THE MANY ELECTRON WAVE EQUATION
IN THE SCHRÖDINGER-PAULI FORM

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1. INTRODUCTION

A generalisation of the Dirac equation for systems containing many electrons will find its applications in several branches of physics and will be of use especially in calculating the relativistic effects in many electron systems as well as in understanding precisely chemical binding and spins in complex molecular systems. It was shown in an earlier paper¹ that by considering a four vector whose components denote respectively the three components of the total momentum and the total energy of a dynamical system, one can obtain a generalisation of the Dirac equation. For a single electron moving in a field, the magnitude of the momentum four vector is equal to \( m \)\( \gamma \), \( m \) being the rest mass of the particle, and the magnitude can also be expressed as \( \sum_{\mu=1}^{4} \gamma_\mu [P_\mu + (e/c) A_\mu] \) where the \( \gamma \)'s are four-dimensional matrices satisfying the relations \( \gamma_\mu \gamma_\nu + \gamma_\nu \gamma_\mu = 2\delta_{\mu\nu} \). Equating these two expressions and making them operate on the state vector \( \psi \), one obtains an alternative elegant method of deriving the Dirac equation. It therefore appears obvious that a natural generalisation of the Dirac equation should proceed from a consideration of the magnitude of the total momentum four vector whose components (three momenta and the energy of the system) represent quantities of utmost physical significance. Such an equation involves no approximation, and it was further shown that a representation of the generalised Dirac equation in the product space of the electrons leads to equation (1) of the present paper which is a generalisation of the Breit equation for systems containing two electrons.

Equation (1) is correct to terms of the order \( (v^2/c^2) \), and includes the retardation effects arising from the fact that the velocity of propagation of interactions is finite in relativity theory and is equal to the velocity of light. The matrices \( a \) are of order \( 4^N \), and the wave function \( \psi \) has also got \( 4^N \) components. Of these, only \( 2^N \) components have large values, the rest being small. For two electron systems, Breit²,³ has earlier obtained an equation satisfied by the four large components, which involves the Pauli matrices only. It is the object of the present paper to generalise Breit's
reduced equation for many electron systems, and to derive an equation in
the $2^N$ large components of the wave equation by eliminating all the remain-
ing small components from equation (1).

II. THE WAVE EQUATION

It has been shown in a previous paper that the many electron wave
equation can be written as

$$\left( P_0 + \frac{e}{c} A_0 \right) + \sum_{i=1}^{N} \sum_{k=1}^{3} a_k^i P_{k}^i + mc \left( \sum_{i=1}^{N} \beta^i \right)$$

$$+ \frac{e^2}{2c} \left[ \sum_{i<j}^{N} \frac{\alpha^i \cdot \alpha^j}{r_{ij}} + \sum_{i<j}^{N} \frac{(\alpha^i \cdot r_{ij})(\alpha^j \cdot r_{ij})}{r_{ij}^3} \right] \Psi = 0 \quad (1)$$

where

$$P_0 = \frac{i\hbar}{c} \frac{\partial}{\partial t} ;$$

$$P_{k}^i = -i\hbar \frac{\partial}{\partial x_{k}^i} ; \quad (2)$$

$$a_k^i = I_4 \times I_4 \times \cdots \times a_k \times I_4 \cdots \times I_4;$$

$$\beta^i = I_4 \times I_4 \times \cdots \times \beta \times I_4 \cdots \times I_4. \quad (3)$$

In the above, the upper suffix $i$ corresponds to the $i$-th electron, and
$(x_1^i, x_2^i, x_3^i)$ denote the co-ordinates of the $i$-th electron. $I_4$ denotes the
unit matrix of order four, and $a_1, a_2, a_3$ and $\beta$ have the representations
(1) of Appendix I. Further in (3), $a_k$ and $\beta$ occur in the $i$-th place and the
$\times$ denotes direct product multiplication. Since the direct product of two
square matrices of orders $m$ and $n$ is of order $mn$, $a_k^i$ and $\beta^i$ are of order
$4^N$. The wave function $\Psi$ has consequently $4^N$ components, and we denote
a general component by $\psi_{i_1, i_2, \cdots, i_N}$, where $i_1, i_2, \cdots, i_N$ are integers which
assume one of the values 1, 2, 3 or 4. These suffixes signify the four different
spin states of the electrons 1, 2, $\cdots$, $N$ respectively.

If the electrons are moving in an external electric field $U$ then $A_0$ is
given by

$$A_0 = \sum_{i=1}^{N} U(r_i) - \sum_{i<j}^{N} \frac{e}{r_{ij}}. \quad (4)$$
Equation (1) was derived on the assumption that the electrons are moving in an electric field only; when a magnetic field is present, we have for $P_k^i$ the following expression.

$$\dot{P}_k^i = -i\hbar \frac{\partial}{\partial x_k^i} + \frac{e}{c} A_k^i$$

where $A_k^i (k = 1, 2, 3)$ are the components of the vector potential for the $i$-th electron.

Now

$$\dot{x}_k^i = [x_k^i, H]$$

where

$$H = -c \left\{ \frac{e}{c} A_0 + \sum_{i=1}^{n} \sum_{k=1}^{3} a_k^i P_k^i + mc \sum_{i=1}^{n} \beta^i 
+ \frac{e^2}{2c} \sum_{i<j} \left[ a_i^\alpha a_j^\beta \frac{x_i^\alpha r_{ij}}{r_{ij}^3} + \frac{(x_i^\alpha r_{ij}) (x_j^\beta r_{ij})}{r_{ij}^3} \right] \right\}.$$  

Further $A_0, A_1, A_2, A_3$ are functions of the positions of the particles or the interelectronic distances and do not involve the momenta. Hence $x_k^i$ commutes with them. Again

$$[x_k^i, P_{s}^m] = \delta_{im} \delta_{ks}$$

so that

$$\left[ x_k^i, \sum_i \sum_k a_k^i P_k^i \right] = a_k^i.$$  

Hence

$$\dot{x}_k^i = -ca_k^i$$

or

$$v^i = -ca^i.$$  

Thus the matrices $a^i$ represent the velocities of the particles as in the one electron theory.
III. First Approximation

Let us consider the $t$-th component of the wave equation where

$$t = \sum_{r=1}^{N} (i_{r} - 1) 4^{N-r}.$$  \hspace{1cm} (10)

The $t$-th component of

$$\left( P_{0} + \frac{e}{c} A_{0} \right) \psi$$ is obviously

$$\left( P_{0} + \frac{e}{c} A_{0} \right) \psi_{i_{1} i_{2} \cdots i_{N}}.$$  \hspace{1cm} (11)

Now $\beta$ is a diagonal matrix with +1 along the first two diagonal elements and -1 along the last two diagonal elements. Thus

$$(\beta^{t} \psi)_{i_{1} i_{2} \cdots i_{N}}$$

$$= \sum_{i^{'}, \cdots , i^{'N}} (\mathbb{I}_{4})_{i_{1}, i^{'1}} (\mathbb{I}_{4})_{i_{2}, i^{'2}} \cdots (\beta)_{i_{r}, i^{'r}, \cdots} (\mathbb{I}_{4})_{i_{N}, i^{'N}} \psi_{i^{'1} \cdots i^{'N}}$$

$$= \sum_{i^{'}, \cdots , i^{'N}} \delta_{i_{1}, i^{'1}} \delta_{i_{2}, i^{'2}} \cdots (\beta)_{i_{r}, i^{'r}, \cdots} \delta_{i_{N}, i^{'N}} \psi_{i^{'1} \cdots i^{'N}}$$

$$= \sum_{i^{'}, \cdots , i^{'N}} (\beta)_{i_{r}, i^{'r}, \psi_{i_{1} \cdots i_{N}} = \epsilon_{r} \psi_{i_{1} \cdots i_{N}}}$$  \hspace{1cm} (12)

where $\epsilon_{r} = +1$ if $i_{r} = 1$ or 2, and is equal to $-1$ if $i_{r} = 3$ or 4. Thus

$$(mc \sum_{r=1}^{N} \epsilon_{r}) \psi_{i_{1} \cdots i_{N}} = mc \left( \sum_{r=1}^{N} \epsilon_{r} \right) \psi_{i_{1} \cdots i_{N}}.$$  \hspace{1cm} (12)

The maximum value of $\sum \epsilon_{r}$ is equal to $N$ and this happens when all the $i_{r}$'s have the values 1 or 2. Similarly when $i_{1}, i_{2}, \cdots, i_{N}$ all assume one of the values 3 or 4, we reach the other extreme value of $\sum \epsilon_{r}$ which is equal to $-N$. The sum $\sum \epsilon_{r}$ takes the $(N + 1)$ values $N, (N - 2), \cdots, -N$ depending on the values of the indices $i_{1}, i_{2}, \cdots, i_{N}$.

In the sequel, we shall use the indices $s_{1}, s_{2}, \cdots, s_{N}$ to denote the numbers 1 or 2 and the indices $l_{1}, l_{2}, \cdots, l_{N}$ to denote the numbers 3 or 4. A general component of the wave function has the form $\psi_{s_{1}, s_{2}, \cdots, l_{N}}$. There are $2^{N}$ components (the large components) of the type $\psi_{l_{1}, l_{2}, \cdots, l_{N}}$ with all the indices having the value 3 or 4; \(\binom{N}{1}\) $2^{N}$ components of the form $\psi_{l_{1}, l_{2}, \cdots, s_{N}}$. \(\binom{N}{1}\)
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in which on index \((s_r)\) is small and the rest are all large; and finally \(\binom{N}{N} 2^N\) components of the form \(\psi_{s_1, ..., s_N}\) with all indices small.

Now in the first approximation,

\[
\left( P_0 + \frac{e}{c} A_0 \right) \sim Nmc.
\]

We have seen that the minimum value of \(mc \sum \epsilon_r\) occurs when all the \(i_r\)'s take the values 3 or 4, and this is equal to \(-Nmc\). Thus

\[
\left[ \left( P_0 + \frac{e}{c} A_0 + mc \sum_{r=1}^{N} \beta^r \right) \psi \right]_{l_1, ..., l_N} = 0
\]

in the first approximation. The components \(\psi_{l_1, ..., l_N}\) in which all the indices have the value 3 or 4 are therefore large. Consider now the component \((l_1, l_2, \cdots s_r, \cdots l_N)\) of the wave equation, in which one index corresponding to the \(r\)-th electron is small and the rest are all large. In this case \(mc \sum_{r=1}^{N} \epsilon_r\) is equal to \(- (N - 2) mc\). The last term in the square bracket in (1) is of one order higher than the rest and we shall neglect it for the time being. We have seen in the appendix that the effect of \(a^r\) on a component \((i_1, i_2, \cdots s_r, \cdots i_N)\) is to transform it into the component \((i_1, i_2, \cdots l_r, \cdots i_N)\) whose \(r\)-th index is a large one and conversely. \(a^r\) thus changes \(s_r\) into \(l_r\), and \(l_r\) into \(s_r\). Thus \((a^r \psi)_{l_1, l_2, \cdots s_r, \cdots l_N}\) is a large component. It can be seen from equation (21) that all the \(\binom{N}{1} 2^N\) components of the type \(\psi_{l_1, l_2, \cdots s_r, \cdots l_N}\) with only one small index are of the order \((v/c)\). In general, a component with \(m\) small indices is of order \((v/c)^m\).

Now \((a^r \psi)_{i_1, s_r, \cdots l_N}\) \((i \neq r)\) is a component which has two indices (the \(i\)-th and the \(r\)-th ones), small and hence is of the order \((v/c)^2\). On the contrary \((a^r \psi)_{l_1, s_r, \cdots l_N}\) is a large component. Thus from (14) of appendix, we see that correct to terms of the order \((v/c)\),

\[
\left( P_0 + \frac{e}{c} A_0 - (N - 2) mc \right) \psi_{l_1, l_2, \cdots s_r, \cdots l_N} + (P^r \sigma^r \psi)_{l_1, \cdots (s_r+2) \cdots l_N} = 0
\]

where

\[
\sigma^r = I_2 \times I_2 \times \cdots \times \sigma \times \cdots I_2.
\]
In the above matrix product, we follow the convention that the elements of $I_2$ as well as $\sigma$ are numbered as 3 and 4 instead of as 1 and 2 as is usually done. If we set

$$\left( P_0 + \frac{e}{c} A_0 \right) = Nmc$$

in equation (13) we get to a first approximation that*

$$\psi_{l_1 l_2 \ldots s_r \ldots l_n} = -\frac{1}{2mc} (P_r \sigma^r \Psi)_{l_1 l_2 \ldots (s_r + 2) \ldots l_n}$$

IV. SECOND APPROXIMATION

Consider now the $(l_1, l_2, \ldots, s_a, \ldots, s_b, \ldots, l_n)$-th component of the wave equation (1). In this, two suffixes $s_a$ and $s_b$ are small and the rest are all large. Hence $mc \Sigma \epsilon_r = -(N - 4) mc$ and thus

$$\left( P_0 + \frac{e}{c} A_0 \right) + mc \sum \epsilon_r \sim 4mc.$$

Now $(a_k \Psi)_{l_1 \ldots s_a \ldots s_b \ldots l_n}$ is equal to a component which involves three small indices, namely $i, a$ and $b$ and is therefore of the order $(v/c)^3$. We are here striving for an approximation of the order $(v/c)^2$ only and hence $(4mc)^{-1} (a_k \Psi)_{l_1 \ldots s_a \ldots s_b \ldots l_n}$ which is of the order $(v/c)^2$ can be neglected. Similarly

$$(4mc)^{-1} \frac{e^2}{cr} (a^i \cdot a^j \Psi)_{l_1 \ldots s_a \ldots s_b \ldots l_n} (i, j \neq a, b)$$

involves four small indices and hence is of the order $(v/c)^3$. Again

$$\frac{1}{4mc} \frac{e^2}{cr} (a^a \cdot a^b \Psi)_{l_1 \ldots s_a \ldots s_b \ldots l_n} (j \neq b)$$

is of the order $(v/c)^4$ and hence can be neglected. Hence the only term in the second summation which is of the order $(v/c)^2$ corresponds to the case for which $i, j = a, b$. Thus correct to terms of the order $(v/c)^2$, we have

$$\left\{ P_0 + \frac{e}{c} A_0 - (N - 4) mc + \sum_{k=1}^n (a_k^a P^a_k^a + a_k^b P^b_k^b) \right. \left. + \frac{e^2}{2c} \left( \frac{a^a \cdot a^b}{r^2_{ab}} + \frac{(s^a \cdot r_{ab}) (s^b \cdot r_{ab})}{r^3_{ab}} \right) \right\} \psi_{l_1 l_2 \ldots s_a \ldots s_b \ldots l_n} = 0.$$ 

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* The representations for $\sigma$ used by Breit are the negative of the Pauli matrices and there will be thus a difference in sign in all terms that depend linearly on $\sigma$ between the results of Breit's paper and the present one, when the latter are reduced to two electron systems.
Now

\[(a_k \alpha^\Psi)_{l_1 l_2 ... s_a ... s_b ... l_N} = \sum_{l_i=3}^4 (\sigma_k)_{s_a+2, l_a} \psi_{l_1 l_2 ... l_a ... s_b ... l_N} = -\frac{1}{2mc} \sum_{l_i=3}^4 (\sigma_k)_{s_a+2, l_a} (P^b \sigma^b \Psi)_{l_1 l_2 ... (s_b+2) ... l_N} \text{ from (15).}\]

Thus

\[\sum_{k=1}^3 (a_k \alpha^\Psi)_{l_1 l_2 ... s_a ... s_b ... l_N} = -\frac{1}{2mc} (P\sigma^a) (P^b \sigma^b \Psi)_{l_1 l_2 ... (s_a+2) ... (s_b+2) ... l_N}. \quad (17 \ a)\]

Similarly

\[\sum_{k} (a_k \beta \Psi)_{l_1 l_2 ... s_a ... s_b ... l_N} = -\frac{1}{2mc} (P^b \sigma^b) (P^a \sigma^a \Psi)_{l_1 l_2 ... (s_a+2) ... (s_b+2) ... l_N}. \quad (17 \ b)\]

From equation (13) (Appendix) it follows that

\[(a_k \alpha^\Psi)_{l_1 l_2 ... s_a ... s_b ... l_N} = \sum_{l_a} \sum_{l_b} (a_k)_{s_a+2, l_a} (\alpha_l)_{s_b+2, l_b} \psi_{l_1 l_2 ... l_a ... l_b ... l_N} = (\sigma_k \alpha \Psi)_{l_1 l_2 ... (s_a+2) ... (s_b+2) ... l_N}. \quad (18)\]

Thus

\[
\left[ \left( \frac{a^a \cdot a^b}{r_{ab}} + \frac{(a^a \cdot r_{ab}) (a^b \cdot r_{ab})}{r_{ab}^3} \right) \psi \right]_{l_1 l_2 ... s_a ... s_b ... l_N} = \left[ \left( \frac{a^a \cdot a^b}{r_{ab}} + \frac{(a^a \cdot r_{ab}) (a^b \cdot r_{ab})}{r_{ab}^3} \right) \psi \right]_{l_1 ... s_a+2 ... s_b+2 ... l_N}. \quad (19)
\]
Hence setting

\[ P_0 + \frac{e}{c} A_0 = Nmc \]

in (16), we get by virtue of (17) and (19) that

\[ \psi_{l_1 \ldots s_a \ldots s_b \ldots s_n} \]

\[ = \frac{1}{4m^2c^2} (P^a \sigma^a) (P^b \sigma^b) \psi_{l_1 \ldots s_a+2 \ldots s_b+2 \ldots s_n} \]

\[ - \frac{e^2}{8mc^2} \left[ \frac{\sigma^a \cdot \sigma^b}{r_{ab}} \psi + \frac{(\sigma^a \cdot r_{ab}) (\sigma^b \cdot r_{ab})}{r_{ab}^3} \psi \right] \psi_{l_1 \ldots s_a+2 \ldots s_b+2 \ldots s_n} \]

(20)

Next the \((l_1 l_2 \cdots s_a \cdots l_n)\)-th component of the wave equation correct to terms of the order \(v^2/c^2\) is given by

\[ \left\{ P_0 + \frac{e}{c} A_0 - (N - 2) mc \right\} \psi_{l_1 \ldots s_a \ldots l_n} \]

\[ + \sum' \sum'_{k} (a_k^i P_k^i) \psi_{l_1 \ldots s_a \ldots l_n} + \left[ \sum'_{k=1} a_k^a P_k^a \psi \right] \]

\[ + \frac{e^2}{2c} \sum'_{i \neq a} \left( a_i^a \cdot a_i^j \right) \left( \frac{\sigma^a \cdot r_{aj}}{r_{aj}^3} \psi \right) \psi_{l_1 \ldots s_a \ldots l_n} = 0. \]  

(21)

Now by the application of equation (20) and of (8), (Appendix), it can be seen that

\( \left( \sum_k a_k^i P_k^i \psi \right) \psi_{l_1 \ldots s_a \ldots l_n} \]

\[ = (\sigma^i P^i) \left[ \frac{1}{4m^2c^2} (P^a \sigma^a) (P^i \sigma^i) \psi \psi \right. \]

\[ - \frac{e^2}{8mc^2} \left( \frac{\sigma^a \cdot \sigma^i}{r_{ia}} + \frac{(\sigma^a \cdot r_{ia}) (\sigma^i \cdot r_{ia})}{r_{ia}^3} \psi \right) \psi_{l_1 \ldots s_a+2 \ldots l_n} \]  

(22)
Again
\[
\left[ \frac{\alpha^a \cdot \alpha^j}{r_{aj}} + \frac{(\alpha^a \cdot r_{aj})(\alpha^j \cdot r_{aj})}{r_{aj}^3} \right]_{l_1, \ldots, l_n} = -\frac{1}{2mc} \left\{ \frac{\sigma^a \cdot \sigma^j}{r_{aj}} + \frac{(\sigma^a \cdot r_{aj})(\sigma^j \cdot r_{aj})}{r_{aj}^3} \right\} (\alpha^i \mathbf{p}^i \psi)_{l_1, \ldots, (s_{a+2}) \ldots l_n} \tag{23}
\]

Thus substituting (22) and (23) in (21) we get
\[
(2mc + f) \psi_{l_1, \ldots, s_a \ldots l_n} + (\mathbf{P}^a \sigma^a \psi)_{l_1, \ldots, (s_{a+2}) \ldots l_n} + \sum_{i \neq a} (\sigma^i \mathbf{p}^i) \times \left[ \frac{1}{4m^2c^2} \left( \mathbf{P}^a \sigma^a \right) \left( \mathbf{P}^i \sigma^i \right) \psi - \frac{e^2}{8mc^2} \left\{ \frac{\sigma^a \cdot \sigma^i}{r_{ia}} + \frac{(\sigma^a \cdot r_{ia})(\sigma^i \cdot r_{ia})}{r_{ia}^3} \right\} \psi \right]_{l_1, \ldots, s_{a+2} \ldots l_n} - \frac{e^2}{4mc^2} \sum_j' \left\{ \frac{\sigma^a \cdot \sigma^j}{r_{aj}} + \frac{(\sigma^a \cdot r_{aj})(\sigma^j \cdot r_{aj})}{r_{aj}^3} \right\} (\alpha^j \mathbf{p}^j \psi)_{l_1, \ldots, s_{a+2} \ldots l_n} = 0 \tag{24}
\]

where we have written
\[
\mathbf{P}^0 + \frac{e}{c} \mathbf{A}_0 = Nmc + f. \tag{25}
\]

Hence we have
\[
\psi_{l_1, l_2, \ldots, s_a \ldots l_n} = -\frac{1}{(2mc + f)^{-1}} (\mathbf{F}_a \psi)_{l_1, \ldots, (s_{a+2}) \ldots l_n} \tag{26}
\]

where
\[
\mathbf{F}_a = \left[ \mathbf{P}^a \sigma^a \right] + \sum_i' \left( \mathbf{P}^i \sigma^i \right) \left\{ \frac{1}{4m^2c^2} \left( \mathbf{P}^i \sigma^i \right) \left( \mathbf{P}^a \sigma^a \right) - \frac{e^2}{8mc^2} \left( \frac{\sigma^a \cdot \sigma^i}{r_{ia}} + \frac{(\sigma^a \cdot r_{ia})(\sigma^i \cdot r_{ia})}{r_{ia}^3} \right) \right\} - \frac{e^2}{4mc^2} \sum_j' \left\{ \frac{\sigma^a \cdot \sigma^j}{r_{ia}} + \frac{(\sigma^a \cdot r_{aj})(\sigma^j \cdot r_{aj})}{r_{aj}^3} \right\} (\alpha^j \mathbf{p}^j) \right]. \tag{27}
\]
Finally on making use of (18) and (23), we find that the \((l_1, l_2 \cdots l_N)\)-th component of the wave equation is given by

\[
\left( P_0 + \frac{e}{c} A_0 - Nmc \right) \psi - \sum_{a=1}^{N} (\sigma^a P^a) (2mc + f)^{-1} F_a \psi
\]

\[
+ \frac{e^2}{2c} \sum_{i<j} \left( \frac{\sigma^i \cdot \sigma^j}{r_{ij}} + \frac{(\sigma^i \cdot r_{ij})(\sigma^i \cdot r_{ij})}{r_{ij}^3} \right) \left\{ \frac{1}{4mc^2} (\sigma^i P^i) (\sigma^j P^j) \right\}
\]

\[
- \frac{e^2}{8mc^2} \left( \frac{\sigma^i \cdot \sigma^j}{r_{ij}} + \frac{(\sigma^i \cdot r_{ij})(\sigma^j \cdot r_{ij})}{r_{ij}^3} \right) \psi \right]_{l_1, \ldots, l_N} = 0. \tag{28}
\]

Equation (28) does not involve any small components and is thus the reduced equation in the large components that we are seeking. It is, however, not in its simplest form since it involves products of the spin matrices. Though the spin matrices have representations of order \(2^N\), it is easy to see that the components of the spin of any electron satisfy the same commutation rules as those associated with the Pauli matrices; the spin matrices corresponding to the different particles of course commute with each other. Again in simplifying equation (28), the following results, which represent a small change in indices of the equations (46), (47) of Breit’s paper, can be made use of:

If

\[
X_{ij} = \frac{\sigma^i \cdot \sigma^j}{r_{ij}} + \frac{(\sigma^i \cdot r_{ij})(\sigma^j \cdot r_{ij})}{r_{ij}^3},
\]

then

\[
X_{ij}^2 = \frac{(6 - 4 \sigma^i \cdot \sigma^j)}{r_{ij}^2} + 2 \frac{(\sigma^i \cdot r_{ij})(\sigma^j \cdot r_{ij})}{r_{ij}^4} \tag{29a}
\]

\[
\frac{e^2}{8m^2c^3} \left[ (P^i \sigma^i) (P^j \sigma^j) X_{ij} + (P^j_\alpha \sigma^i) X_{ij} (P^j \sigma^i) + (P^j_\sigma \sigma^j) X_{ij} (P^j \sigma^i) 
\right.
\]
\[
+ X_{ij} (P^i \sigma^i) (P^j \sigma^j)]
\]

\[
= \frac{e^2}{2m^2c^3} \left[ r_{ij}^{-1} (P^i P^j) + \sum_{k} \sum_{l} (x_{k}^i - x_l^i) (x_{k}^j - x_l^j) P^k_\alpha P^l_\sigma \right]
\]
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\[ + \frac{e^2}{8m^2c^3} (P^i\sigma^i) (P^j\sigma^j) X_{ij} \]

\[ + \left( \frac{e^2}{2m^2c^3} \right) \{ (P^i r_{ij}^{-1}) \times P^j, \sigma^i \} + (P^j r_{ij}^{-1}) \times P^i, \sigma^j \}. \quad (29\ b) \]

Again

\[ \frac{1}{4m^2c^2} (P^a\sigma^a) (2mc + f)^{-1} (P^i\sigma^i)^2 (P^a\sigma^a) \]

\[ = \frac{1}{8m^3c^3} (P^a)^2 (P^i)^2. \quad (29\ c) \]

The second term in the right-hand side of the (29 b) contains singularities at \( r_{ij} = 0 \), and its behaviour at this point needs to be investigated carefully. For example making use of the relation

\[ (a\mathbf{\tau}) (b\mathbf{\tau}) = (ab) + i (a \times b) \cdot \sigma, \]

we have

\[ \left( \frac{e^2}{8m^2c^3} \right) (P^i\sigma^i) (P^j\sigma^j) (\sigma^i\sigma^j) r_{ij}^{-1} \]

\[ = \frac{e^2}{8m^2c^3} \{ (P^i P^j) (1 - \sigma^i \cdot \sigma^j) - i (P^i \times P^j) \cdot (\sigma^i - \sigma^j) \]

\[ + (P^i\sigma^j) (P^j\sigma^i) \} r_{ij}^{-1}. \]

In view of the presence of the factor \( (e^2/8m^2c^3) \), we can neglect \( (e/c) A_i \) in \( P_i \) in the above term and write \( P_i = -i\hbar \nabla_i \). Further, \( \nabla_j = -\nabla_i \), as far as the effect of these operators on \( r_{ij}^{-1} \) is concerned, and thus \( (P^i P^j) r_{ij}^{-1} = -4\pi\hbar^2 \delta (r_{ij}) \). The behaviour of the term \( (P^i\sigma^i) (P^j\sigma^j) X_{ij} \) at the singular point has been investigated by Sucher and Foley, and by making use of their result, we can write

\[ (P^i\sigma^i) (P^j\sigma^j) X_{ij} = H_{\text{sp},ij} \]

\[ = -2\hbar^2 \left( \frac{1}{r_{ij}^4} \right) \left[ (\sigma^i \cdot \sigma^j) - 3 \frac{(\sigma^i r_{ij}) (\sigma^j r_{ij})}{r_{ij}^4} \right] - \frac{8\pi}{3} (\sigma^i \sigma^j) \delta (r_{ij}) \]

\[ (29\ d) \]
where the dash indicates that in evaluating the first term one should exclude a small sphere surrounding the vector \( r_i \). If \( E \) represents the energy of the system, and \( V = A_0 \), then

\[
P_0 + \frac{e}{c} A_0 = \frac{E + eV}{c}
\]

and hence

\[
f = P_0 + \frac{e}{c} A_0 - Nmc = \left( \frac{E + eV - Nmc^2}{c} \right).
\]

(25a)

We have finally

\[
\sum_{a=1}^{N} (\sigma^a \mathbf{p}^a) (2mc + f)^{-1} (\sigma^a \mathbf{p}^a)
\]

\[
= \frac{1}{2mc} \left[ \sum_{i=1}^{N} (\mathbf{p}^i)^2 + \frac{e \hbar}{c} \sum_{i=1}^{N} (\mathbf{H}^i \sigma^i) \right] - \frac{1}{4m^2c^2} \sum_{i=1}^{N} \left( \frac{E + eV - Nmc^2}{c} \right) (\mathbf{p}^i)^2 - \frac{ie\hbar}{c} \mathbf{p}^i \cdot \mathbf{\sigma}^i
\]

\[
- \frac{e \hbar}{c} \mathbf{\sigma}^i \cdot \mathbf{p}^i \cdot \mathbf{\sigma}^i
\]

(30)

where

\[
\mathbf{H}^i = \text{curl } \mathbf{A}^i \quad \text{and} \quad \mathbf{\sigma}^i = - \text{grad}^i V.
\]

Substituting the equations (29) to (30) in (28) and solving for \( (E + eV - Nmc^2) \), we get after some simplification that

\[
\left[ \frac{E + eV - Nmc^2}{c} \right] \left( \frac{1}{2mc} \sum_{i=1}^{N} (\mathbf{p}^i)^2 + \left( \frac{1}{8\pi m^2c^2} \right) (\mathbf{p}^i)^4
\]

\[
- \left( \frac{e \hbar}{4\pi mc^2} \right) \sum_{i=1}^{N} (\sigma^i \mathbf{H}^i) - \left( \frac{e \hbar}{8\pi m^2c^2} \right) \sum_{i} \left( i\mathbf{p}^i \cdot \mathbf{\sigma}^i + \mathbf{\sigma}^i \times \mathbf{p}^i \cdot \mathbf{\sigma}^i \right)
\]
Many Electron Wave Equation in Schrödinger-Pauli Form

\[ + \sum_{i < s} \left\{ \left( \frac{e^2}{2m^2c^2} \right) \left[ r^{-1}_{is} (P_i P_s) + \sum_{jk} (x_j^i - x_j^s) (x_k^i - x_k^s) \right. \right. \]

\[ \times P_j^i P_k^s \right \} - \left( \frac{e^2 \hbar^2}{4m^2c^2} \right) \left[ \frac{\sigma_i^i \sigma_s^s}{r_{is}} - 3 \left( \frac{\sigma_i^i r_{is}}{r_{is}^2} (\sigma_s^s r_{is}) \right) \right] \]

\[ - \frac{8\pi}{3} (\sigma_i^i \delta (r_{is})) + \left( \frac{i e^2}{2m^2c^2} \right) \left( \langle P_i^r_{is}^{-1} \rangle \times P_i^s \sigma^i \right) \]

\[ + \langle P_i^r_{is}^{-1} \rangle \times P_i^s \sigma^i \right \} \Psi = 0. \tag{31} \]

In this equation the bracket \( \langle \rangle \) indicates that the operators operate only within the \( \langle \rangle \).

V. THE REDUCED EQUATION IN THE LARGE COMPONENTS

Equation (31) is what one obtains on reducing the wave equation (1) to its large components. In his investigations on the relativistic wave equation for two electron systems, Breit (1932) has discussed in detail the validity of the term \( (e^4/16mc^2) X_{12}^2 \) (the last term in 31) which involves neither the momentum operator nor the Planck's constant. He came to the conclusion that the Breit equation yields results consistent with field theory for energy calculations provided the last term in it is taken into account to the first order by perturbation theory working with sixteen components. Such a calculation will lead to all the terms in (31) excepting the last sum involving the terms \( (e^4/16mc^2) X_{ij}^2 \). Since the arguments of Breit on the validity of this sum are quite general and are not restricted to two-electron systems only, we shall not repeat them here and shall content ourselves with stating that the correct wave equation is the one obtained by leaving out the sum \( (e^4/16mc^2) \sum X_{ij}^2 \) in equation (31). If we set \( \epsilon = E - Nmc^2 \), then \( \epsilon \) denotes the observable energy of the system, as its rest energy is equal to \( Nmc^2 \). Thus the wave equation for many electron systems is given by

\[ \left\{ \epsilon - \sum_{i=1}^{N} \frac{(P_i)^2}{2m} + eV + \left( \frac{1}{8m^3c^2} \right) \sum_{i=1}^{N} (P_i)^4 \right. \]

\[ - \left( \frac{e\hbar}{2mc} \right) \sum_i (\sigma^i H^i) - \left( \frac{e\hbar}{8\pi m^2c^2} \right) \sum_i g^i \times P_i \sigma^i \]
The first three terms in the above equation constitute the Schrödinger equation for many electron systems. The fourth and fifth terms give respectively the relativistic variation of mass with velocity and the interaction energy between the spins and the magnetic field acting on them. The sixth term in the square bracket gives the well-known spin-orbit coupling energy. The term

\[\left(-\frac{e^2\hbar}{4\pi m^2c^2} \sum_{i,s} (\nabla i r_{is}^{-1}) \times \mathbf{p}^s \cdot \sigma^i\right) - \left(\frac{ie\hbar}{4\pi m^2c^2} \sum_i \mathbf{p}^i \cdot \sigma^i\right)\]

\[+ \left(\frac{e^2}{2m^2c^2} \sum_{i<s} \left[\frac{\mathbf{p}^i \cdot \mathbf{p}^s}{r_{is}} + \sum_{js} (x_j^i - x_j^s) (x_k^i - x_k^s) P_j^i P_k^s\right]\right)
\]

\[-\left(\frac{e^2\hbar^2}{4m^2c^2} \sum_{i<s} \left[\frac{1}{r_{is}^3} (\sigma^i \cdot \sigma^s - 3 \frac{(\sigma^i r_{is})(\sigma^s r_{is})}{r_{is}^2})\right]\right)
\]

\[-\frac{8\pi}{3} (\sigma^i \sigma^s) \delta (r_{is})\]\n
The seventh term is imaginary and does not lend itself easily to physical interpretation. It is characteristic of Dirac theory, and can also be written as

\[\sum_i + \frac{ie\hbar}{8\pi m^2c^2} \sigma^i \cdot \mathbf{p}^i,\]

and the expectation values of both the expressions will be equal as pointed out by Bethe and Salpeter. This term also involves singularities of the type \(\delta (r_i)\) and \(\delta (r_{ij})\). The last two terms give respectively the orbit-orbit and the spin-spin interactions.

We can replace \(\mathbf{P}_i\) by its \(-i\hbar \nabla i\) in all terms of the equation (32) excepting the term \(-\Sigma (\mathbf{P}_i^2/2m)\) and this term has the value

\[\sum_i \left\{\frac{\hbar^2}{(2m)} \nabla_i^2 - \frac{c}{cm} A_i \cdot \mathbf{p}_i - \frac{e^2}{2mc^2} (A^i)^2\right\}.\]
One may notice that when there is no external magnetic field, the symmetry of the equation (31) is the same as that of the potential field \( V \), and the wave function \( \Psi \) also will thus exhibit this symmetry.

VI. THE SPIN STATES

If the wave function \( \Psi \) is normalised so that \( \int \Psi^* \Psi \, d\tau = 1 \) where \( d\tau = dx_1 \cdots dx_N \) denotes an element of volume in the configuration space and \( \Psi^* \) is the transpose of \( \Psi \), then \( \Psi^* \Psi \, d\tau \) can be interpreted as the probability of finding the electrons 1, 2 \( \cdots \) \( N \) in the volume elements \( dx_1, dx_2, dx_N \) respectively. In particular, \( \Psi^2 \) denotes the probability of finding all the electrons with parallel spins and of finding the electrons 1, 2 \( \cdots \) \( N \) respectively in the volume elements \( dx_1, \cdots dx_N \). Similarly \( (\sum \psi^2_{l_1 l_2 \cdots l_N}) \) where the summation covers all the components for which \( m \) out of the \( N \) numbers \( l_i \) have the value 3 and the rest the value 4, denotes the probability of finding \( m \) electrons with spins quantised along the positive direction of the \( z \)-axis and the remaining \( (N - m) \) electrons with spins quantised in the opposite direction. The number of terms in the above summation is obviously

\[
\binom{N}{m} = \frac{N!}{(N - m)! m!}
\]

Thus the number of terms contained in the probability distributions of finding \( N, (N - 1) \cdots 0 \) electrons having the positive spin are given by the different terms of the binomial expansion \( (1 + 1)^N \). If \( N \) is even, obviously the term having the greatest value corresponds to the case for which \( m = (N/2) \) or to the case wherein each electron finds its spin compensated by another electron of the opposite spin. It must however be borne in mind that in an approximation that ignores terms of the order \( \left( \frac{v^2}{c^2} \right) \), the wave function is an eigenfunction of \( S^2 \) and \( S_z \), and thus the components which correspond to the solution of the Schrödinger equation will have the largest values; the other components can be expected to have the order of magnitude of the relativistic corrections.

Now to satisfy the Pauli Exclusion Principle, the wave function should be anti-symmetric with respect to an interchange of any two electrons. From (32) we see that the Hamiltonian remains invariant under any permutation of the space co-ordinates as well as the spin co-ordinates. Thus Pauli’s Exclusion Principle will be satisfied if the components of \( \Psi \) satisfy the following relations:

\[
\psi_{i_1 \cdots l_i \cdots l_N}(x_1 \cdots x_i \cdots x_j \cdots x_N) = - \psi_{i_1 \cdots l_j \cdots l_i \cdots l_N}(x_1 \cdots x_i \cdots x_j \cdots x_N)
\]

\( (i, j = 1, 2, \cdots N) \).  

(33)
If \( l_i = l_j \) or in other words if the spins of the \( i \)-th and the \( j \)-th electrons are the same, the function \( \psi_{l_1, l_2, ..., l_j, ..., l_N} \) is anti-symmetric in the co-ordinates of these two electrons. Thus the Exclusion Principle demands that the components should be anti-symmetric with respect to the co-ordinates of all electrons that have the same spin, while they can behave as a mixture of symmetric and anti-symmetric functions as far as interchange of electrons with opposite spins are concerned. In both cases equations (33) give the conditions which Pauli’s Exclusion Principle demands on the components of the wave function. As an example, the Heitler-London theory for the hydrogen molecule corresponds to the case for which the two anti-symmetric components \( \psi_{a3} \) and \( \psi_{a4} \) are identically equal to zero while \( \psi_{a4} \) and \( \psi_{a3} \) are taken as symmetric functions satisfying the relation \( \psi_{a4} (1, 2) = - \psi_{a3} (2, 1) \).

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**Summary**

The paper deals with the reduction of the generalised Dirac equation for a system containing \( N \) electrons to its \( 2^N \) large components. The wave equation for many electron systems has been derived in its Schrödinger-Pauli form, and this includes higher order relativistic effects such as the mass change of the particles with their velocities, the spin-orbit, the orbit-orbit and the spin-spin interactions. A few remarks are made on the physical interpretation of the components of the wave function and the relations which they should obey in order to satisfy the Pauli Exclusion Principle.

**References**

Many Electron Wave Equation in Schrödinger-Pauli Form

APPENDIX

If \((x_1, x_2, \ldots, x_m)\) are components of a vector \(r\) in a vector space \(R\) of dimension \(m\), and similarly if \((y_1, y_2, \ldots, y_n)\) denote the components of a vector \(\eta\) in a vector space \(G\) of dimension \(n\), then the direct product of \(R \times G\) is of dimensions \(mn\) and is associated with the transformation properties of the vector \(z = r \times \eta\) whose components are given by \(z_l = z_{ik} = x_i y_k\) \((l = 1, 2, \ldots, mn)\). With the linear correspondences \(A\) in \(R\) and \(B\) in \(G\): 

\[
x'_i = \sum_i a_{i'i} x_i; \quad y'_{k'} = \sum_k b_{k'k} y_k
\]

is associated the linear correspondence \(C = A \times B\) in the product space:

\[
x'_i y'_{k'} = \sum_{i,k} a_{i'i} b_{k'k} x_i y_k
\]

or

\[
z'_i = \sum_i c_{i'i} z_i; \quad c_{i'i} = a_{i'i} b_{i'i}
\]

(A)

if we associate the numbers \(l\) and \(l'\) with the pairs \((ik)\) and \((i'k')\). For the sake of definiteness, we arrange the components \(x_i y_k\) in such a way that a component \(x_i y_k\) precedes another component \(x_i' y_{k'}\) if \(i < i'\), and when \(i = i'\) if \(k < k'\). The same convention will be adopted to evaluate the direct product of \(N\) matrices also. Thus a component \(\psi_{i_1 i_2 \ldots i_N}\) of the wave function will precede another component \(\psi_{j_1 j_2 \ldots j_N}\) if \(i_1 < j_1\), and when \(i_1 = j_1\); \(i_2 = j_2\); \(\ldots\); \(i_N = j_N\) then \(\psi_{i_1 i_2 \ldots i_N}\) precedes \(\psi_{j_1 j_2 \ldots j_N}\) if \(i_{N+1} < j_{N+1}\). The matrices \(a_k\) and \(\beta\) are given by

\[
a_k = \begin{pmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{pmatrix}; \quad \beta = \begin{pmatrix} I_2 & 0 \\ 0 & -I_2 \end{pmatrix}
\]

(1)

where \(\sigma_1, \sigma_2, \sigma_4\) are the Pauli matrices and \(I_2\) is the unit matrix of order 2. Further for the Pauli matrices, we choose the usual representations

\[
\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}
\]

(2)

Now if \(A = (a_{ij})\) and \(B = (b_{kl})\) are two square matrices of order \(m\) and \(n\) respectively, then the direct product can be represented as the partitioned matrix

\[
A \times B = \begin{pmatrix} a_{11}B & a_{12}B & \cdots & a_{1m}B \\ a_{21}B & a_{22}B & \cdots & a_{2m}B \\ \cdots & \cdots & \cdots & \cdots \\ a_{m1}B & a_{m2}B & \cdots & a_{mm}B \end{pmatrix}
\]

(3)
Further the direct product of $i$ unit matrices of order four is a unit matrix of order $4^i$. Hence from (3, section II) and (3), we see that $a_{k_i}$ is given by a partitioned matrix of order $4^{i-1}$; we have

$$a_{k_i} = egin{pmatrix}
  a_{k_i} & 0 & \cdots & 0 \\
  0 & a_{k_i} & \cdots & 0 \\
  \vdots & \vdots & \ddots & \vdots \\
  0 & 0 & \cdots & a_{k_i}
\end{pmatrix}
$$

(4)

In the above, each element is a matrix of order $4^{N-i+1}$ and $a_{k_i}$ is given by the matrix

$$a_{k_i} = \left( \begin{array}{cc}
  0 & \sigma_k \times I_{N_i} \\
  \sigma_k \times I_{N_i} & 0
\end{array} \right)
$$

(5)

where $N_i = 4^{N-i}$ and $I_{N_i}$ is a unit matrix of order $4^{N-i}$. Similarly $b_i$ is given by the following partitioned diagonal matrix of order $4^{i-1}$

$$b_i = \begin{pmatrix}
  b_i & 0 & \cdots & 0 \\
  0 & b_i & \cdots & 0 \\
  \vdots & \vdots & \ddots & \vdots \\
  0 & 0 & \cdots & b_i
\end{pmatrix}
$$

(6)

where

$$b_i = \beta \times I_{N_i} = \begin{pmatrix}
  I_{N_i} & 0 & 0 & 0 \\
  0 & I_{N_i} & 0 & 0 \\
  0 & 0 & -I_{N_i} & 0 \\
  0 & 0 & 0 & -I_{N_i}
\end{pmatrix}.
$$

(7)

Now

$$a_{k_r} = I_4 \times I_4 \times \cdots \times a_k \times \cdots \times I_4.
$$

From a generalisation of the equations (A) to $N$ vectors, we see that

$$(a_{k_r} \Psi)i_{i_1}, \ldots, i_N = \sum_{i_1, \ldots, i_N} (I_4)_{i_{i_1}, \cdots, i_N} (a_{k})_{i_{i_1}, \cdots, i_N} (I_4)_{i_{i_1}, \cdots, i_N} \Psi_{i_{i_1}, \cdots, i_N}
$$

(8)

$$= \sum_{i_1, \ldots, i_N} \delta_{i_{i_1}, \cdots, i_N} (a_{k})_{i_{i_1}, \cdots, i_N} \Psi_{i_{i_1}, \cdots, i_N}
$$

$$= \sum_{i_{i_1}, \ldots, i_N} (a_{k})_{i_{i_1}, \cdots, i_N} \Psi_{i_{i_1}, \cdots, i_N}$$

$$= \sum_{i_{i_r}} (a_{k})_{i_{i_r}} \Psi_{i_{i_r}, \ldots, i_{i_r}, \ldots, i_N}$$

(8)
Many Electron Wave Equation in Schrödinger-Pauli Form

The same result could be proved with the aid of the matrix for \( \alpha_k \) given by (4) but this is more tedious.

If \( A_1, A_2, \ldots A_N \) and \( B_1, B_2, \ldots B_N \) are matrices of the same order, then
\[
(A \times A_1 \times A_2) = AB \times A_1B_1
\]
Hence applying the above result to one more matrix, we get
\[
(A \times A_1 \times A_2) (B \times B_1 \times B_2) = [(A \times A_1) (B \times B_1)] \times A_2B_2
\]
Thus \( A \times A_1 \cdots \times A_N \) \( B \times B_1 \cdots \times B_N \) \( = AB \times A_1B_1 \cdots \times A_NB_N. \)

Thus we find that
\[
\alpha_k^r \alpha_1^s = I_4 \times I_4 \times \cdots \times \alpha_k \times \cdots \times \alpha_l \times \cdots \times I_4
\]
Again we find that the matrices \( \alpha_k^r \) satisfy the commutation rules
\[
\alpha_k^r \alpha_1^r + \alpha_1^r \alpha_k^r = 2\delta_k k_l.
\]
From (11) we find that
\[
\sum_{i_1 \cdots i_n} (I_4)_{i_1 \cdots i_n} \psi_{i_1 \cdots i_n} = \sum_{i_1 \cdots i_n} \delta_{i_1 i_1} \cdots (\alpha_k)_{i_1 \cdots i_n} \cdots (\alpha_l)_{i_1 \cdots i_n} \psi_{i_1 \cdots i_n}
\]
\[
= \sum_{i_1 \cdots i_n} \delta_{i_1 i_1} \cdots (\alpha_k)_{i_1 \cdots i_n} \cdots (\alpha_l)_{i_1 \cdots i_n} \psi_{i_1 \cdots i_n}
\]
\[
= \sum_{i_1 \cdots i_n} \delta_{i_1 i_1} \cdots (\alpha_k)_{i_1 \cdots i_n} \psi_{i_1 \cdots i_n}
\]
Now \( \alpha_k \) is of the form \( \begin{pmatrix} 0 \\ \sigma_k \end{pmatrix} \) and thus if \( i_1 = 1 \) or 2, we have \( (\sigma_k)_{i_1 i_1} = 0 \)
for \( i_1 = 1 \) or 2 and it is equal to \( (\sigma_k)_{i_1 i_1} = 0 \) for \( i_1 = 3 \) or 4. Similarly when \( i_1 = 3 \) or 4, we have \( (\sigma_k)_{i_1 i_1} = 0 \) if \( i_1 = 1 \) or 2, and is equal to zero if \( i_1 = 3 \) or 4. Thus from (8) we see that the effect of \( \alpha_k^r \) on \( \psi \) is to transform a component \( (i_1, i_2, \cdots i_n) \) into another component \( (i_1, i_2, \cdots i_n) \) whose \( r \)-th index is large if \( i_r \) is small and \textit{vice versa}. In other words, if \( i_r \) is large (having the value 3 or 4) then \( \alpha_1^r \) transforms it into a small one and conversely \( \alpha_1^r \) transforms a component whose \( r \)-th index is small into a component whose \( r \)-th index is large.

If now we follow the convention that the row and column indices of the two-dimensional Pauli matrices be denoted by the numbers 3 and 4 instead of by 1 and 2, then it follows from (8) that
\[
(\alpha_k^r \psi)_{i_1 i_2 \cdots i_n} = \sum_{i_1 \cdots i_n} (\alpha_k)_{i_1 \cdots i_n} \psi_{i_1 i_2 \cdots i_n}
\]
\[
= \sum_{i_1 \cdots i_n} (\sigma_k)_{i_1 \cdots i_n} \psi_{i_1 i_2 \cdots i_n}
\]
\[
= (\sigma_k^r \psi)_{i_1 i_2 \cdots i_n}(\sigma_{r+2}) \cdots i_n.
\]