquad (H - W)\, \psi_{44} = 0 \qquad (11)$$

where H is the non-relativistic Hamiltonian of the system. The above equations are satisfied by four different states of the system in each of which all components, excepting one, are zero. Thus, solutions of (11) exist which have the form

$$\psi_1 = [\psi_{33}, 0\ \ 0, 0]; \qquad\qquad \psi_2{}' = [0, \psi_{34}, 0, 0]$$
$$\psi_3{}' = [0, 0, \psi_{43}, 0]; \qquad\qquad \psi_4 = [0, 0, 0, \psi_{44}]$$

Since the spin-orbit coupling terms are neglected in the Hamiltonian (6, Appendix I), one can see that both

$$M_x = m_x{}^I + m_x{}^{II} \qquad \text{and} \qquad S_x = \frac{\hbar}{2}\,(\sigma_x{}^I + \sigma_x{}^{II})$$

are constants of motion in this case, and further ψ_1 and ψ_4 are states belonging to the eigenvalues $\hbar$ and $-\hbar$ of S_x respectively, whereas the states $\psi_2{}'$ and $\psi_3{}'$ have zero as the eigenvalue of S_x. From the form of ψ_{34} and ψ_{43} in (10), one can see that the states

$$\psi_2 = \psi_2{}' + \psi_3{}' = [0, \psi_{34}, \psi_{43}, 0]$$

and

$$\psi_3 = \psi_2{}' - \psi_3{}' = [0, \psi_{34}, -\psi_{43}, 0]$$

have the eigenvalue M for the x-component of the total orbital angular momentum and zero for the x-component of the total spin angular momentum. Further if

$$\Sigma^2 = \tfrac{1}{4}\,[(\sigma_x{}^I + \sigma_x{}^{II})^2 + (\sigma_y{}^I + \sigma_y{}^{II})^2 + (\sigma_z{}^I + \sigma_z{}^{II})^2]$$

one can verify from (3) that the states ψ_1, ψ_2 and ψ_4 are eigenstates of Σ^2 belonging to the eigenvalue 2 (or the value 1 for Σ), and the state ψ_3 has the eigenvalue zero for Σ. The former set of states are thus the well-known triplet states of two electron systems whereas the state ψ_3 represents the singlet state.

Now according to the Pauli Exclusion Principle, every state should be anti-symmetric with respect to an exchange of the two electrons. An exchange operator, which we denote by P, interchanges the spin states of the two electrons as well as their positions and thus under its influence, a component of the state ψ_{mn} (1, 2) gets transformed into ψ_{nm} (2, 1). The state

$$\psi = [\psi_{33}(1, 2), \psi_{34}(1, 2), \psi_{43}(1, 2), \psi_{44}(1, 2)]$$

therefore changes into $\psi = [\psi_{33}(2, 1), \psi_{43}(2, 1), \psi_{34}(2, 1), \psi_{44}(2, 1)]$ under the influence of P. In order to satisfy the Exclusion Principle, the following relations should therefore be obeyed by the components of a state: (1) $\psi_{33}(2, 1) = -\psi_{33}(1, 2)$; (2) $\psi_{34}(2, 1) = -\psi_{43}(1, 2)$ and (3) $\psi_{44}(2, 1) = -\psi_{44}(1, 2)$. One can see that the states ψ_1 and ψ_4 will be anti-symmetric if the components ψ_{33} and ψ_{44} are anti-symmetric functions of the position of the two electrons. Since ψ_{34} and ψ_{43} are solutions of the same Schroedinger equation in the Russel-Saunders approximation, the state ψ_2 will be anti-symmetric if its components ψ_{34} and ψ_{43} are such that $\psi_{34}(1, 2) = \psi_{43}(1, 2) = -\psi_{34}(2, 1) = -\psi_{43}(2, 1)$, and similarly the state ψ_3 will be anti-symmetric if

$$\psi_{34}(1, 2) = \psi_{34}(2, 1) = -\psi_{43}(1, 2) = -\psi_{43}(2, 1)$$

(a) *The symmetric and anti-symmetric states.*—Let $\psi_{nlm}(r_{a_1})$ ...... denote a complete set of eigenfunctions of a hydrogen atom whose nucleus is at position A. Then these functions form a complete basis for the expansion of any arbitrary single-valued function of the position $r_1 = (x_1, y_1, z_1)$ of the electron 1. Similarly, the set of eigenfunctions ($\psi_{n'l'm'}(r_{b_2})$ of a hydrogen atom with its nucleus in position B form a complete set of eigenfunctions for the expansion of an arbitrary function of the position r_2 of the electron 2. Then, by a well-known theorem,[4] the set of functions

$$\psi_{nlm}(r_{a_1}) \, \psi_{n'l'm'}(r_{b_2}) \begin{pmatrix} n = 1, 2 \ldots\ldots\ldots \\ n' = 1, 2 \ldots\ldots\ldots \end{pmatrix}$$

form a complete basis for the expansion of an arbitrary function $\psi(r_1, r_2)$ of the two electrons, that vanishes when $r_1 \to \infty$ and $r_2 \to \infty$. Thus we can write

$$\psi(r_1, r_2) = \sum_{nn'} F_{nn'} \, \psi_n(r_{a_1}) \, \psi_{n'}(r_{b_2}) \tag{12}$$

where we have written n and n' for the set of three quantum numbers (n, l, m) and (n', l', m') of the hydrogen atoms.

Now if the wave function $\psi\,(\mathbf{r_1}, \mathbf{r_2})$ is symmetric with respect to an interchange of the two electrons, we get from (12) by interchanging the suffixes (1) and (2) that

$$\psi\,(\mathbf{r_1}, \mathbf{r_2}) = \sum_{nn'} F_{nn'}\,\psi_n\,(\mathbf{r}_{a_2})\,\psi_{n'}\,(\mathbf{r}_{b_1}) \tag{13}$$

The above equation alternatively follows from the expansion of $\psi\,(\mathbf{r_1}, \mathbf{r_2})$ in terms of the set of functions $\psi_n\,(\mathbf{r}_{a_2})\,\psi_{n'}\,(\mathbf{r}_{b_1}) \ldots$ which also form a complete basis for the expansion of a function of the two electrons.

By adding (12) and (13)* we see that any symmetric function of the electrons 1 and 2 can be written as

$$\psi^+\,(\mathbf{r_1}, \mathbf{r_2}) = \sum_{nn'} f_{nn'}\,[\psi_n\,(\mathbf{r}_{a_1})\,\psi_{n'}\,(\mathbf{r}_{b_2}) + \psi_n\,(\mathbf{r}_{a_2})\,\psi_{n'}\,(\mathbf{r}_{b_1}) \tag{14}$$

where $f_{nn'} = \frac{1}{2} F_{nn'}$. The suffix $+$ has been used to indicate that the function ψ is symmetric with respect to an interchange of the electrons.

In the same way we can see that an anti-symmetric function $\psi^-\,(\mathbf{r_1}, \mathbf{r_2})$ of the electrons has the form

$$\psi^-\,(r_1, r_2) = \sum_{nn'} g_{nn'}\,[\psi_n\,(\mathbf{r}_{a_1})\,\psi_{n'}\,(\mathbf{r}_{b_2}) - \psi_n\,(\mathbf{r}_{a_2})\,\psi_{n'}\,(\mathbf{r}_{b_1})] \tag{15}$$

(b) *The singlet state.*—We have seen before that the singlet state ψ_3 is represented by the vector $[0, \psi_{34}{}^+, -\psi_{34}{}^+, 0]$ where $\psi_{34}{}^+$ is a symmetric function of the two electrons. Now from the equations (10) it follows that ψ_{34} has the form given by

$$\psi_{34} = f_{34}\,(r_1, r_2, \theta_1, \theta_2)\,e^{i\,(m_1\phi_1 + m_2\phi_2)} \tag{10 a}$$

where m_1 and m_2 are integers satisfying the relation $m_1 + m_2 = M$. Thus the general form of ψ_{34} consists of a superposition of terms of the type (10 a) for all integral values of m_1 and m_2 satisfying the condition $m_1 + m_2 = M$.

Let us consider the case where the component of the total angular momentum parallel to the axis of the molecule is zero, *i.e.*, $m_1 + m_2 = 0$ or $m_1 = -m_2$. It is well known that the ground state of the hydrogen molecule belongs to this species. Thus from (14) and (10 a) it follows that the eigenfunction of the ground state is given by

$$\psi_{34}{}^+\,(\mathbf{r_1}, \mathbf{r_2}) = \sum_{nlm}\,\sum_{n'l'} f_{nn'}\,[\psi_{nlm}\,(\mathbf{r}_{a_1})\,\psi_{n'l'-m}\,(\mathbf{r}_{b_2})$$
$$+ \psi_{nlm}\,(\mathbf{r}_{a_2})\,\psi_{n'l'-m}\,(\mathbf{r}_{b_1})] \tag{16}$$

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* We assume the absolute convergence of these series.

The first term of the above series is

$$[\psi_{100}(r_{a_1})\,\psi_{100}(r_{b_2}) + \psi_{100}(r_{a_2})\,\psi_{100}(r_{b_1})] \tag{17}$$

which is the well-known Heitler-London wave function. This function explains qualitatively in a satisfactory manner the chemical binding of the hydrogen molecule, but quantitatively it gives a value of 3·14 e.v. for the binding energy of the molecule, the observed value being 4·72 e.v. The quantitative inaccuracy of the Heitler-London function is not surprising when we recall that it is only the first term in the expansion of the wave function in terms of symmetric wave functions built from the hydrogen atomic orbitals. Since the discrepancy between the energy value derived from (17) and the experimentally observed one is not very large, one can hope that the series (16) converges rather rapidly and that the addition of a few more terms to (17) will lead one to the correct value for the binding energy of the molecule.

(c) *The triplet states.*—As an example of the triplet states, consider the state ψ_1 which is described by a non-vanishing anti-symmetric component $\psi_{33}^-(r_1, r_2)$ and three vanishing components. From (10) we have

$$\psi_{33} = f_{33}(r_1, r_2, \theta_1, \theta_2)\,e^{i\,(m_1\phi_1 + m_2\phi_2)} \tag{18}$$

where $m_1 + m_2 = (M - 1)$.

Since the component of the total spin angular momentum for this state is $\hbar$, the component of the total orbital angular momentum is equal to $(M - 1)\hbar$. The general form of ψ_{33} will consist of a superposition of terms of the type (18) for all integral values of m_1 and m_2 satisfying the relation $m_1 + m_2 = (M - 1)$. Thus from (15) it follows that ψ_{33}^- is given by

$$\psi_{33}^-(r_1, r_2) = \sum_{nlm}\sum_{n'l'm'} g_{nn'}\,[\psi_{nlm}(r_{a_1})\,\psi_{n'l'm'}(r_{b_2})$$

$$- \psi_{nlm}(r_{a_2})\,\psi_{n'l'm'}(r_{b_1})] \tag{19}$$

where $m + m' = (M - 1)$.

In other words, the state ψ_1 is a superposition of all anti-symmetric molecular states for which the component of the total orbital angular momentum is equal to $(M - 1)\hbar$. In the same way we can obtain the wave function for the state ψ_4 by superposing anti-symmetric molecular states have the eigenvalue $(M + 1)\hbar$ for the component of the total orbital angular momentum parallel to the axis of the molecule.

Regarding the state ψ_2 we shall consider the particular case $M = 0$. ψ_2 is described by the vector $[0, \psi_{34}^-, \psi_{34}^-, 0]$ where ψ_{34}^- is anti-symmetric

with respect to an interchange of the two electrons. From (15) and (10 a) it follows that the form of ψ_{34}^{-} is given by

$$\psi_{34}^{-}\,(r_1, r_2) = \sum_{nlm} \sum_{n'l'} g_{nn'}\,[\psi_{nlm}\,(r_{a_1})\,\psi_{n'l'-m}\,(r_{b_2})$$

$$- \psi_{nlm}\,(r_{a_2})\,\psi_{n'l'-m}\,(r_{b_1})\qquad\qquad (20)$$

The first term of the above series is

$$[\psi_{100}\,(r_{a_1})\,\psi_{100}\,(br_2) - \psi_{100}\,(ar_2)\,\psi_{100}\,(r_{b_1})]\qquad\qquad (21)$$

It is a well-known fact that this function leads to an unstable chemical state.

(*d*) *The case of* C_2 *and* O_2.—From (19) or (20), it follows that the wave function for a triplet state is a superposition of a number of terms each of which is anti-symmetric with respect to an interchange of the two electrons. Further, all the terms in a series belong to the same species, *i.e.*, the states belonging to these terms have all the same eigenvalue for the x-component of the total orbital angular momentum.

According to the Heitler-London theory, the ground state of the hydrogen molecule is the singlet state and the triplet states are unstable. The theory therefore requires as an essential condition for a stable bond that the spins of the two electrons should be antiparallel. This rule is obeyed by a large class of molecules, but nevertheless, exceptions are also present of which we may cite the examples of C_2 and O_2. The ground state of C_2 is the state designated in spectroscopic notation by $^3\Pi_u$ whereas for oxygen, the ground state is $^3\Sigma_g^-$. Oxygen is in addition paramagnetic. Heitler[6] and Nordheim-Poschl[7] showed that by adding to the wave function (21) a few more terms of the same species, or in other words, by taking into account the interaction between states of the same species, the deviations between theory and experiment can be removed. Now in the Russel-Saunders approximation, Σ has the value 1 for the triplet states and Σ_z has the values 1, 0, -1 respectively for the states ψ_1, ψ_2 and ψ_4. Further each term in (19) or (20) corresponds to the same value of the component of the total orbital angular momentum parallel to the axis of the molecule. The expansion (19) is, therefore, nothing but a superposition of states of the same species. Relativistic theory offers thus a clear explanation of the facts relating to C_2 and O_2 and brings about naturally the concept of interaction of states of the same species.

VI. Strong Spin-Orbit Coupling

The discussion of the last section holds good only for the case of Russel-Saunders coupling. Strictly speaking, the Russel-Saunders coupling and the

j-j coupling are two extreme ideal cases and the coupling in most cases is intermediate. When the spin-orbit interaction is strong compared to the electrostatic interaction of the two electrons, the above discussion will break down. In such a case, only the component of the total angular momentum along the axis is a constant of motion and none of the quantities Σ, Σ_x and M_x is a constant of motion. An eigenstate of the energy will be an eigenstate of J_x also and conversely every state of the system will specify, besides the energy, only the *x*-component of the total angular momentum. For the case of strong spin-orbit coupling, the usual spectroscopic notation which presumes that all the quantities Σ, Σ_x and M_x are constants of motion, is therefore inconsistent with theoretical considerations and requires modification.

When the spin-orbit coupling is strong, the solution of the equations (7, Appendix I) will lead to non-zero values for all the four components of the wave function. Further it follows from equations (6) and (7) of Appendix I that a state will be anti-symmetric with respect to an interchange of electrons only if the components have the following properties:

(1) $\psi_{33}(2, 1) = -\psi_{33}(1, 2)$;

(2) $\psi_{34}(2, 1) = -\psi_{43}(1, 2)$;

(3) $\psi_{44}(2, 1) = -\psi_{44}(1, 2)$.

Thus ψ_{33} and ψ_{44} are anti-symmetric functions, while ψ_{34} or ψ_{43} can be a mixture of both symmetric and anti-symmetric functions. The form of the former components is therefore given by (15) while the latter can be expanded as a series of the type (12). Now the energy of the system is given by

$$W = \frac{\int \psi^* H \psi \, d\tau_1 d\tau_2}{\int \psi^* \psi \, d\tau_1 d\tau_2} \tag{22}$$

where ψ^* is the transpose of the vector ψ and is given by the *row* vector $[\psi_{33}^*, \psi_{34}^*, \psi_{43}^*, \psi_{44}^*]$.

In practice, the computation of the energy will be facilitated if (1) the series for the function ψ_{33}, etc., are terminated at a particular point and their coefficients determined by the variational principle and (2) if use is made of the tables giving the values of exchange, coulomb and other related integrals.[8, 9, 10]

We can now interpret the quantities ψ_{33}^2, $\psi_{34}^2 + \psi_{43}^2$ and ψ_{44}^2 as the probabilities of finding the spins of the electrons respectively (1) parallel to the *x*-axis, (2) opposite to each other and (3) parallel to the negative direction of the *x*-axis. The ground state of the molecule will be the state having the

least value for the energy of all the states, subject to the condition that it is stable besides.

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APPENDIX I

For the sake of easy reference, we collect here some of the results and equations of Breit that are made use of in the paper. The relativistic wave equation of Breit is given by

$$
\left[
\begin{array}{l}
p_0 + \sum_{k=1,2,3} (a_k{}^{I} p_k{}^{I} + a_k{}^{II} p_k{}^{II}) + (a_4{}^{I} + a_4{}^{II})\, mc \\[2mm]
\quad + \dfrac{e^2}{2cr} \left\{ \sum_k a_k{}^{I} a_k{}^{II} + \dfrac{(a^{I} \cdot r)(a^{II} \cdot r)}{r^2} \right\}
\end{array}
\right] \psi = 0
\qquad (1)
$$

Here p_0, p^{I} and p^{II} are given by equations (2) of Section II. The wave function ψ has sixteen components which are denoted by ψ_{mn} ($m, n = 1, 2, 3, 4$). The matrices a^{I} and σ^{II} are the usual Dirac matrices, but now they operate on the suffixes I and II respectively. They are given by

$$
a_1 = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix} ; \qquad
a_2 = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} ;
$$

$$
\qquad (2)
$$

$$
a_3 = \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{pmatrix} ; \qquad
a_4 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}
$$

If we set

$$
a_1 = \rho_1 \sigma_1 ; \qquad a_2 = \rho_1 \sigma_2 ; \qquad a_3 = \rho_1 \sigma_3 ,
\qquad (3)
$$

where

$$
\sigma_1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} ; \qquad
\sigma_2 = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} ;
$$

$$\sigma_3 = \begin{pmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{pmatrix} ; \quad \rho_1 = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}$$

equation (1) becomes

$$\left\{ \begin{aligned} & p_0 + \rho_1{}^{I} (\sigma^{I} \cdot \mathbf{p}^{I}) + \rho_1{}^{II} (\sigma^{II} \cdot \mathbf{p}^{II}) + (\alpha_4{}^{I} + \alpha_4{}^{II}) \, mc \\ & + \frac{e^2}{2cr} \left[(\rho_1{}^{I}\sigma^{I} \cdot \rho_1{}^{II}\sigma^{II}) + \frac{(\rho_1{}^{I}\alpha^{I} \cdot \mathbf{r})(\rho_1{}^{II}\alpha^{II} \cdot r)}{r^2} \right] \end{aligned} \right\} \psi = 0 \qquad (5)$$

It follows that the Hamiltonian of the system is given by equation (5) of Section II.

Next the Breit equation in the Schroedinger-Pauli form is given by

$$\left\{ E - 2mc^2 + eV - \frac{1}{2m} [(p^{I})^2 + (p^{II})^2] + \frac{(p^{I})^4 + (p^{II})^4}{8m^3c^3} \right.$$

$$+ \frac{e^2}{2m^2c^2} [r^{-1} (\mathbf{p}^{I}, \mathbf{p}^{II}) + r^{-3} (x_i{}^{II} - x_i{}^{I})(x_j{}^{II} - x_j{}^{I}) \, p_i{}^{I} p_j{}^{II}]$$

$$+ \frac{eh}{4\pi mc} [(\mathbf{H}^{I}, \sigma^{I}) + (\mathbf{H}^{II}, \sigma^{II})] + \frac{ehi}{8\pi m^2c^2} [(\mathscr{E}^{I}, \mathbf{p}^{I}) + (\mathscr{E}^{II}, \mathbf{p}^{II})]$$

$$+ \frac{eh}{8\pi mc^2} \left[\left(\mathscr{E}^{I} \times \frac{\mathbf{p}^{I}}{m}, \sigma^{I} \right) + \left(\mathscr{E}^{II} \times \frac{\mathbf{p}^{II}}{m}, \sigma^{II} \right) \right.$$

$$\left. + 2e \left(\frac{\mathbf{r}^{I} - \mathbf{r}^{II}}{r^3} \times \frac{\mathbf{p}^{II}}{m}, \sigma^{I} \right) + 2e \left(\frac{\mathbf{r}^{II} - \mathbf{r}^{I}}{r^3} \times \frac{\mathbf{p}^{I}}{m}, \sigma^{II} \right) \right]$$

$$\left. - \left(\frac{eh}{4\pi mc} \right)^2 \langle (\nabla^{II}\sigma^{I})(\nabla^{I}\sigma^{II}) \, r^{-1} \rangle \right\} \psi = 0 \qquad (6)$$

where

$$\mathbf{H}^{I} = \text{curl } \mathbf{A}^{I}, \quad \mathbf{H}^{II} = \text{curl } \mathbf{A}^{II}$$

$$\mathscr{E}^{I} = - \text{grad}^{I} V = - \left(\frac{\partial}{\partial x^{I}}, \frac{\partial}{\partial y^{I}}, \frac{\partial}{\partial z^{I}} \right) V ;$$

$$V = \phi^{I} + \phi^{II} - \frac{e}{r} .$$

$\langle\ \rangle$ means the differential operators $\mathbf{p}^{\mathrm{I}}$, $\mathbf{p}^{\mathrm{II}}$ apply only within the $\langle\ \rangle$. The σ's are the Pauli matrices and have the representations given by

$$\sigma_x = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} ; \quad \sigma_y = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} ; \quad \sigma_z = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

Let us write

$$\mathbf{E} - 2mc^2 = \mathbf{W};$$

$$\mathbf{A} = e\mathbf{V} - \frac{1}{2m}\{(p^{\mathrm{I}})^2 + (p^{\mathrm{II}})^2\} + \frac{(p^{\mathrm{I}})^4 + (p^{\mathrm{II}})^4}{8m^3c^3}$$

$$+ \frac{e^2}{2m^2c^2}[r^{-1}\,\mathbf{p}^{\mathrm{I}}\cdot\mathbf{p}^{\mathrm{II}} + \Sigma\,r^{-3}(x_i^{\mathrm{II}} - x_i^{\mathrm{I}})(x_j^{\mathrm{II}} - x_j^{\mathrm{I}})\,p_i^{\mathrm{I}}p_j^{\mathrm{II}}]$$

$$+ \frac{ehi}{8\pi m^2c^2}\{(\mathscr{E}^{\mathrm{I}}, \mathbf{p}^{\mathrm{I}}) + (\mathscr{E}^{\mathrm{II}}, \mathbf{p}^{\mathrm{II}})\}.$$

$$\mathbf{B}^{\mathrm{I}} = \frac{eh}{8\pi mc^2}\left[\mathscr{E}^{\mathrm{I}} \times \frac{\mathbf{p}^{\mathrm{I}}}{m} + 2e\frac{\mathbf{r}^{\mathrm{I}} - \mathbf{r}^{\mathrm{II}}}{r^3} \times \frac{\mathbf{p}^{\mathrm{II}}}{m}\right] = (\mathrm{B}_x^{\mathrm{I}}, \mathrm{B}_y^{\mathrm{I}}, \mathrm{B}_z^{\mathrm{I}})$$

$$\mathbf{B}^{\mathrm{II}} = \frac{eh}{8\pi mc^2}\left[\mathscr{E}^{\mathrm{II}} \times \frac{\mathbf{p}^{\mathrm{II}}}{m} + 2e\frac{\mathbf{r}^{\mathrm{II}} - \mathbf{r}^{\mathrm{I}}}{r^3} \times \frac{\mathbf{p}^{\mathrm{I}}}{m}\right] = (\mathrm{B}_x^{\mathrm{II}}, \mathrm{B}_y^{\mathrm{II}}, \mathrm{B}_z^{\mathrm{II}})$$

and

$$-\left(\frac{eh}{4\pi mc}\right)^2 \langle(\nabla^{\mathrm{II}}, \sigma^{\mathrm{I}})(\nabla^{\mathrm{I}}, \sigma^{\mathrm{II}})\,r^{-1}\rangle = \Sigma\,C_{xy}\sigma_x^{\mathrm{I}}\sigma_y^{\mathrm{II}}$$

where

$$C_{xy} = -\left(\frac{eh}{4\pi mc}\right)^2 \frac{\partial}{\partial x^{\mathrm{II}}}\frac{\partial}{\partial y^{\mathrm{I}}}\,r^{-1}.$$

Then the equation (6) is equivalent to the following four equations:

$$(\mathrm{A} + \mathrm{B}_x^{\mathrm{I}} + \mathrm{B}_x^{\mathrm{II}} + C_{xx} + \mathrm{W})\,\psi_{33} + (\mathrm{B}_y^{\mathrm{II}} - i\mathrm{B}_z^{\mathrm{II}} + C_{xy} - iC_{xz})\,\psi_{34}$$
$$+ (\mathrm{B}_y^{\mathrm{I}} - i\mathrm{B}_z^{\mathrm{I}} + C_{yx} - iC_{zx})\,\psi_{43} + (C_{yy} - C_{zz}$$
$$- i\overline{C_{yz} + C_{zy}})\,\psi_{44} = 0.$$

$$(\mathrm{B}_y^{\mathrm{II}} + i\mathrm{B}_z^{\mathrm{II}} + C_{xy} + iC_{xz})\,\psi_{33} + (\mathrm{A} + \mathrm{B}_x^{\mathrm{I}} - \mathrm{B}_x^{\mathrm{II}} - C_{xx} + \mathrm{W})\,\psi_{34}$$
$$+ (C_{yy} + C_{zz})\,\psi_{43} + (\mathrm{B}_y^{\mathrm{I}} - i\mathrm{B}_z^{\mathrm{I}} - C_{yx} + iC_{zx})\,\psi_{44} = 0$$

$$\tag{7}$$

$$(\mathrm{B}_y^{\mathrm{I}} + i\mathrm{B}_z^{\mathrm{I}} + C_{yx} + iC_{zx})\,\psi_{33} + (C_{yy} + C_{zz})\,\psi_{34}$$
$$+ (\mathrm{A} + \mathrm{B}_x^{\mathrm{II}} - \mathrm{B}_x^{\mathrm{I}} - C_{xx} + \mathrm{W})\,\psi_{43} + (\mathrm{B}_y^{\mathrm{II}} - i\mathrm{B}_z^{\mathrm{II}} - C_{xy}$$
$$+ iC_{xz})\,\psi_{44} = 0$$

$$(C_{yy} - C_{zz} + i\overline{C_{yz} + C_{zy}})\,\psi_{33} + (B_y{}^I + iB_z{}^I - C_{yx} - iC_{zx})\,\psi_{34}$$
$$+ (B_y{}^{II} + iB_z{}^{II} - C_{xy} - iC_{xz})\,\psi_{43} + (A - B_x{}^I - B_x{}^{II}$$
$$+ C_{xx} + W)\,\psi_{44} = 0.$$

Appendix II

Proof of the relation $J_x H - H J_x = 0$.—We have seen that the Hamiltonian for a hydrogen molecule is given by

$$H = - e\,(\phi^I + \phi^{II}) + \frac{e^2}{r} - \rho_1{}^I c\,(\sigma^I \cdot \mathbf{p}^I) - \rho_1{}^{II} c\,(\sigma^{II} \cdot \mathbf{p}^{II})$$

$$- m_0 c^2\,(a_4{}^I + a_4{}^{II}) - \frac{e^2}{2r}\left\{\rho^I\sigma^I \cdot \rho_1{}^{II}\sigma^{II}) + \frac{(\rho_1\sigma^I \cdot \mathbf{r})\,(\rho_1{}^{II}\sigma^{II} \cdot \mathbf{r})}{r^2}\right\}$$

$$\tag{1}$$

where

$$\phi^I = e\left(\frac{1}{r_{a_1}} + \frac{1}{r_{b_1}}\right) \qquad \text{and} \qquad \phi^{II} = e\left(\frac{1}{r_{a_2}} + \frac{1}{r_{b_2}}\right);$$

r is the interelectronic distance. Each of the angular momentum variables $m_x{}^I$ and $m_x{}^{II}$ commutes with r_{a_1}, r_{b_1}, r_{a_2} and r_{b_2} and hence with the potentials ϕ^I and ϕ^{II}. Further

$$[m_x{}^I + m_x{}^{II}, r^2) = [m_x{}^I + m_x{}^{II}, \varSigma\, x_1{}^2 + \varSigma\, x_2{}^2 - 2\,\varSigma\, x_1 x_2]$$
$$= - 2\,(y_1 z_2 - y_2 z_1) - 2\,(y_2 z_1 - y_1 z_2) = 0 \tag{2}$$

$(m_x{}^I + m_x{}^{II})$ commutes with r^2 and hence with any function of r^2, particularly with $1/r$ and $1/r^3$.

Now

$$i\hbar\,(\dot{m}_x{}^I + \dot{m}_x{}^{II}) = (m_x{}^I + m_x{}^{II})\,H - H\,(m_x{}^I + m_x{}^{II}) \tag{3}$$

Since $(m_x{}^I + m_x{}^{II})$ commutes with ϕ^I, ϕ^{II}, $1/r$ and $1/r^3$, we have

$$i\hbar\,(\dot{m}_x{}^I + \dot{m}_x{}^{II}) = - c\rho_1{}^I\,\{m_x{}^I(\sigma^I \cdot \mathbf{p}^I) - (\sigma^I \cdot \mathbf{p}^I)\,m_x{}^I\}$$
$$- c\rho_1{}^{II}\,\{m_x{}^{II}(\sigma^{II} \cdot \mathbf{p}^{II}) - (\sigma^{II} \cdot \mathbf{p}^{II})\,m_x{}^{II}\}$$

$$- \frac{e^2}{2r^3}\left\{\begin{matrix}(m_x{}^I + m_x{}^{II})\,(\rho_1{}^I\sigma^I \cdot \mathbf{r})\,(\rho_1{}^{II}\sigma^{II} \cdot \mathbf{r}) \\ - (\rho_1{}^I\sigma^I \cdot \mathbf{r})\,(\rho_1{}^{II}\sigma^{II} \cdot \mathbf{r})\,(m_x{}^I + m_x{}^{II})\end{matrix}\right\} \tag{4}$$

Now

$$\{m_x{}^I(\sigma^I \cdot \mathbf{p}^I) - (\sigma^I \cdot \mathbf{p}^I)\,m_x{}^I\} = (\sigma^I, m_x{}^I\mathbf{p}^I - \mathbf{p}^I m_x{}^I)$$
$$= i\hbar\,(\sigma_2 p_3 - \sigma_3 p_2)^I \tag{5}$$

Similarly

$$\{m_x^{II} (\sigma^{II} \cdot p^{II}) - (\sigma^{II} \cdot p^{II}) m_x^{II}\} = i\hbar (\sigma_2 p_3 - \sigma_3 p_2)^{II} \tag{6}$$

Next the following Poisson bracket relations can be verified:

$$\left[m_x^I + m_x^{II}, \frac{(x_2 - x_1)(y_2 - y_1)}{r^3} \right] = \frac{(x_2 - x_1)(z_2 - z_1)}{r^3} ;$$

$$\left[m_x^I + m_x^{II}, \frac{(x_2 - x_1)(z_2 - z_1)}{r^3} \right] = \frac{(x_2 - x_1)(y_2 - y_1)}{r^3} ;$$

$$\left[m_x^I + m_x^{II}, \frac{(y_2 - y_1)(z_2 - z_1)}{r^3} \right] = \left[\frac{[(z_2 - z_1)^2 - (y_2 - y_1)^2]}{r^3} \right] ;$$

$$\left[m_x^I + m_x^{II}, \frac{(y_2 - y_1)^2}{r^3} \right] = \frac{2(y_2 - y_1)(z_2 - z_1)}{r^3} ;$$

$$\left[m_x^I + m_x^{II}, \frac{(z_2 - z_1)^2}{r^3} \right] = \frac{-2(y_2 - y_1)(z_2 - z_1)}{r^3} . \tag{7}$$

Hence if we denote the components of the vectors $\rho_1^I \sigma^I$ and $\rho_1^{II} \sigma^{II}$ by

$$(a_x^I, a_y^I, a_z^I) \quad \text{and} \quad (a_x^{II}, a_y^{II}, a_z^{II}),$$

we get from (3), (4), (5), (6) and (7) that

$$i\hbar (\dot{m}_x^I + \dot{m}_x^{II})$$

$$= - i\hbar c\rho_1^I (\sigma_2 p_3 - \sigma_3 p_2)^I - i\hbar c\rho_1^{II} (\sigma_2 p_3 - \sigma_3 p_2)^{II}$$

$$- \frac{i\hbar e^2}{2r^3} \left\{ \begin{array}{l} (a_x^I a_y^{II} + a_y^I a_x^{II})(x_2 - x_1)(z_2 - z_1) \\ - (a_x^I a_z^{II} + a_z^I a_x^{II})(x_2 - x_1)(y_2 - y_1) \\ + (a_y^I a_z^{II} + a_z^I a_y^{II})[(z_2 - z_1)^2 - (y_2 - y_1)^2] \\ + 2(a_y^I a_y^{II} - a_z^I a_z^{II})(y_2 - y_1)(z_2 - z_1) \end{array} \right\} \tag{8}$$

Next we have

$$(\sigma_x^I \sigma^I - \sigma^I \sigma_x^I, \mathbf{p}^I) = 2i (\sigma_3 p_2 - \sigma_2 p_3)^I$$

$$(\sigma_x^{II} \sigma^{II} - \sigma^{II} \sigma_x^{II}, \mathbf{p}^{II}) = 2i (\sigma_3 p_2 - \sigma_2 p_3)^{II} \tag{9}$$

Also

$$\left[\sigma_x^I + \sigma_x^{II}, \frac{(\rho_1^I \sigma^I \cdot \rho_1^{II} \sigma^{II})}{r^3} \right] = 0 \tag{10}$$

A2

Further

$$\sigma_x{}^{\mathrm{I}} (\rho_1{}^{\mathrm{I}} \mathbf{\circ}^{\mathrm{I}} \cdot \mathbf{r}) (\rho_1{}^{\mathrm{II}} \mathbf{\circ}^{\mathrm{II}} \cdot \mathbf{r}) - (\rho_1{}^{\mathrm{I}} \mathbf{\circ}^{\mathrm{I}} \cdot \mathbf{r}) (\rho_1{}^{\mathrm{II}} \mathbf{\circ}^{\mathrm{II}} \cdot \mathbf{r}) \sigma_x{}^{\mathrm{I}}$$

$$= 2i \{a_z{}^{\mathrm{I}} (y_2 - y_1) - a_y{}^{\mathrm{I}} (z_2 - z_1)\} \{a_x{}^{\mathrm{II}} (x_2 - x_1)$$

$$+ a_y{}^{\mathrm{II}} (y_2 - y_1) + a_z{}^{\mathrm{II}} (z_2 - z_1)\}$$

$$\sigma_x{}^{\mathrm{II}} (\rho_1{}^{\mathrm{I}} \mathbf{\circ}^{\mathrm{I}} \cdot \mathbf{r}) (\rho_1{}^{\mathrm{II}} \mathbf{\circ}^{\mathrm{II}} \cdot \mathbf{r}) - (\rho_1{}^{\mathrm{I}} \mathbf{\circ}^{\mathrm{I}} \cdot \mathbf{r}) (\rho_1{}^{\mathrm{II}} \mathbf{\circ}^{\mathrm{II}} \cdot \mathbf{r}) \sigma_x{}^{\mathrm{II}}$$

$$= 2i \{a_z{}^{\mathrm{II}} (y_2 - y_1) - a_y{}^{\mathrm{II}} (z_2 - z_1)\} \{a_x{}^{\mathrm{I}} (x_2 - x_1)$$

$$+ a_y{}^{\mathrm{I}} (y_2 - y_1) + a_z{}^{\mathrm{I}} (z_2 - z_1)\} \qquad (11)$$

From (9), (10) and (11), we get

$$i\hbar (\dot{\sigma}_x{}^{\mathrm{I}} + \dot{\sigma}_x{}^{\mathrm{II}})$$

$$= (\sigma_x{}^{\mathrm{I}} + \sigma_x{}^{\mathrm{II}}) \mathrm{H} - \mathrm{H} (\sigma_x{}^{\mathrm{I}} + \sigma_x{}^{\mathrm{II}})$$

$$= - 2ic\rho_1{}^{\mathrm{I}} (\sigma_3 p_2 - \sigma_2 p_3)^{\mathrm{I}} - 2ic\rho_1{}^{\mathrm{II}} (\sigma_3 p_2 - \sigma_2 p_3)$$

$$- \frac{2ie^2}{2r^3} \left\{ \begin{array}{l} (a_x{}^{\mathrm{I}}a_z{}^{\mathrm{II}} + a_z{}^{\mathrm{I}}a_x{}^{\mathrm{II}}) (y_2 - y_1) (x_2 - x_1) \\ + (a_z{}^{\mathrm{I}}a_y{}^{\mathrm{II}} + a_z{}^{\mathrm{II}}a_y{}^{\mathrm{II}}) \{(y_2 - y_1)^2 - (z_2 - z_1)^2\} \\ + 2 (a_z{}^{\mathrm{I}}a_z{}^{\mathrm{II}} - a_y{}^{\mathrm{I}}a_y{}^{\mathrm{II}}) (y_2 - y_1) (z_2 - z_1) \\ - (a_y{}^{\mathrm{I}}a_x{}^{\mathrm{II}} + a_y{}^{\mathrm{II}}a_x{}^{\mathrm{I}}) (z_2 - z_1) (x_2 - x_1) \end{array} \right\} \quad (12)$$

From (8) and (12) it follows that

$$\dot{m}_x{}^{\mathrm{I}} + \dot{m}_x{}^{\mathrm{II}} + \frac{\hbar}{2} (\dot{\sigma}_x{}^{\mathrm{I}} + \dot{\sigma}_x{}^{\mathrm{II}}) = 0.$$

Or, in other words,

$$\mathrm{J}_x = m_x{}^{\mathrm{I}} + m_x{}^{\mathrm{II}} + \frac{\hbar}{2} (\sigma_x{}^{\mathrm{I}} + \sigma_x{}^{\mathrm{II}}) \text{ is a constant of motion.}$$

Fields possessing cylindrical symmetry.—Though the above result has been proved for the case of a hydrogen molecule only, it holds good in general for any system of two electrons moving in a field possessing cylindrical symmetry. If the x-axis is chosen as the axis of symmetry, the potentials ϕ^{I} and ϕ^{II} in this case are functions of two variables only, i.e., $\phi^{\mathrm{I}} = \phi^{\mathrm{I}} (x_1, r_1)$ and $\phi^{\mathrm{II}} = \phi^{\mathrm{II}} (x_2, r_2)$, r_1 and r_2 being the distances of the electrons from the origin. Since $\mathrm{M}_x = m_x{}^{\mathrm{I}} + m_x{}^{\mathrm{II}}$ commutes with all the variables x_1, x_2, r_1 and r_2, it commutes with the first term in the Hamiltonian (1). The remaining terms do not involve ϕ^{I} or ϕ^{II} and are the same as for the hydrogen molecule. Thus for a system of two electrons moving in a field of cylindrical symmetry, the component of the total angular momentum along the axis of symmetry is a constant of motion. Since for most diatomic molecules and individual bonds in complex molecules the charge cloud approximately satisfies cylindrical symmetry, the above result can be applied to such cases also.