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ELECTRONIC WAVE FUNCTIONS

VI. SOME THEOREMS FACILITATING THE EVALUATION OF SCHRÖDINGER INTEGRALS OF VECTOR-COUPLED FUNCTIONS

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CONTENTS

The theorems reported here provide some powerful additional relations to the general theory of the reduction of Schrödinger integrals completed in part V. One result of these is to establish a number of relations between the various vector-coupling coefficients and thus to reduce considerably the labour of calculation of these. A second result is to provide a method of evaluating the two-electron electrostatic integrals which is a complete alternative to the c^k method which has generally been used previously. This appears to be simpler and more powerful. A third result is only applicable to a restricted class of integrals and only to particular terms in the formulas for these, but where applicable it makes trivial the evaluation of the terms concerned and actually simplifies about three-quarters of the integrals normally occurring. These methods have been found to be extremely useful in the convergent variational calculations of atomic wave functions, and will also be applicable to all problems which require the evaluation of Schrödinger integrals between vector-coupled functions.

1. Introduction

This series of investigations is being made in accordance with the opinion that the convergent variational calculation of wave functions of atoms and molecules can be performed much more simply than is generally realized. The numerical calculations which have already been completed and will be reported later amply justify this view for the case of atoms. When allowance is made for the increased accuracy, the calculations appear to be proportionately shorter than non-convergent calculations. However, these calculations would be prohibitively laborious for all atoms more complicated than boron without a small number of mathematical relations, whose justification is extremely involved, although their use is much simpler. These relations are purely mathematical identities and not particular to any atom or physical picture. A general scheme of these relations sufficient for any problem was completed in part V, but if these are supplemented with a few others which are more particular, but still applicable to all atoms, the labour of evaluating the Schrödinger integrals is reduced to less than a quarter of what it would be otherwise. It is these more particular relations which will be derived here. It is unfortunate that the exposition

of these increases the amount of theory before the practical application, but these methods both decrease the actual labour and simplify very much the description of the calculation for any particular atom. It may be noted that the theory which has been, and is being, developed is not specialized in parts to particular types of atoms; all the theory is used for any single atom, unless this is sufficiently simple, as for the beryllium atom (part II), to be performed without the theory. The subsequent atoms only use the same general theory applied to different integrals.

The simplest relations which will be derived here are those relating to various vector-coupling coefficients. A number of such coefficients were defined in the general theory, and it was suggested that the values of these should be calculated and tabulated. The same coefficients will be used repeatedly in calculations for different atoms. It will be shown that there are several very simple relations between the values of any one coefficient with different arguments, and between different coefficients. These relations both reduce the necessary numerical calculation and serve as checks. The following examples expressed in the original notations, which will be repeated below, illustrate this type of relation:

$$X(L, M, a, b, m) = (-1)^{a+b-L} X(L, -M, a, b, -M+m), \tag{1}$$

$$W\begin{pmatrix} a & b \\ c & d \end{pmatrix} L\ K = U\begin{pmatrix} b & a & c & d \\ L & & & K \end{pmatrix} \mathrm{i}^{2(d-b-L)}. \tag{2}$$

Some such relations of X and U coefficients will be derived in § 3, of U and W in § 4, and of V in § 6. One or two of these relations, such as equation (1), are effectively already known, but most are new.

Probably the most important relations in this paper are those of § 5, which provide a method of evaluating the two-electron integrals previously denoted by

$$[p_{12}/r_{12} \,||\, x_r x_s \,|\, x_t x_u]^{LS}. \tag{3}$$

The only method known previously which is equivalent to this is the c^k method (see Condon & Shortley 1935, p. 174). The new method appears to be simpler and more fundamental, and is much more appropriate in the present formulation.

The final method which is worked out is only a short way of evaluating certain terms of Schrödinger integrals for which the general theory has already been given. It expresses the integrals concerned in a form

$$(\psi \,|\, H \,|\, \psi') = (\psi \,|\, \mathrm{inv} \,|\, \psi')\ (\text{a constant}) + \text{other terms}. \tag{4}$$

The invariant portion $(\psi \,|\, \mathrm{inv} \,|\, \psi')$ has the significance that it is sufficiently simple to be written down by a memorized rule and at the same time it contains the greater part of the total integral. The general theory is still required for the residual terms, but frequently need only be applied to a lower-order problem. The method does not apply to all integrals, but its value for the approximate three-quarters to which it does apply is considerable. No equivalent relation of this generality has previously been known, although the equivalent of applying this to some simple and specialized integrals is described in Condon & Shortley (1935, p. 177). The necessary theorems will be derived in a form in which they are applicable to some molecular problems.

It is necessary to carry out most of the present analysis in the very general notations introduced previously, and this will be reviewed in § 2, together with some other convenient abbreviations.

2. Notation and nomenclature

A set of functions $\phi(m)$ with $m = -l, -l+1, \ldots, l$ will, as previously, be called a connected set of eigangs when they satisfy the usual relations

$$(L_x + iL_y)\,\phi(m) = \sqrt{[(l-m)\,(l+m+1)]}\,\phi(m+1), \quad \text{etc.}, \tag{5}$$

for a given set of angular operators L_x, L_y, L_z.

If $\phi(m_1, m_2)$ is a doubly-connected set of eigangs under the sets of operators $\mathbf{L}_1$ and $\mathbf{L}_2$, then the notations

$$\phi\theta(L, M, 1, 2) \quad \text{or} \quad \phi\theta_{12}^{LM} = \sum_m \phi(m, M-m)\, X(L, M, l_1, l_2, m) \tag{6}$$

will be used. The X's are coefficients with a formal definition chosen to make $\phi\theta_{12}^{LM}$ a connected set under the operators $(\mathbf{L}_1 + \mathbf{L}_2)$. Considerable liberty will be taken with the suffixes of the type 12 which serve to indicate the m suffixes or arguments of the ϕ which are to be coupled. If these are otherwise obvious, they will be omitted. In complicated cases any symbols obviously related to the suffixes to be coupled will be used. This fundamental operation will generally be designated as the vector coupling of m_1 and m_2.

The spectroscopic notations ^{1}S, ^{3}S, ^{1}P, etc., each specify an l and s value according to the code $l = 0, 1, 2$, for S, P, D, etc., and the suffix has value $2s+1$. It is convenient to use a modified form of this in which the $2s+1$ suffix is written after the letter to designate a double coupling $\theta^{LM}\theta^{SU}$ of two doubly-connected sets of eigangs of orbital and spin angular operators L and S. If necessary, the M and U values will be written as in $\mathrm{D}^3(M, U)$, but they can generally be omitted. The later position of the suffix is very convenient, since it avoids the necessity for brackets in such cases as $d^2\mathrm{D}^1$ and in more complicated cases.

The coefficients X, U, W, V will be used as in previous parts, but will be effectively redefined when used. For the sake of compactness the following alternative forms of representation will be used where convenient:

$$\left.\begin{aligned} W\begin{pmatrix} a & c \\ b & d \end{pmatrix} e\, f\Big) &= W(a, b \mid c, d \mid e, f), \\ U\begin{pmatrix} a & b & c & d \\ & e & & f \end{pmatrix} &= U(a, b, c, d \mid e, f), \\ V\begin{pmatrix} a & & d \\ b & c & e \end{pmatrix} f\Big) &= V(a, b \mid c \mid d, e \mid f). \end{aligned}\right\} \tag{7}$$

The notation $P(x_1, x_2, \ldots \mid y_1, y_2, \ldots)$ will be used to denote the operation of replacing x_1 by y_1, x_2 by y_2, etc. The notations $\delta(x, y)$ and $\delta(x_1, x_2, \ldots \mid y_1, y_2, \ldots)$ will be used to denote unity when $x = y$ and $x_i = y_i$ respectively, and otherwise zero. The notation

$$qt(x_1, x_2, \ldots / y_1, y_2, \ldots)$$

will denote some quantity dependent on the x_i but independent of the y_i. $\sigma(x)$ will denote i^{2x}, which is thus $(-1)^x$ when x is integral. f^* will denote the conjugate complex of f, but $\bar{f}$ will always be defined explicitly, except in the case of a connected set of eigangs, when

$$\bar{a}(m) = \sigma(m)\, a^*(-m). \tag{8}$$

t_i will denote a set of variables x_i, y_i, z_i, v_i, where x_i, y_i, z_i are ordinary spatial variables but v_i is the spin variable which can only assume two values.

The result of the complete integration summation operation f^*Qg will be denoted as usual by $(f|\,Q\,|g)$. As introduced previously, the notations

$$\left(Q\left\|\begin{matrix}F\\G\end{matrix}\right.\right) \quad \text{or} \quad (Q\,\|\,FG) \tag{9}$$

will be used when F and G are functions of the corresponding sets of variables t_i and t_i', and where Q is some operator which removes corresponding pairs t_j, t_j' to mean the removal of all remaining t_i, t_i' by $\int \mathrm{d}t_i P(t_i'\,|\,t_i)$ operators. The same notations will be used when the elementary sets are just x, y, z or v.

3. Some properties of the X coefficients

The relations derived in this section are of the first type described above. In this case the most important results are already known, but they have been re-derived in accordance with the present scheme of analysis for the sake of completeness. The justification from other formal treatments would be nearly as complicated.

The X vector-coupling coefficients were defined by a minimum necessary set of conditions in part IV and then were shown to satisfy some corresponding symmetric relations. It is convenient to state this complete set, containing the definition, as a theorem without proof. It is effectively justified by theorem 8, part III. The subsequent theorems follow by detailed analysis of this.

Theorem 1. The coefficients $X(L, M, m)$, or $X(L, M, a, b, m)$ for the conventional vector coupling of eigangs with first values a and b satisfy

$$X(a+b, a+b, a) = 1, \quad \sum_m X(L, M, m)\, X(L', M', m) = \delta(L, M\,|\,L', M'), \tag{10}$$

$$N^-(L, M)\, X(L, M-1, m) = N^-(a, m+1)\, X(L, M, m+1) + N^-(b, M-m)\, X(L, M, m), \tag{11}$$

$$N^+(L, M)\, X(L, M+1, m) = N^+(a, m-1)\, X(L, M, m-1) + N^+(b, M-m)\, X(L, M, m), \tag{12}$$

$$\sum_m m X(L+1, L, m)\, X(L, L, m) > 0, \tag{13}$$

$$N^-(L, M) = N^+(L, M-1) = N^+(L, -M) = N^-(L, -M+1) = \sqrt{[(L+M)\,(L-M+1)]}. \tag{14}$$

These relations are still valid when some X coefficients are non-existent if these are regarded as zero.

Theorem 2. $$X(L, L, a, b, m) = \sigma(a-m)\,|\,X(L, L, a, b, m)\,|. \tag{15}$$

Proof. If relation (12) is examined for the case $M = L$ the left-hand side is zero, and hence

$$X(L, M, m-1) = -X(L, M, m)\, N^+(b, M-m)/N^+(a, m-1), \tag{16}$$

so that
$$X(L, L, m)/|\,X(L, L, m)\,| = \sigma(a-m)\, k_L, \tag{17}$$

where
$$k_L = X(L, L, a)/|\,X(L, L, a)\,|. \tag{18}$$

If $A(t_1)$ and $B(t_2)$ denote two connected sets of eigangs of the operators $\mathbf{L}_1$ and $\mathbf{L}_2$ respectively with first values a and b, then it follows from relation (13) that

$$\begin{aligned}0 &< \sum_m mX(L+1,L,m)\,X(L,L,m)\,N^-(L+1,L+1)\\ &= (AB\theta^{L+1,L}\,|\,L_{1z}\,|\,AB\theta^{L,L})\,N^-(L+1,L+1)\\ &= (\{L_1^- + L_2^-\}\,AB\theta^{L+1,L+1}\,|\,L_{1z}\,|\,AB\theta^{L,L})\\ &= (AB\theta^{L+1,L+1}\,|\,-L_1^+ + L_{1z}(L_1^+ + L_2^+)\,|\,AB\theta^{L,L})\\ &= -\sum_m^{L+1} X(L+1,L+1,m)\,X(L,L,m-1)\,N^+(L,m-1)\\ &= \sum_m |\,X(L+1,L+1,m)\,|\,|\,X(L,L,m-1)\,|\,N^+(L,m-1)\,k_L k_{L+1}. \end{aligned} \tag{19}$$

The first equalities are obtained by trivial changes of form, and the last follows by use of relation (18). Hence

$$k_L = 1/k_{L+1} = k_{L+1} = k_{a+b} = 1, \tag{20}$$

and substitution in (17) gives the theorem.

THEOREM 3.
$$X(L,M,a,b,m) = \sigma(a+b-L)\,X(L,-M,a,b,-m), \tag{21}$$
$$X(L,M,b,a,M-m) = \sigma(a+b-L)\,X(L,M,a,b,m). \tag{22}$$

Proof. It is simplest to show immediately that all the $X(L,M,m)$ with the lowest permissible m values, for a given L but different M values, have the same sign. Let $X(L,M,m')$ and $X(L,M+1,m'')$ be such coefficients. Then it is only possible for $m'' = m'$ or $m'' = m'+1$. When $m'' = m'$ it follows by equation (12) that

$$N^+(L,M)\,X(L,M+1,m') = N^+(b,M-m'')\,X(L,M,m''), \tag{23}$$

since $X(L,M,m''-1)$ does not exist when m'' is the lowest term. Hence the two lowest terms have the same sign. When $m'' = m'+1$ it follows by equation (11) that

$$N^-(L,M+1)\,X(L,M,m') = N^-(a,m'+1)\,X(L,M+1,m'+1), \tag{24}$$

since $X(L,M+1,m')$ does not exist, since $m'+1$ is the lowest term. Hence the two lowest coefficients always have the same sign. Consider the two lowest coefficients $X(L,L,L-b)$ and $X(L,-L,-a)$. It follows from theorem 2 that the sign of the first is $\sigma(a+b-L)$, and this must also be the sign of the second.

Let $Y(M,m)$ be defined by

$$\sigma(a+b-L)\,Y(M,m) = X(L,-M,-m), \tag{25}$$

so that $Y(L,a)$ is positive and

$$0 = N^+(a,-m-1)\,Y(L,-m-1) + N^+(b,L+m)\,Y(L,-m) \tag{26}$$

follows from equation (11) by replacing N^- quantities by the N^+ quantities. If m' is written for $-m$ in this last relation these conditions with

$$\sum_m Y^2(L,m) = 1 \tag{27}$$

determine the $Y(L,m)$ and are exactly the same as the conditions for $X(L,L,m)$ obtained in theorem 2. Hence

$$X(L,L,m) = Y(L,m). \tag{28}$$

Exactly similarly the equation found to derive the $Y(M,m)$ from $Y(L,m)$ can be shown to be the same as the equation deriving the $X(L,M,m)$ from $X(L,L,m)$ and so generally

$$X(L,M,m) = Y(L,m). \tag{29}$$

By the definition of the Y coefficients this is the first assertion of the theorem. The second assertion has already been established in theorem 7, part V, but is included for completeness.

THEOREM 4. $$X(0,0,a,a,m) = \sigma(a-m)/\sqrt{(2a+1)}. \tag{30}$$

Proof. It follows by putting $L = M = 0$ in equation (12) that

$$0 = N^+(a,m-1)\,X(0,0,m-1) + N^+(a,-m)\,X(0,0,m), \tag{31}$$

and since $$N^+(a,m-1) = N^+(a,-m),$$

that all these coefficients have the same absolute magnitude.

The signs stated in the theorem follow from theorem 2, and the absolute magnitudes stated are required to satisfy the normalization relation.

4. PROPERTIES OF U AND W COEFFICIENTS

It will be shown that the U and W coefficients, which were defined to be the coefficients of two very useful transformations, are closely related. This does not avoid the necessity of tabulating these separately, since they are used in circumstances in which it would be troublesome to have to perform trivial numerical transformations. However, the relation is useful either for evaluation or for checking numerical values. The symmetry properties of the U and W can conveniently be obtained in conjunction with this analysis, and these reduce the necessary tables to about a quarter of the length otherwise required.

It is convenient to establish first a fairly obvious property of multiple vector coupling, but which is applicable to such a wide range of circumstances that it is convenient to be able to use it without repeated explanation. This property is the completeness of what have been called progressive systems of vector-coupled functions. A formal definition of these was given in part V, but the intuitive construction of such systems is probably simpler than this. Let $\phi(m_1, m_2, \ldots)$ be a multiply-connected set of eigangs and let vector-coupled eigangs be formed by coupling the (a_1)th and the (a_2)th suffixes to give a suffix designated as m_{n+1}. Let there be an arbitrary number of repetitions of such couplings to give m_{n+1}, $m_{n+2}, \ldots$, etc., either the original suffixes or any of the newly generated suffixes being coupled. Then the system of functions formed by including all $l_{n+1}, l_{n+2}, \ldots$ and all uncoupled m values is a progressive system. The final functions are only linear combinations of the original $\phi(m_1, m_2, \ldots)$, and it is convenient to use a symbolic operator

$$\theta(l_1, l_2, \ldots \,|\, l_{n+1}, a_1, a_2 \,|\, l_{n+2}, a_3, a_4 \,|\, \ldots), \quad \text{etc.},$$

to designate such a linear combination. This is a generalization of the θ for a single vector coupling. The theorem which is required shows the completeness of such systems and the

invariance of the generalized U coefficients for expressing functions of one such system in terms of the functions of another system.

THEOREM 5. A progressive system of vector-coupled multiple eigangs is a complete orthonormal system of functions. The summation operators of one progressive system of vector coupling can be expressed as linear combinations of the operators of any other system by

$$\theta(l_1, l_2, \ldots \mid a, p_1, q_1 \mid b, p_2, q_2 \mid c, p_3, q_3 \mid \ldots \mid L, M, p_n, q_n) = \sum_{A,B,C,\ldots} \theta(l_1, l_2, \ldots \mid A, P_1, Q_1 \mid B, P_2, Q_2 \mid \ldots) \times U(l_1, l_2, \ldots \mid a, p_1, q_1 \mid b, p_2, q_2 \mid \ldots \parallel A, P_1, Q_1 \parallel B, P_2, Q_2 \mid \ldots), \quad (32)$$

where

$$U(l_1, l_2, \ldots \mid a, p_1, q_1 \mid \ldots \parallel A, P_1, Q_1 \mid \ldots) = U(l_1, l_2, \ldots \mid A, P_1 Q_1 \mid \ldots \mid a, p_1, q_1 \mid \ldots) = [\phi\theta(a, p_1, q_1 \mid \ldots) \mid \phi\theta(A, P_1 Q_1 \mid \ldots)] = qt(/M). \quad (33)$$

The U coefficients are unique and serve for the reciprocal expansion. The theorem is also valid if a number of suffixes $L_1, M_1, L_2, M_2, \ldots$ are left uncoupled and if L, M is taken to mean this set.

Proof. Consider any multiply-connected set of eigangs $\phi(m_1, m_2, \ldots, m)$ with first eigang values $l_1, l_2, \ldots$. If ϕ' denote the vector-coupled eigangs $\phi\theta(L, M, p_1, q_1)$ including all possible values of L, then any term of the original ϕ can be expressed in terms of the ϕ' by

$$\phi(m_1, \ldots, m_p, m_q, \ldots) = \sum_L X(L, m_p + m_q, l_p, l_q, m_p)\, \phi\theta(L, m_p + m_q, p_1, q_1). \quad (34)$$

However, any member of ϕ' can similarly be expressed as a linear combination of ϕ'' formed by applying a further vector coupling, and by repetitions of this argument any member of ϕ can be expressed as linear combinations of any complete set formed by repeated vector couplings. Since a second progressive set can be expressed in terms of the $\phi(m_1, m_2, \ldots)$ it can also be expressed as a linear combination of the first progressive system.

In the second place, it is apparent that any two different members of one progressive system are orthogonal, since they must differ by some l or m value and there is thus a corresponding L operator for which they will have different eigenvalues. The functions are normal, since vector coupling of normal eigangs always gives normal eigangs (theorem 8, part IV).

If a function f can be expressed as a linear combination of orthonormal functions g_r, then the unknown coefficients can be evaluated by multiplication by g_r^* and integration to give

$$f = \sum_r g_r (g_r \mid f). \quad (35)$$

If the functions $\phi\theta(\ldots \mid a, p_1, q_1 \mid \ldots)$ are written for f and another progressive system $\phi\theta(\ldots \mid A, P_1, Q_1 \mid \ldots)$ for g_r, the relation of the theorem follows. The coefficients satisfy $(g_r \mid f_s) = (f_s \mid g_r)$, since all the X coupling coefficients are real. The possibility of writing the identity in terms of the operators and of the uniqueness of the coefficient follows immediately by use of theorem 7, part IV, where the total coefficients of any particular non-degenerate eigenfunction in a null quantity was shown to be zero.

THEOREM 6. If the elementary U coefficients are defined, as in part V, to satisfy

$$\theta^{e}_{ab}\theta^{LM}_{ec} = \sum_{f} \theta^{f}_{bc}\theta^{LM}_{af} U\begin{pmatrix} a & b & c & L \\ e & & f & \end{pmatrix}, \tag{36}$$

the values of the only existing coefficients for $L = 0$ are given by

$$U\begin{pmatrix} a & b & c & 0 \\ c & & a & \end{pmatrix} = 1. \tag{37}$$

Proof. In the case $L = 0$ the only possible value for e is c, since this must be coupled with c to give 0, and similarly the only possible value for f is a. Hence there is only one coefficient and one term in the f expansion. When the operators are applied to a given $\phi(m_1, m_2, m_3)$ the coefficient of any given $\phi(m_1, m_2, m_3)$ must be the same on each side of the equation and the implication of this for the particular term $\phi(a, c-a, -c)$ will be examined. The left-hand coefficient is

$$X(c, c, a, b, a)\, X(0, 0, c, c, c), \tag{38}$$

both factors of which are positive by theorem 2. The right-hand side coefficient is

$$U(a, b, c, 0, c, a)\, X(0, 0, a, a, a)\, X(a, -a, b, c, c-a). \tag{39}$$

The first X is positive by theorem 2, and the second X is similarly seen to be positive if it is replaced by theorem 3, giving

$$X(a, -a, b, c, c-a) = X(a, a, c, b, c). \tag{40}$$

Hence the U coefficient must be positive and the value $+1$ follows, since the magnitude unity is required in order that both progressively coupled functions are normalized in accordance with theorem 5.

THEOREM 7. The U coupling coefficients satisfy

$$U\begin{pmatrix} a & b & c & d \\ e & & f & \end{pmatrix} = U\begin{pmatrix} d & c & b & a \\ e & & f & \end{pmatrix} = U\begin{pmatrix} c & b & a & d \\ f & & e & \end{pmatrix}, \tag{41}$$

thus, in general, giving eight equal coefficients, and also

$$\theta^{e}_{ab}\theta^{e}_{cd}\theta^{00}_{ab,cd} = \sum_{f} \theta^{f}_{bc}\theta^{f}_{ad}\theta^{00}_{bc,ad} U\begin{pmatrix} a & b & c & d \\ e & & f & \end{pmatrix} \sigma(d-f-a). \tag{42}$$

Proof. If A, B, C, D denote connected sets of eigangs with first eigang values a, b, c, d, and are functions of different variables which do not change, it follows that

$$(DCBA\theta^{e}_{DC}\theta^{a}_{eB}\theta^{00}_{aA} \mid DCBA\theta^{f}_{CB}\theta^{a}_{Df}\theta^{00}_{aA}) \tag{43}$$

$$= (ABCD\theta^{e}_{CD}\theta^{a}_{Be}\theta^{00}_{Aa} \mid ABCD\theta^{f}_{BC}\theta^{a}_{fD}\theta^{00}_{aA}) \tag{44}$$

$$= (ABCD\theta^{e}_{AB}\theta^{e}_{CD}\theta^{00}_{AB,CD} \mid ABCD\theta^{f}_{BC}\theta^{d}_{Af}\theta^{00}_{dD}) \tag{45}$$

$$= (ABCD\theta^{e}_{AB}\theta^{d}_{eC}\theta^{00}_{dD} \mid ABCD\theta^{f}_{BC}\theta^{d}_{Af}\theta^{00}_{dD}) \tag{46}$$

$$= (ABC\theta^{e}_{AB}\theta^{dM}_{eC} \mid ABC\theta^{f}_{BC}\theta^{dM}_{Af}) \tag{47}$$

$$= U(abcd \mid ef) \tag{48}$$

$$= (ABCD\theta^{e}_{AB}\theta^{e}_{CD}\theta^{00}_{AB,CD} \mid ABCD\theta^{f}_{BC}\theta^{f}_{AD}\theta^{00}_{AD,BC})\, \sigma(f+a-d) \tag{49}$$

$$= (CBA\theta^{e}_{BA}\theta^{dM}_{Ce} \mid CBA\theta^{f}_{CB}\theta^{dM}_{fA}). \tag{50}$$

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The first equality follows from a consideration of the repeated application of theorem 3 to any set of eigangs $A, B, \ldots$ coupled to a final L value, when it is obvious that the function with all couplings reversed is $\sigma(L-a-b-\ldots)$ times the original independently of intermediate couplings. The two equal changes within the integral thus cancel. The second and third equalities are obtained by changes of order of coupling and relations of the type $U(a\,b\,c\,0\,|\,c\,a) = 1$. The fourth equality follows by elementary considerations, or explicitly by theorem 9, part IV, and the identity of the resulting expression with the U coefficient results from the definition and theorem 5. The alternative expression (49) is obtained from a trivial alteration of the coupling in (45), and (50) follows from the complete reversal of coupling in (47) by the above rule.

Expressions (43) and (45) differ by complete reversal of order of a, b, c, d, and (47) and (50) by a reversal of a, b, c. Hence these changes give U coefficients with equal values and establish the first part of the theorem. The equality of expressions (48) and (49) in conjunction with theorem 5 establish the second identity.

THEOREM 8. If the W coefficients are defined, as in part IV, to satisfy

$$F\begin{pmatrix} A^* & B^* \\ C & D \end{pmatrix} \begin{matrix} \theta_{AB}(L,M) \\ \theta_{CD}(L,M) \end{matrix} = \sum_{\bar{L}} W\begin{pmatrix} a & b \\ c & d \end{pmatrix} L\bar{L} F\begin{pmatrix} \bar{A} & \bar{B} \\ C & D \end{pmatrix} \begin{matrix} \theta_{AC}(\bar{L},\bar{M}) \\ \bar{\theta}^*_{BD}(\bar{L},\bar{M}) \end{matrix}, \tag{51}$$

where F is some integral operator satisfying

$$\left.\begin{aligned} F\begin{pmatrix} A^* & B^* \\ C & D \end{pmatrix} \begin{matrix} \theta_{AB}(L,M) \\ \theta_{CD}(L',M') \end{matrix} &= \delta(L,L')\,\delta(M,M')\,qt(/M), \\ F\begin{pmatrix} \bar{A} & \bar{B} \\ C & D \end{pmatrix} \begin{matrix} \theta_{AC}(L,M) \\ \bar{\theta}^*_{BD}(L',M') \end{matrix} &= \delta(L,L')\,\delta(M,M')\,qt(/M), \end{aligned}\right\} \tag{52}$$

then

$$W\begin{pmatrix} a & b \\ c & d \end{pmatrix} L\bar{L} = U\begin{pmatrix} b & a & c & d \\ L & & \bar{L} & \end{pmatrix} \sigma(d-b-L)\sqrt{\left(\frac{2\bar{L}+1}{2L+1}\right)}. \tag{53}$$

Proof. It is possible to express the first form of coupled F integral in terms of the second form by means of the following succession of changes, so that the resultant coefficients can be equated to the W coefficients

$$F\begin{pmatrix} A^* & B^* \\ C & D \end{pmatrix} \begin{matrix} \theta^{LM}_{AB} \\ \theta^{LM}_{CD} \end{matrix} = \sum_{M} \frac{\sigma(M)}{(2\bar{L}+1)} F\begin{pmatrix} \bar{A} & \bar{B} \\ C & D \end{pmatrix} \begin{matrix} \theta^{L,-M}_{BA} \\ \theta^{LM}_{CD} \end{matrix} \tag{54}$$

$$= \frac{\sigma(-L)}{\sqrt{(2L+1)}} F\begin{pmatrix} \bar{A} & \bar{B} \\ C & D \end{pmatrix} \begin{matrix} \theta^{L}_{BA}\theta^{00}_{BA,CD} \\ \theta^{L}_{CD} \end{matrix} \tag{55}$$

$$= \frac{\sigma(-L+d-\bar{L}-b)}{\sqrt{(2L+1)}} \sum_{\bar{L}} F\begin{pmatrix} A & B \\ C & D \end{pmatrix} \begin{matrix} \theta^{\bar{L}}_{AC}\theta^{00}_{AC,BD} \\ \theta^{\bar{L}}_{BD} \end{matrix} U\begin{pmatrix} b & a & c & d \\ L & & \bar{L} & \end{pmatrix} \tag{56}$$

$$= \sum_{\bar{L}}\sum_{M} \frac{\sigma(-L+d-\bar{L}-b+\bar{L}-M)}{\sqrt{[(2\bar{L}+1)\,(2L+1)]}} F\begin{pmatrix} \bar{A} & \bar{B} \\ C & D \end{pmatrix} \begin{matrix} \theta^{LM}_{AC} \\ \theta^{\bar{L},-M}_{BD} \end{matrix} U\begin{pmatrix} b & a & c & d \\ L & & \bar{L} & \end{pmatrix} \tag{57}$$

$$= \sum_{\bar{L}} \sigma(d-b-L)\sqrt{\left(\frac{2\bar{L}+1}{2L+1}\right)} F\begin{pmatrix} \bar{A} & \bar{B} \\ C & D \end{pmatrix} \begin{matrix} \theta^{\bar{L}M}_{AC} \\ \bar{\theta}^{*\bar{L}M}_{BD} \end{matrix} U\begin{pmatrix} B & A & C & D \\ L & & \bar{L} & \end{pmatrix}. \tag{58}$$

Expression (54) was obtained by theorem 3 giving

$$\begin{aligned} a^*b^*\theta^{LM} &= \sigma(M)\,\Sigma\bar{a}(-m)\,\bar{b}(-M+m)\,X(L,M,a,b,m) \\ &= \sigma(M)\,\Sigma\bar{a}(-m)\,\bar{b}(-M+m)\,X(L,-M,b,a,-M+m) \\ &= \sigma(M)\,\bar{a}\bar{b}\theta^{L,-M}_{ba}, \end{aligned} \tag{59}$$

and then by dividing by $(2L+1)$ and summing over M, since the integral is independent of M. Expression (55) was obtained by the explicit formula for $X(0,0,L,L,M)$. Expression (56) follows from the special change of coupling of theorem 7, and expression (57) from the expansion of the last coupling with values of $X(0,0,L,L,M)$. Expression (58) results from the independence of the integral on M and by the replacement $\sigma(-M)\,\theta^{L,-M} = \bar{\theta}^{*LM}$. The comparison of this last expansion with the W coefficient expansion gives the values stated in the theorem.

THEOREM 9. The values of W coefficients with symmetrically altered arguments are given by

$$W\begin{pmatrix} c & d \\ a & b \end{pmatrix} e\, f = W\begin{pmatrix} a & b \\ c & d \end{pmatrix} e\, f\, \sigma(2d-2b), \tag{60}$$

$$W\begin{pmatrix} b & a \\ d & c \end{pmatrix} e\, f = W\begin{pmatrix} a & b \\ c & d \end{pmatrix} e\, f\, \sigma(a+b-c-d). \tag{61}$$

Proof. These results follow trivially by the expression of the W in terms of the U coefficients, the change of order of the arguments of this by theorem 7 and the re-expression of the result in terms of the W coefficient.

THEOREM 10.

$$\sum_f U\begin{pmatrix} a & b & c & d \\ & e & & f \end{pmatrix} U\begin{pmatrix} a & b & c & d \\ & g & & f \end{pmatrix} = \delta(e,g), \tag{62}$$

$$\sum_f W\begin{pmatrix} a & b \\ c & d \end{pmatrix} e\, f\,(-1)^{a+b-e}\, W\begin{pmatrix} a & c \\ b & d \end{pmatrix} f\, g\,(-1)^{a+c-f} = \delta(e,g). \tag{63}$$

Proof. The first identity follows directly from the expansion of $\theta^e_{ab}\,\theta^{dM}_{ec}$ in terms of the alternative couplings and the re-expansion of these back in terms of the original type of couplings. The second identity is obtained by replacing the U coefficients by their W equivalents by theorem 8.

COMMENT. The theorems derived above are very useful for reducing the preliminary work for the calculation of Schrödinger integrals. However, their theoretical significance is not great, and the results are much more important than the methods of proof.

5. THE EVALUATION OF THE FUNDAMENTAL TWO-ELECTRON INTEGRALS

In the general method for the reduction of all integrals of the operator $\sum_{i>j} 1/r_{ij}$ given in part V, the reduction was considered complete when the integrals had been expressed in terms of two-electron integrals of the form

$$[p_{12}/r_{12} \,\|\, x_r x_s \,|\, x_t x_u]^{LS} = [p_{12}/r_{12} \,\|\, \bar{x}_r(t_1)\, x_s(t_1')\, \bar{x}_t(t_2)\, x_u(t_2')]\, \theta^{LSMU}_{rs}\, \bar{\theta}^{*LSMU}_{tu}, \tag{64}$$

where p_{12} denotes either 1 or $P(t_1', t_2' \,|\, t_2', t_1')$. These integrals could be evaluated by the expansions of the θ summations followed by the evaluation of each term of the type

$$[x_r^*(m_1,u_1)\, x_t^*(m_2,u_2) \,|\, 1/r_{12} \,|\, x_s(m_3,u_3)\, x_u(m_4,u_4)] \tag{65}$$

by the well-known procedure using the $c^k(l,m,l',m')$ tables (see Condon & Shortley 1935, p. 174). However, this is very laborious, and it will be shown below that the unexpanded

integrals can be evaluated directly and are actually simpler and more fundamental quantities than the particular terms of such an expansion. This evaluation does not depend on the c^k tables, which are not required for any part of the present scheme of analysis. The first results will be expressed in terms of some coefficients denoted by Q^L and Q^{LK} which can be calculated very simply, without summations, from the X and W coefficients. These are the actual coefficients in the expansions of the above integrals in terms of integrals depending only on the radial functions. These results are obtained by the following detailed theorems, some of which will be of value for other topics.

It will be convenient to use notations such as

$$[G_{12}\,\|\,x_r x_s\,|\,x_t x_u]^L \quad \text{and} \quad [G_{12}\,\|\,x_r x_s\,|\,x_t x_u]^S \tag{66}$$

exactly as in equation (64), but with the couplings confined respectively to the L or S components instead of both L and S as in the original case. The integration operation may be different in different cases but will correspond just to the variables of which the x_r, etc., are functions.

To avoid repetition of the well-known properties of spherical harmonics and spin functions two theorems will now be quoted without proof. If necessary, the effective justification of these can be found in Condon & Shortly (1935, pp. 54 and 50 respectively).

THEOREM 11. Let $s_\alpha(v, v')$ with $\alpha = x, y, z$ denote the matrices

s_x

$v \backslash v'$	$\frac{1}{2}$	$-\frac{1}{2}$
$\frac{1}{2}$	0	$\frac{1}{2}$
$-\frac{1}{2}$	$\frac{1}{2}$	0

s_y

$v \backslash v'$	$\frac{1}{2}$	$-\frac{1}{2}$
$\frac{1}{2}$	0	$-\frac{1}{2}i$
$-\frac{1}{2}$	$\frac{1}{2}i$	0

s_z

$v \backslash v'$	$\frac{1}{2}$	$-\frac{1}{2}$
$\frac{1}{2}$	$\frac{1}{2}$	0
$-\frac{1}{2}$	0	$-\frac{1}{2}$

(67)

Let s_α denote the operators $$s_\alpha = \sum_{v'} s_\alpha(v, v')\, P(v\,|\,v') \tag{68}$$

acting on functions of v; and $s_{i\alpha}$ the corresponding operators acting on functions of v_i. Then a set $\mathbf{s}$ constitutes a set of angular operators and the functions $\mu_{\frac{1}{2}}(v)$ and $\mu_{-\frac{1}{2}}(v)$, or α and β as they are usually denoted, defined by

$$\alpha(\tfrac{1}{2}) = \beta(-\tfrac{1}{2}) = 1, \quad \alpha(-\tfrac{1}{2}) = \beta(\tfrac{1}{2}) = 0 \tag{69}$$

form a connected set of eigangs of $\mathbf{s}$ with first eigang value $s = \frac{1}{2}$.

COMMENT. A trivial algebraic proof is sufficient, but is not really significant, since the $s_\alpha(v, v')$ were effectively constructed to give just this property.

THEOREM 12. Let the spherical harmonics $S^{lm}(\theta, \phi)$ be defined for integral values of l and m with $l \geqslant |m|$ by

$$S^{lm} = \frac{e^{im\phi}\,(-1)^l}{\sqrt{(2\pi)}} \sqrt{\left(\frac{(2l+1)\,(l+m)!}{2(l-m)!}\right)} \frac{1}{2^l l!} \frac{1}{\sin^m\theta} \frac{d^{l-m}}{d(\cos\theta)^{l-m}} \sin^{2l}\theta. \tag{70}$$

Then S^{lm} constitute a connected set of eigangs of the angular operators $\mathbf{L} = (-i)\,\mathbf{r} \wedge (\partial/\partial\mathbf{r})$ with eigang values l, m, and there are no functions of θ, ϕ other than numerical multiples of these which are eigangs of $\mathbf{L}$. It also follows that

$$S^{LM} = i^{2M}\,(S^{L,-M})^*, \tag{71}$$

these latter being the quantities which according to the earlier notation could be denoted as $\overline{S}^{LM}$.

COMMENT. In atomic wave-function calculations of the type under consideration all the actual single-electron functions used will be of the type $Aa\mu$, where A denotes a function of the radial variable r, a a spherical harmonic and μ one of the above spin eigangs. It could be proved that all connected sets of eigangs L and S are of this type, but this is not necessary for the present argument. The following theorems will contribute to the evaluation of the required integrals when the x_r, etc., are of the types $Aa\mu$, $Bb\mu$, etc. This will be performed by considering the integral operators with respect to the r and v variables separately, since it is obvious that the complete integral is just a product of two such integrals.

THEOREM 13. The following integrals exist only for $S = 0$, or 1, and have the values

$$[\|\mu\mu\,|\,\mu\mu]^S = -2\delta(S,0), \quad [P_{12}\|\mu\mu\,|\,\mu\mu]^S = -1, \tag{72}$$

where $$P_{12} = P(t_1', t_2'\,|\,t_2', t_1').$$

Proof. The following values follow directly from the definitions of the X coefficients

$$\left.\begin{aligned} X(1,1,\tfrac{1}{2},\tfrac{1}{2},1) = 1, \quad X(0,0,\tfrac{1}{2},\tfrac{1}{2},-\tfrac{1}{2}) = -1/\sqrt{2}, \\ X(1,0,\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}) = X(1,0,\tfrac{1}{2},\tfrac{1}{2},-\tfrac{1}{2}) = X(0,0,\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}) = 1/\sqrt{2}. \end{aligned}\right\} \tag{73}$$

The insertion of these in the full expansion of the integrals gives the values in the theorem.

THEOREM 14. If a and b denote connected sets of spherical harmonics, then

$$\begin{aligned} a(\theta,\phi)\,b(\theta,\phi)\,\theta^{LM} &= S^{LM}(\theta,\phi)\,X(L,0,L_a,L_b,0)\,\sqrt{[(2L_a+1)\,(2L_b+1)/4\pi(2L+1)]} \\ &= 0 \quad \text{if} \quad (L_a+L_b-L) \text{ is odd.} \end{aligned} \tag{74}$$

Proof. It is apparent that

$$\begin{aligned} &\mathbf{L}_1\,a(\theta_1,\phi_1)\,b(\theta_1,\phi_1)\,\theta^{LM} \\ &\quad = \mathbf{L}_1 P(\theta_2,\phi_2\,|\,\theta_1,\phi_1)\,a(\theta_1,\phi_1)\,b(\theta_2,\phi_2)\,\theta^{LM} \\ &\quad = P(\theta_2,\phi_2\,|\,\theta_1,\phi_1)\,(\mathbf{L}_1+\mathbf{L}_2)\,a(\theta_1,\phi_1)\,b(\theta_2,\phi_2)\,\theta^{LM}, \end{aligned} \tag{75}$$

and hence by taking $P(\theta_2,\phi_2\,|\,\theta_1,\phi_1)$ for the operator K in theorem 10, part IV, it follows that $ab\theta^{LM}$ are a connected set of eigangs of $\mathbf{L}$ with eigang values L, M. Hence by theorem 12 these must be a multiple of the S^{LM}. The numerical coefficient can be obtained by considering the ratio of the values of these functions at the point $\theta = \phi = 0$. Let a_0, b_0, S_0^{LM} denote the values at this point. Since $\cos\theta = 1$ it follows for positive M that

$$\begin{aligned} &S^{LM}(0,0)\,(-1)^L\sqrt{\left(\frac{2(L-M)!\,2\pi}{(2L+1)\,(L+M)!}\right)}\,2^L L! \\ &\quad = \left[\frac{1}{(1+x)^{\frac{1}{2}M}\,(1-x)^{\frac{1}{2}M}}\,\frac{\mathrm{d}^{L-M}}{\mathrm{d}x^{L-M}}\,(1+x)^L\,(1-x)^L\right]_{x=1} \\ &\quad = [(L!/M!)\,(-1)^{L-M}\,(1-x)^{\frac{1}{2}M}\,(1+x)^{\frac{1}{2}(L-M)} + \text{higher powers of } (x-1)]_{x=1} \\ &\quad = 0 \quad \text{when } M>0 \\ &\quad = (-1)^L L\,2^L \quad \text{when } M = 0. \end{aligned} \tag{76}$$

The values for negative M will similarly be zero by theorem 12, and it follows that

$$S_0^{LM}(0,0) = \delta(M,0)\,\sqrt{[(2L+1)/4\pi]}, \tag{77}$$

and $$ab\theta^{LM}/S^{LM} = a_0 b_0 \theta^{L0}/S_0^{L0} = \sqrt{[(2L_a+1)\,(2L_b+1)/4\pi(2L+1)]}\,X(L,0,L_a,L_b,0), \tag{78}$$

as stated in the theorem. The result when (L_a+L_b-L) is odd follows immediately from the symmetry properties of the X coefficients, since $X(L, 0, L_a, L_b, 0)$ is equal to minus itself in this case and the result thus vanishes.

THEOREM 15.

$$[1/r_{12} \| AaBb \mid CcDd]^L = J^L_{ab} J^L_{cd} [A^*B \mid C^*D]^L, \tag{79}$$

where

$$\begin{aligned} J^L_{ad} &= X(L, 0, L_a, L_b, 0) \sqrt{[(2L_a+1)(2L_b+1)]/(2L+1)} \\ &= 0 \quad \text{if} \quad (L_a+L_b-L) \text{ is odd}, \end{aligned} \tag{80}$$

and

$$[f \mid g]^L = \iint \mathrm{d}r_1 \, \mathrm{d}r_2 f(r_1) \, g(r_2) \, \{r_1, r_2\}^L, \tag{81}$$

where

$$\left.\begin{aligned} \{r_1, r_2\}^L &= r_1^{L+2}/r_2^{L-1} \quad \text{for} \quad r_2 > r_1 \\ &= r_2^{L+2}/r_1^{L-1} \quad \text{for} \quad r_1 > r_2. \end{aligned}\right\} \tag{82}$$

Proof. It is necessary to assume the well-known expansion

$$1/r_{12} = \sum_{L, M} [4\pi/(2L+1)] \, [S^{LM}(\theta_1, \phi_1)]^* \, S^{LM}(\theta_2, \phi_2) \, \{r_1, r_2\}^L / r_1^2 r_2^2. \tag{83}$$

By the introduction of the J's defined above into the preceding theorem, it follows that

$$\begin{aligned} a(\theta, \phi) \, b(\theta, \phi) \, \theta^{LM} &= S^{LM}(\theta, \phi) \, J^L_{ab} \sqrt{[(2L+1)/4\pi]}, \\ c(\theta, \phi) \, d(\theta, \phi) \, \bar{\theta}^{*LM} &= [S^{LM}(\theta, \phi)]^* \, J^L_{cd} \sqrt{[(2L+1)/4\pi]}. \end{aligned} \tag{84}$$

From the definition of the $(\|\ )$ operation and the execution of the $P(t' \mid t)$ operations it thus follows

$$\begin{aligned} &[1/r_{12} \| AaBb \mid CcDd]^L \\ &\quad = \int \ldots \int \mathrm{d}r_1 \, \mathrm{d}r_2 \, \mathrm{d}(\cos\theta_1) \, \mathrm{d}(\cos\theta_2) \, \mathrm{d}\phi_1 \, \mathrm{d}\phi_2 \{A^*(r_1) \, B(r_1) \, C^*(r_2) \, D(r_2) \, r_1^2 r_2^2 \\ &\qquad \times S^{LM}(\theta_1, \phi_1) \, [S^{LM}(\theta_2, \phi_2)]^* \, J^L_{ab} J^L_{cd} [(2L+1)/4\pi] / r_{12}\}. \end{aligned} \tag{85}$$

The insertion of the expansion for $1/r_{12}$ and the orthonormality of the S^{LM} thus gives the value stated in the theorem, the zero result occurring as in the preceding theorem.

THEOREM 16. If a, b, c and d denote sets of functions of r which are connected sets of eigangs of $\mathbf{L}$, and if G_{12} denotes the selective form of a Hermitian operator which commutes with $\mathbf{L}_1+\mathbf{L}_2$, then

$$[G_{12} p_{12} \| AaBb \mid CcDd]^L = \sum_K W \begin{pmatrix} L_a & L_b \\ L_d & L_c \end{pmatrix} LK \Big) (-1)^{L_a+L_d-K} [G_{12} p_{12} P_{12} \| AaDd \mid CcBb]^K. \tag{86}$$

Proof. It follows from theorems 3 and 12 that

$$\begin{aligned} \bar{a}b\theta^{LM} &= \bar{a}\bar{b}\theta^{LM} = \mathrm{i}^{2M} \sum_m a^*(-m) \, b^*(-M+m) \, X(L, M, L_a, L_b, m) \\ &= \mathrm{i}^{2M} \sum_m a^*(-m) \, b^*(-M+m) \, X(L, -M, L_a, L_b, -m) \, (-1)^{L_a+L_b-L} \\ &= \mathrm{i}^{2M} a^* b^* \theta^{L, -M} (-1)^{L_a+L_b-L}, \end{aligned} \tag{87}$$

and

$$\bar{c}d\bar{\theta}^{*LM} = \mathrm{i}^{-2M} cd\theta^{L, -M} = \mathrm{i}^{-2M} cd\theta^{L, -M}_{dc} (-1)^{L_c+L_d-L}. \tag{88}$$

Hence

$$[Gp_{12} \| AaBb \mid CcDd]^L = \left(G_{12} p_{12} \middle\| \begin{matrix} A^* & a^* & C^* & c \\ B & b^* & D & d \end{matrix}\right) \theta^{LM}_{ab} \theta^{LM}_{dc} (-1)^{L_a+L_b+L_c+L_d}. \tag{89}$$

If the operator F is defined to be

$$F\begin{pmatrix} a^*(m_1) & b^*(m_2) \\ d(m_3) & c(m_4) \end{pmatrix} = \left(G_{12}p_{12}\middle\| \begin{matrix} A^*a^*(m_1) & C^*c(m_4) \\ B\, b^*(m_2) & D\, d(m_3) \end{matrix}\right), \tag{90}$$

it follows that F satisfies the first condition of theorem 17, part IV. It also follows that F satisfies the second necessary condition, since

$$\begin{aligned} F\begin{pmatrix} ab \\ dc \end{pmatrix} \theta^{L'M'}_{adbc}{}^{LM} &= \left(G_{12}p_{12}P_{12}\middle\| \begin{matrix} A^* & aC^* & c \\ Dd & & Bb \end{matrix}\right) \theta^{L'M'}_{ad}\, \bar{\theta}^{*LM}_{bc} \\ &= \delta(L', L)\, \delta(M', M)\, qt(/M). \end{aligned} \tag{91}$$

Hence theorem 17, part IV, can be applied to the function F to change the coupling from $ab\theta$, $dc\theta$ to $ad\theta$, $bc\theta$. If this transformation is combined with a change of order of $bc\theta$ coupling to $cb\theta$ and P_{12} inserted with corresponding change in the serial order of Dd and Cc, the statement of the theorem is obtained.

THEOREM 17. The fundamental two-electron integrals for atoms can be expressed

$$\left.\begin{aligned} [1/r_{12}\,\|\, Aa\mu Bb\mu \,|\, Cc\mu Dd\mu]^{LS} &= \delta(S, 0)\, Q(ab\,|\,cd\,|\,L)\, [A^*B\,|\,C^*D]^L, \\ [-P_{12}/r_{12}\,\|\, Aa\mu Bb\mu \,|\, Cc\mu Dd\mu]^{LS} &= \sum_K Q(ab\,|\,cd\,|\,LK)\, [A^*D\,|\,C^*B]^K, \end{aligned}\right\} \tag{92}$$

where

$$Q(ab\,|\,cd\,|\,L) = -2J^L_{ab}\, J^L_{cd};$$

$$Q(ab\,|\,cd\,|\,LK) = W\begin{pmatrix} L_a & L_b & LK \\ L_d & L_c \end{pmatrix} J^K_{ad} J^K_{bc}, \tag{93}$$

where J^L_{ad} and $[f\,|\,g]^L$ are defined as in theorem (15).

Proof. This assertion is merely a combination of the results of previous theorems. The given integrals must first be expressed as products of an L integral and an S integral, the values of the latter being -2 and -1 respectively by theorem 13. The expression for the first L integral is given directly by theorem 15. The second is obtained by putting $-P_{12}/r_{12}$ for $G_{12}p_{12}$ in theorem 16, which gives a linear combination of integrals of the first type as a result. (L_a+L_d-L) can be taken as even, since the resulting terms vanish if this is not so.

COMMENT. The above analysis expresses all the two-electron integrals required for atoms in terms of integrals of the radial factors of the single-electron functions and in terms of the Q coefficients. The Q coefficients are defined in terms of other quantities, but since only comparatively few are required, these will be tabulated and used as numerical data. The wisdom of this is illustrated by the fact that for extensive calculations on atomic states, up to those of $3p$ shell, only fifty such coefficients have been used. No general formula for the radial integrals can be given, since these might involve very different types of functions in different applications. However, for the case of the polynomial exponential functions which are used in the accompanying numerical investigations general formulas can be obtained and have been given in part II. Formulas for the corresponding single-electron functions are also given there, so that the analysis of this section has reduced the evaluation of all the fundamental integrals required for converging calculations of atomic wave functions to comparatively simple and stereotyped procedures.

6. The symmetry properties of the V coefficients

It will now be shown that $$V^{LS}_{PQrs} = V^{LS}_{QPsr} \tag{94}$$ is satisfied by the coefficients which were defined in part IV in order to expand the density kernels of pairs of connected sets of eigangs such as A and B and thus to formulate the reduction of complicated integrals. This result shows that it is not necessary to pay attention to the order in which the initial pair of functions occurs, and also that it is only necessary to tabulate half of the possible coefficients. The result is established by two theorems, the first of which contains the main content of the analysis.

Theorem 18. If the V coefficients are defined for integral values of $a-b$ to satisfy

$$\begin{matrix} A \\ B \end{matrix}\left(\left\| \begin{matrix} C \\ C \end{matrix}\right) \overline{\theta}^{e}\,\theta^{LM}_{ef} = \begin{matrix} \overline{A} \\ B \end{matrix} \theta^{LM}_{AB}\, V(a,b\,|\,c\,|\,e,f\,|\,L), \tag{95}$$

then $$V(a,b\,|\,c\,|\,e,f\,|\,L) = V(b,a\,|\,c\,|\,f\;e\,|\,L), \tag{96}$$

where a, b, c are the first eigang values of the connected sets A, B, C and e, f of the vector couplings.

Proof. It follows from the change of coupling properties shown earlier and the definition of the a^n quantities that

$$\begin{aligned} AC\overline{\theta}^{LM} &= \sigma(M)\, A^{*}C^{*}\theta^{L,\,-M} \\ &= \sigma(M) \sum_{m} A^{*}(m)\, C^{*}(-M-m)\, X(L,-M,a,c,m) \\ &= \sum_{m} \overline{A}(-m)\, \overline{C}(M+m)\, X(L,M,c,a,M+m) \\ &= \overline{A}\overline{C}\theta^{LM}_{CA}. \end{aligned} \tag{97}$$

Let A_1, B_1, C_1, C_2 be any connected sets of eigangs with first values a, b, c. Let the coefficients J be defined to satisfy

$$C_1 A_1 \theta^{e} B_1 C_2 \theta^{f} \theta^{LM} = \sum_{l,\,m,\,m_1,\,m_2} J(l,m,m_1,m_2)\, A_1 B_1 \theta^{lm} C_1(m_1)\, C(m_2)\, \sigma(-m_1), \tag{98}$$

an expansion which is always possible since any uncoupled term could be expressed as such a linear combination. Then since

$$(\|\,\overline{C}(m_1)\, C(m_2)) = \sigma(m_1)\, \delta(-m_1, m_2) \tag{99}$$

by the meaning of these notations, it follows that the straightforward evaluation of the V coefficient by expansion of the first couplings in the theorem, followed by integration and identification of A with $\overline{A}_1$, $\overline{C}$ with C_1, etc., yields

$$V(a,b\,|\,c\,|\,e,f\,|\,L) = \sum_{m} J(L,M,m,-m). \tag{100}$$

Similarly, if J' are defined by

$$C_2 B_1 \theta^{f} A_1 C_1 \theta^{e} \theta^{LM} = \sum_{l,\,m,\,m_1,\,m_2} J'(l,m,m_1,m_2)\, B_1 A_1 \theta^{lm} C_2(m_1)\, C_1(m_2)\, \sigma(-m_1), \tag{101}$$

then $$V(b,a\,|\,c\,|\,f,e\,|\,L) = \sum_{m} J'(L,M,m,-m). \tag{102}$$

However, it follows that

$$\begin{aligned} C_1 A\theta^{e} B C_2 \theta^{f} \theta^{LM} &= C_2 B\theta^{f} A C_1 \theta^{e} \theta^{LM} \sigma(a+b+2c-L) \\ &= \sum_{l,\,m,\,m_1,\,m_2} \sigma(2c-L+l-m_1+m_2)\, J'(l,m,m_1,m_2)\, AB\theta^{lm} C_1(m_2)\, C_2(m_1)\, \sigma(-m_2). \end{aligned} \tag{103}$$

Hence $$V(a,b\,|\,c\,|\,e,f\,|L) = \sum_m \sigma(2c+2m)\,J'(L,M,-m,m) = V(b,a\,|\,c\,|\,f,e\,|\,L), \qquad (104)$$
since $c+m$ must be integral.

THEOREM 19. If P and Q denote conventional vector-coupled antisymmetric functions constructed from single electron eigangs x_r, and the V coefficients are defined by the density kernel expansion,

$$R(t,t')\,\bar{P}Q\theta_{PQ}(L,M,S,U) = \sum_{rs} V^{LS}_{PQrs}\,\bar{x}_r(t)\,x_s(t')\,\theta_{rs}(L,M,S,U), \qquad (105)$$

then
$$V^{LS}_{PQrs} = V^{LS}_{QPsr}. \qquad (106)$$

Proof. Consider the calculation of the V_{PQ} and V_{QP} coefficients according to the reduction method of § 5, part V. It is then apparent that the coefficients at every stage of the reduction have the same values for both PQ and QP cases. First, if the order of the coupling has to be altered and Q expressed by means of U coefficients as a linear combination of Q'_i the U's are real, and the same for Q and Q^*. The η^{LS}_{ik}, which enable $a^n\phi$ functions to be expanded in terms of $a^{n-1}\phi$ functions, are also real and the same expansion results in both cases. Finally, the elementary V coefficients were shown to be independent of this ordering by the preceding theorem.

DISCUSSION. It is useful to note that the result of this analysis, together with those on W and Q coefficients, shows that all the W, V, Q coefficients used in the analysis of $(\psi\,|\,H\,|\,\psi')$ have exactly the same numerical values of those used in the analysis of $(\psi'\,|\,H\,|\,\psi)$. This means that in all tabulations of these quantities only the combination ψ, ψ', or its equivalent, need be entered, independently of the order.

7. A SHORT EVALUATION OF CERTAIN INVARIANT PORTIONS OF SCHRÖDINGER INTEGRALS

Since a general method of reducing all Schrödinger integrals to one- and two-electron integrals has been given, there is no logical necessity for any addition to this. However, a relation will be derived below which makes it possible to write down a considerable portion of many such integrals merely by inspection. The relation makes it possible to write down the $(A\,|\,K\,|\,B)$, $(A\,|\,V\,|\,B)$, $[A^*B\,|\,C^*D]^0$ and some other special terms by inspection. The remaining $[A^*B\,|\,C^*D]^L$ expressions will require the general theory, but frequently only for lower-order integrals. The method is not applicable to all integrals, but is sufficiently widely so that the labour of integral evaluation is reduced to about a quarter of what it would be otherwise. Formulas which correspond to a very special case, special symmetric integrals, of the following relation have been known before (see Condon & Shortley 1935, p. 182), but the use of these would only effect a very much smaller saving than the relation given below.

It appears most useful to state the definitions and theorems in the general form applying to the sectioned co-detors introduced in part III. They are then applicable to certain molecular calculations as well as for the present atomic requirements. It is, however, worth noting that for application to atoms the general classes of elementary functions x_r will be just the connected sets of eigangs of the form $Aa\mu$, etc. For example, if

$$\psi = \mathscr{A}sA^2\mathrm{S}^1sB^2\mathrm{S}^1pA^4\mathrm{S}^1$$

it would be convenient to take $x_1 = sA$, $x_2 = sB$, $x_3 = pA$, when the n_r would have the values $n_1 = 2$, $n_2 = 2$, $n_3 = 4$. In such cases the m suffix of the following definition and theorem would have to take values corresponding to all pairs of values of the ordinary eigang suffixes m and u.

DEFINITION. Let x_r $(r = 1, 2, \ldots)$ denote various classes of orthonormal single-electron functions. Let ψ and ψ' denote two co-detors constructed from these elementary functions with configuration n_r and n'_r respectively. Then a row of symbols y_1, y_2, y_3 written above a corresponding row $y'_1, y'_2, \ldots$ will be called a correspondence of ψ, ψ' when

(i) each y is one of the symbols x_r,

(ii) n_1 of the y_k are equal to x_1, n_2 to x_2, etc., and n'_1 of the y'_k to x_1, n'_2 to x_2, etc.,

(iii) there are as many x_1 symbols under x_1 symbols, x_2 under x_2, etc., as possible, and the first pair with $y_k \neq y'_k$ consists of the first x_r for which $n_r > n'_r$ over the first x_r for which $n_r < n'_r$.

Let $\sum_i J_i + \sum_{i>j} G_{ij}$ be some symmetric operator for which

$$[J \| x_r x_s] \equiv \left(J \left\| \begin{matrix} x_r^*(m_1) \\ x_s(m_2) \end{matrix} \right.\right) = \delta(m_1, m_2)\, qt(/m_1), \tag{107}$$

$$[G \| x_r x_s \mid x_t x_u] = \left(G \left\| \begin{matrix} x_r^*(m_1) & x_t^*(m_3) \\ x_s(m_2) & x_u(m_4) \end{matrix} \right.\right) = \delta(m_1, m_3 \mid m_2, m_4)\, qt(/m_1, m_3), \tag{108}$$

where m_1, etc., label the different members of the classes x_r and the short notations on the left-hand side will be used subsequently.

Then the invariant is defined to be

$$(\text{inv} \| \psi\psi') = \sum_k [J \| y_k y'_k]\, \sigma_k + \sum_{k>1} [G \| y_k y'_k \mid y_1 y'_1]\, \sigma_{kl}, \tag{109}$$

where $\sigma_k = 0$ if there is any other pair $y_m \neq y'_m$ with $k \neq m$, and $\sigma_{kl} = 0$ if there is a pair $y_m \neq y'_m$ with $k \neq m \neq l$, but otherwise σ_k and σ_{kl} are unity. Any integral $[J \| xx]$ or $[G \| xx \mid xx]$ which does not occur in the invariant will be called a variant integral.

THEOREM 20. If ψ, ψ' and $\sum_i J_i + \sum_{i>j} G_{ij} = F$ satisfy the invariant conditions, then

$$(F \| \psi\psi') = C(\text{inv} \| \psi\psi') + \text{variant integrals}, \tag{110}$$

where C is a constant, and $C = (\psi \mid \psi')$ when $\psi = \psi'$.

Proof. Let ψ be expressed as a linear combination of serial products of which

$$j = z_1(t_1)\, z_2(t_2)\, z_3(t_3) \ldots z_k(t_k) \ldots \tag{111}$$

denotes a typical term. Let j' and z'_r be related similarly to ψ'. Let j' be written below j. Consider the case when the vertical pairs in j, j' are exactly the same as those in the ψ, ψ' correspondence pattern, the order of occurrence of the pairs being ignored. Consider first the special case of this when the m value of each z_k is the same as that of z'_k, that is, that the number labels of the functions within the x_r classes are the same in each vertical pair. Then any such $(F \mid jj')$ is equal to the invariant, since any vertical pair z_k, z'_k will give an integral $[J \| z_k z'_k]$ by the operator J_k provided that there is no other pair $z_l \neq z'_l$, in which case multiplication by this orthogonality integral would give zero. The corresponding G integrals will be similarly obtained. In the other subcase when j, j' have the correspondence pattern but

there is some $m_k \neq m'_k$, it follows that $(F \| jj') = 0$, since each factor integral containing z_k, z_k will be zero whether these occur in a J, G, or orthogonality integral.

Consider now the case when a particular integral, say $[J \| x_1 z']$, occurs in both the invariant and in any given $(F \| jj')$. Then there must be the $x_1 z'$ pair in both j, j' and the correspondence patterns, and there must be $n_1 - 1$ pairs (x_1, x_1), n_2 pairs (x_2, x_2), and so on, in both. Hence j, j' and the correspondence pattern must be the same. The same deduction holds if a G integral is common to both. Hence all j, j' pairs without the correspondence pattern contain only variant integrals. However, $(F \| \psi\psi')$ is a linear combination of $(F \| jj')$ integrals and so can only be a multiple of the invariant plus variant integrals. The coefficient $(\psi \mid \psi')$ follows in the case $\psi = \psi'$ since the $(F \| jj')$ integrals equal to the invariant are those with $j = j'$ and it is apparent that if

$$\psi = \sum_k C_k j_k, \tag{112}$$

then

$$(F \| \psi\psi') = \sum_k C_k C_k^* (\text{inv} \| \psi\psi') + \text{variants} \tag{113}$$

and

$$(\psi \mid \psi') = \sum_k C_k C_k^*. \tag{114}$$

THEOREM 21.

$$\left(\frac{\{r_1, r_2\}^0}{r_1^2 r_2^2} \middle\| \begin{matrix} A^*a^*(m_1)\,\mu^*(u_1) & C^*c^*(m_3)\,\mu^*(u_3) \\ Bb(m_2)\,\mu(u_2) & Dd(m_4)\,\mu(u_4) \end{matrix} \right)$$
$$= \delta(L_a, L_c, m_1, u_1, m_3, u_3 \mid L_b, L_d, m_2, u_2, m_4, u_4)\,[A^*B \mid C^*D]^0. \tag{115}$$

Proof. Since $\{r_1, r_2\}^0 / r_1^2 r_2^2$ commutes with L_1, S_1, L_2, S_2 it follows that the integral vanishes if $L_a \neq L_b$, etc., giving all the necessary equalities shown in the δ. When these conditions are satisfied it follows that $[a(m) \mid b(m)] = 1$, since a and b then denote the same spherical harmonic. Finally, the radial integral denoted by $[A^*B \mid C^*D]^0$ is the only residual factor if the integration is performed as usual in polar co-ordinates.

DEFINITION. It is very convenient to use a notation

$$id[AB \mid CD] = [AB \mid CD]^0 + \sum_k Q(ab \mid cd \mid 0K)\,[AD \mid CB]^K / Q(ab \mid cd \mid 0). \tag{116}$$

DEFINITION. The Schrödinger Hamiltonian can be written

$$H = \sum_i J_i + \sum_{i>j} G_{ij} + \sum_{L=1} \sum_{M=-L}^{L} \sum_{i>j} \frac{\{r_i, r_j\}^L}{r_i^2 r_j^2} S^{LM}(\theta_i, \phi_i)\,[S^{LM}(\theta_j, \phi_j)]^*, \tag{117}$$

where

$$G_{ij} = \{r_i, r_j\}^0 / r_i^2 r_j^2.$$

The invariant of $(\psi \mid \sum_i J_i + \sum_{i>j} G_{ij} \mid \psi')$ will be called the primary Schrödinger invariant. However, it is very convenient to define a more complicated function as the fundamental or secondary Schrödinger invariant. This is derived from the primary invariant by replacing certain of the $[G \| x_r x_s \mid x_t x_u]$ or $[x_r x_s \mid x_t x_u]^0$ as they were shown to be by theorem 21 by the corresponding $id[x_r x_s \mid x_t x_u]$ according to the following conditions. If ψ and ψ' contain respectively component functions η and η' which (i) depend on the same numbers of variables, (ii) have $L = S = 0$, (iii) depend only on some sets x_r which do not otherwise occur in ψ and ψ', then all the $[x_r x_s \mid x_t x_u]^0$ for which either x_r, x_s or x_t, x_u, but not both, belong to η, η' must be replaced by $id[x_r x_s \mid x_t x_u]$. There may be different pairs η, η' of this type in a

given ψ, ψ', and if the conditions hold with respect to any such pair the replacement must be made.

It must be noted that any integrals which do not occur in an invariant expression when all *id* terms are written out in full will be designated as variant terms, and so these will actually be different for the primary or secondary invariants.

It must not be assumed that the extra terms of the secondary invariant arise just from the extra terms of H. They come partly from this and partly from the variant terms of $\sum_i J_i + \sum_{i>j} G_{ij}$.

THEOREM 22. If ψ and ψ' are conventional vector-coupled functions, then, if inv denotes either Schrödinger invariant, it follows that

$$(\psi \,|\, H \,|\, \psi') = C(\text{inv} \,\|\, \psi\psi') + \text{variant terms}, \tag{118}$$

where C is a constant equal to 1 when $\psi = \psi'$.

Proof. It follows from the two preceding theorems that

$$(\psi \,|\, \sum_i J_i + \sum_{i>j} G_{ij} \,|\, \psi') = C(JG \text{ invariant} \,\|\, \psi\psi') + \text{variant terms}, \tag{119}$$

where this invariant consists of the $[J \,\|\, x_r x_s]$ and $[A^*B \,|\, C^*D]^0$ appropriate to the correspondence pattern. If the extra terms $\{r_i, r_j\}^L / r_1^2 r_2^2$ with $L \neq 0$ are included to give the complete Schrödinger Hamiltonian, the extra integrals are all of the types $[A^*B \,|\, C^*D]^L$ and hence only contribute to the variant terms so that

$$(\psi \,|\, H \,|\, \psi') = C(JG \text{ invariant} \,\|\, \psi\psi') + \text{variant terms}. \tag{120}$$

Now consider the evaluation of the given integral by means of the general analysis developed in parts III, IV and V, and in particular the central $V^{LS}V^{LS}W^{L}W^{S}$ expansion. For any case where two groups η and η' with $L = S = 0$ are coupled vertically, only one term with $L = S = 0$ occurs in the expansion and so only terms of the type

$$[(1 - P_{12})/r_{12} \,\|\, x_r x_s \,|\, x_t x_u]^{00} = Q^0 id[x_r x_s \,|\, x_t x_u] \tag{121}$$

can occur between these η, η' groups and the other parts of ψ and ψ'. Hence the integrals concerned can only occur in the *id* combination. Since the coefficient of the first integral of the *id* is just that of the primary invariant, the coefficients of the other integrals are similarly fixed. Hence the theorem holds as stated, since when these terms are included in the invariant they are no longer to be considered as variant terms by the definition.

COMMENT. In order to illustrate the practical use of the invariant the details of three examples which have been calculated for the ground state of an F atom will be given. Let

$$\left.\begin{aligned} \phi_1 &= \mathscr{A} sA^2\mathrm{S}^1 sB^2\mathrm{S}^1 pA^3\mathrm{S}^4 pB^2\mathrm{P}^3\mathrm{P}^2, \\ \phi_2 &= \mathscr{A} sA^2\mathrm{S}^1 sBsC\mathrm{S}^1 pA^3\mathrm{S}^4 pB^2\mathrm{P}^3\mathrm{P}^2, \\ \phi_3 &= \mathscr{A} sA^2\mathrm{S}^1 sBsC\mathrm{S}^1 pA^4\mathrm{P}^3 pB\mathrm{P}^2, \end{aligned}\right\} \tag{122}$$

where $\mathscr{A}$ denotes all the antisymmetric ω operators included in conventional vector-coupled functions. It will be assumed that the radial factors of the functions sA, sB, etc., are all real, since it is always convenient to make them so in practice. The above functions illustrate the convenience of using the modified spectroscopic notation of S^4 instead of $^4\mathrm{S}$ as mentioned

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in § 2. Let $[sAsB]$ denote $(sA\,|-\frac{1}{2}\nabla^2-Z/r\,|\,sB)$, and inv the fundamental Schrödinger invariant, when it follows by application of the last theorem that

$$\left.\begin{aligned}(\phi_1\,|\,\mathrm{inv}\,|\,\phi_1) &= 2[sAsA]+2[sBsB]+3[pApA]+2[pBpB]+[sAsA\,|\,sAsA]^0\\ &\quad+[sBsB\,|\,sBsB]^0+3[pApA\,|\,pApA]^0+[pBpB\,|\,pBpB]^0\\ &\quad+4id[sAsA\,|\,sBsB]+6id[sAsA\,|\,pApA]+4id[sAsA\,|\,pBpB]\\ &\quad+6id[sBsB\,|\,pApA]+4id[sBsB\,|\,pBpB]+6[pApA\,|\,pBpB]^0,\\ (\phi_1\,|\,\mathrm{inv}\,|\,\phi_2) &= [sBsC]+[sBsC\,|\,sBsB]^0+2id[sBsC\,|\,sAsA]\\ &\quad+3id[sBsC\,|\,pApA]+2id[sBsC\,|\,pBpB],\\ (\phi_1\,|\,\mathrm{inv}\,|\,\phi_3) &= id[sBsC\,|\,pApB].\end{aligned}\right\}\qquad(123)$$

It follows by the reduction theorems as specified in part V, and the fact that only the variant terms, denoted var, need be calculated, that

$$\left.\begin{aligned}(\phi_1\,|\,H\,|\,\phi_1) &= (\phi_1\,|\,\mathrm{inv}\,\phi_1)+(sA^2S^1\,|\,\mathrm{var}\,|\,sA^2S^1)+(sB^2S^1\,|\,\mathrm{var}\,|\,sB^2S^1)\\ &\quad+(pA^3S^4pB^2P^3P^2\,|\,\mathrm{var}\,|\,pA^3S^4pB^2P^3P^2)\\ &= (\phi_1\,|\,\mathrm{inv}\,|\,\phi_1)-\tfrac{3}{5}[pApA\,|\,pApA]^2-\tfrac{1}{5}[pBpB\,|\,pBpB]^2+\tfrac{2}{3}[pApB\,|\,pBpA]^0\\ &\quad+\tfrac{4}{15}[pApB\,|\,pBpA]^2,\\ (\phi_1\,|\,H\,|\,\phi_2) &= C(\phi_1\,|\,\mathrm{inv}\,|\,\phi_2)+(sB^2S^1\,|\,\mathrm{var}\,|\,sBsCS^1)\\ &= \sqrt{2}\,(\phi_1\,|\,\mathrm{inv}\,|\,\phi_2),\\ (\phi_1\,|\,H\,|\,\phi_3) &= C(\phi_1\,|\,\mathrm{inv}\,|\,\phi_3) = (4/\sqrt{3})\,(\phi_1\,|\,\mathrm{inv}\,|\,\phi_3).\end{aligned}\right\}\qquad(124)$$

From these examples it should be appreciated how the use of the invariant enables so many of the simpler terms in actual integrals to be written down by inspection, and leaves a smaller number of difficult terms to be evaluated by the general reduction theory. This, however, does not apply at all to a small proportion of integrals in which the functions are very differently vector coupled.

8. Discussion

The preceding analysis completes the general basic theory which it is simplest to present before the description of the numerical calculations to be given in the following parts. The whole analytical scheme provides methods of expressing any Schrödinger integral required for a poly-detor variational treatment of any atom as a linear combination of two-electron radial integrals with coefficients determined by stereotyped procedures. It is, of course, equally applicable to the Schrödinger integrals required for less general calculations on atomic spectra. The scheme contains more relations than are necessary, since these reduce numerical calculation and tabulation and provide a powerful short method for a special, but wide, class of integrals. This latter method, derived in § 7, effectively evaluates the terms of the integrals which might be regarded as corresponding to the associated non-antisymmetric functions without vector coupling. The residual terms require the general theory, but fortunately are much fewer in number.

The other important part of the scheme developed above is a method of evaluating all the electrostatic integrals dependent on spherical harmonics, and provides a more systematic method than known previously.

In practice this scheme has proved even more serviceable than was expected, and probably considerably more than appears from the general theory. By its method it appears quite feasible to tabulate the formulas for all the Schrödinger integrals required for the lower states of all existent atoms for calculations of an accuracy superior to that of the Hartree-Fock solutions.

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