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ELECTRONIC WAVE FUNCTIONS

VIII. A CALCULATION OF THE GROUND STATES Na^+, Ne AND F^-

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CONTENTS

The wave functions and energies of the ground states of Na^+, Ne and F^- have been calculated using the variational method applied to a linear combination of Slater determinants. The wave functions are probably more accurate than any others previously reported for these ions. Some innovations in the method of calculation have been examined and have provided interesting empirical experience. The expansions of the relevant Schrödinger matrix elements are derived. This is the first time that a convergent method of calculation has been applied to systems of such complexity.

1. Introduction

In this part the calculation of wave functions for three ions, in states which approximate to that conventionally described as $1s^2 2s^2 2p^6$, is described. The method used, which has been applied to beryllium in a previous paper of this series and for which an extensive scheme for the evaluation of Schrödinger integrals has been developed in preceding parts, is the variational method applied to a linear combination of Slater determinants. The aim was both to obtain useful data on the structure of these ions and to find the most practical ways of applying the general theory to complex atoms. Three reasons were responsible for the particular choice of ions. First, they occur in the free vapour, liquid and solid states, and there is strong reason for believing that for these ions the wave functions for the latter states will differ only slightly from that for the former states. Thus the free-state wave functions could be used as approximations to the wave functions for the ions in the liquid or solid state, or as a first approximation in a more accurate calculation of these. Secondly, these ions were sufficiently complicated that the calculation of their wave functions would necessitate the most general theory and methods throughout. Thirdly, a previous calculation by Fock & Petraschen (1934) for Na^+ on the Hartree-Fock basis, for which the energy was given, was available. The results of the calculations have demonstrated the practicability of the application of the method to complex atoms, and provided a considerable amount of empirical knowledge on the relative efficiency of different types of functions for improving the accuracy of wave functions for many-electron atoms.

2. Notation and nomenclature

Relativistic corrections will be neglected in the present calculations which will be based on the Schrödinger Hamiltonian, which with its components as for atoms will be denoted by

$$H = \sum_i K_i - Z\sum_i V_i + \sum_{i>j} M_{ij} = -\tfrac{1}{2}\sum \nabla_i^2 - Z\sum_i (1/r_i) + \sum_{i>j} (1/r_{ij}), \qquad (1)$$

where corresponding terms are to be identified.

When a linear combination of co-detors $\sum_r Y_r \Phi_r$ is said to approximate to a stationary state, or wave function, of H according to the variational method, this will imply that

$$\sum_s H_{rs} Y_s - EY_r = 0, \qquad (2)$$

where $H_{rs} = (\Phi_r \mid H \mid \Phi_s)$ and E is a constant called the energy of the approximation.

The term 'connected sets of eigangs' will be used to designate sets of functions which are simultaneously eigenfunctions of operators L^2 and L_z, or S^2 and S_z, with the usual phase conventions as specified in part IV. Electronic functions will consist of doubly-connected sets of eigangs, such as $A(m, u)$, where m is the eigenvalue of L_z and u of S_z. The notation θ^{LS} will be used as previously to denote a double-vector coupling such as

$$AB\theta^{LSMU} = \sum_{mu} A(m, u)\, B(M-m, U-u)\, X(L, M, L_A, L_B, m)\, X(S, U, S_A, S_B, u), \qquad (3)$$

where the X coefficients were effectively defined to make the resulting functions connected sets of eigangs of the operators $L_1 + L_2$ and $S_1 + S_2$. Particular θ^{LS} operators will be denoted by the modified spectroscopic notations $\mathrm{S}^1, \mathrm{S}^3, \ldots, \mathrm{P}^1, \mathrm{P}^2$, etc., where S, P, D, ..., are written respectively for $L = 0, 1, 2, \ldots$, and the suffix denotes the value of $2S+1$. It has been found extremely convenient to place the suffix after the letter instead of before as in the usual spectroscopic notation, since then all the complicated vector-coupled functions can be written without ambiguity when all brackets are omitted.

The Φ_r are constructed by the vector coupling of connected sets of eigangs, each set depending only on a single set of variables of the type x_i, y_i, z_i, v_i, denoted by t_i. The notation $sA, sB, pA, \ldots$, will be used to denote such elementary sets where the first letter signifies the L value by the spectroscopic code and $S = \frac{1}{2}$. Such pairs as sA denote single sets and are used for particular sets of numerical functions.

In some of the present calculations the elementary eigangs sA, sB and pA were constructed so that they corresponded approximately to the orbitals conventionally described as $1s$, $2s$ and $2p$ respectively. This was purely a matter of convenience, being in no way theoretically necessary (see part II, § 7).

What has been called the serial convention will be used so that a function known to depend on t_i variables, but written without these variables, will be understood to have the arguments $t_1, t_2, t_3, \ldots$, reading from left to right.

The terminal operator ω will be used to denote just those partial antisymmetry operators $\sum \sigma_u P_u$ required to make the function on which they operate completely antisymmetric.

In accordance with these conventions the Φ_r will be denoted by such symbols as

$$sA^2\mathrm{S}^1\, sBsC\mathrm{S}^1\, pA^6\mathrm{S}^1\, \omega, \tag{4}$$

where reference must be made to part V for the general definition of the particular linear combinations of vector-coupled functions denoted by $sA^2\mathrm{S}^1$ and pA^n.

In the expansion of the integrals H_{rs} it is only necessary to consider the type of integral

$$[A^*\, B \mid C^*\, D]^L = \iint \mathrm{d}r_1\, \mathrm{d}r_2 \bar{A}^*(r_1)\, \bar{B}(r_1)\, \bar{C}^*(r_2)\, \bar{D}(r_2)\, \{r_1, r_2\}^L, \tag{5}$$

where

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

where $\bar{A}(r)$, etc., denote the radial variation of the respective sets of functions A, B, etc. The coefficients of the other integrals are very few and follow trivially from these. The actual functions used in all the present calculations have real radial functions so that $\bar{A}^* = \bar{A}$. In accordance with this the above integrals will be written $[AB \mid CD]^L$, but on the isolated occasions when distinction must be made the first functions in each enclosure will be referred to as A^* and C^*.

Two combinations of these integrals related to a given H_{rs} were defined and called invariants in part VI, which must be consulted for these and the related notations. The invariant of $(\Phi_r \mid H \mid \Phi_s)$ will be denoted by $(\Phi_r \mid \mathrm{inv} \mid \Phi_s)$, and the variant by $(\Phi_r \mid \mathrm{var} \mid \Phi_s)$. The coefficient of the invariant in $(\Phi_r \mid H \mid \Phi_s)$, when this is expressed as the sum of invariant and variant quantities, will be denoted by $C(\Phi_r, \Phi_s)$.

3. Derivation of the Schrödinger integral formulas

The most important stage of a variational calculation using antisymmetric vector-coupled functions is the expression of the Schrödinger matrix elements between pairs of these functions as linear combinations of one- and two-electron integrals of the types $(A \mid K - ZV \mid B)$ and $[AB \mid CD]^L$. The formulas for the latter integrals are relatively simple and have been given in part II. To obtain the linear coefficients of these expressions use will be made of the integral formulas derived in part VII, which correspond roughly to component parts of those required here. The labour of integral evaluation is greatly reduced by using five theorems, which will be established below. The theorems follow from the general theory but are more of the nature of summaries of processes which would be set out repeatedly for different integrals, both here and in the future, if they were not set out once completely explicitly. Although they might be guessed from particular cases, their proofs in the general case are not always easy.

Some of the theorems (those concerning the formulas for classes of specially related integrals which occur in problems such as the present one) make it possible to obtain the formulas for all members of a class by trivial modifications of the formula for a single member. The labour saved by using these theorems is considerable. In the present calculations the formulas for about one-third of the integrals required may be obtained by their use.

The theorems will be established first, and then some particular integrals will be considered successively. Any required integral is either a member of these, or can be trivially derived from one of these by theorems given here or previously, or is zero.

THEOREM 1. If A and A' denote two similar connected sets of co-detors and B and B' another such pair with all their elementary functions orthogonal to those of A and A', then

$$(AB\theta^{LS}\omega \mid H \mid A'B'\theta^{LS}\omega) = C_A C_B(\text{invariant}) + \text{variant terms}, \tag{6}$$

where C_A and C_B are the invariant coefficients of the pairs A, A' and B, B' respectively.

Proof. For simplicity and clarity the M and U values of the functions $A(M, U)$, $AB\theta^{LSMU}$, etc., will be omitted, since all the integrals concerned will follow the usual behaviour of vanishing for two unequal M or U values, and of being independent of the M and U values.

The proof will be performed for a particular type of invariant operator $\sum\limits_{ij} G_{ij}$ (see theorem 20, part VI) with $G_{ij} = J_i J_j$, where J_i is one of the simpler types of invariant operator such as the kinetic energy operator. This proof is quite general, since the quoted theorem showed that all the invariant coefficients were independent of the particular operators considered. When the ω operators are removed in the usual manner by theorem 14, part III, and an obvious extension of theorem 9, part IV, is applied to the result it follows that

$$\begin{aligned}(AB\theta^{LS}\omega \mid \sum_{ij} J_i J_j \mid A'B'\theta^{LS}\omega)\\ = (A \mid \sum_{ij} J_i J_j \mid A')(B \mid B') + (A \mid A')(B \mid \sum_{ij} J_i J_j \mid B') + 2(A \mid \sum_i J_i \mid A')(B \mid \sum_j J_j \mid B')\\ + \text{exchange terms}, \end{aligned} \tag{7}$$

where it is understood that the summations range over all the variables of the particular integral in which each of these occurs. The particular form of the third term was obtained by means of the identity

$$(AB\theta^{LS} \mid PQ \mid A'B'\theta^{LS}) = (A \mid P \mid A')(B \mid Q \mid B'), \tag{8}$$

which can be seen to be valid either from first principles or by the argument of theorem 9, part IV, for operators P and Q which commute with the L and S operators and which depend only on the variables of A and B respectively.

If the configurations of B and B' are the same, then the first terms of (7) contribute the terms $C_A \operatorname{inv}_A (B \mid B')$ to the total integral. Then the coefficient of the total invariant is $C_A C_B$, since if inv_A does exist it occurs with coefficient unity in the total invariant, and if it vanishes, so does the total invariant. The same result must be true if A and A' have the same configuration, and it only remains to examine the case when there is one non-coincidence in each of the pairs A, A' and B, B'. Let these non-coincidences be denoted by a, a' and b, b' respectively. In this case $(a \mid J \mid a')$ occurs in $(A \mid \sum\limits_i J_i \mid A')$ with coefficient C_A and $(b \mid J \mid b')$ in $(B \mid \sum\limits_i J_i \mid B')$ with coefficient C_B, and it follows that $2(a \mid J \mid a')(b \mid J \mid b')$ occurs in the total integral with coefficient $C_A C_B$. It follows from the definition that this term is just the total invariant, and hence the theorem has been justified for all cases in which it is not trivially true by the vanishing of the invariant.

Theorem 2. If A, A', B and B' are functions with S^1 symmetry satisfying the conditions of theorem 1, then

$$(AB\mathrm{S}^1\,\omega\,|\,\mathrm{var}\,|\,A'B'\mathrm{S}^1\,\omega) = (A\,|\,\mathrm{var}\,|\,A')\,(B\,|\,B') + (B\,|\,\mathrm{var}\,|\,B')\,(A\,|\,A'), \tag{9}$$

and

$$\begin{aligned}(AB\mathrm{S}^1\,\omega\,|\,H\,|\,A'B'\mathrm{S}^1\,\omega) = {} & C(A,A')\,C(B,B')\,(AB\mathrm{S}^1\,\omega\,|\,\mathrm{inv}\,|\,A'B'\mathrm{S}^1\,\omega)\\ & + (A\,|\,\mathrm{var}\,|\,A')\,(B\,|\,B') + (B\,|\,\mathrm{var}\,|\,B')\,(A\,|\,A').\end{aligned} \tag{10}$$

Proof. By the usual removal of the ω operator and the fact that all contributions to the integral arising from different S^1 groupings are contained in the invariant, the result follows.

Comment. Two particular results follow from this theorem, the first of which will be used repeatedly below. Using the fact that $(s^2\mathrm{S}^1\,|\,\mathrm{var}\,|\,s^2\mathrm{S}^1) = 0$ from table 9, part VII, it follows from (*b*) that

$$(sA^2\mathrm{S}^1\,sB^2\mathrm{S}^1\,X\mathrm{S}^1\,\omega\,|\,\mathrm{var}\,|\,sA^2\mathrm{S}^1\,sB^2\mathrm{S}^1\,Y\mathrm{S}^1\,\omega) = (X\,|\,\mathrm{var}\,|\,Y), \tag{11}$$

where X and Y are similar connected sets of co-detors with S^1 symmetry, with all their elementary functions orthogonal to sA and sB.

Using the fact that

$$C(sA^2\mathrm{S}^1\,sBsC\mathrm{S}^1\,\omega,\; sAsC\mathrm{S}^1\,sB^2\mathrm{S}^1\,\omega) = -1 \tag{12}$$

and

$$(sA^2\mathrm{S}^1\,sBsC\mathrm{S}^1\,\omega\,|\,\mathrm{var}\,|\,sAsC\mathrm{S}^1\,sB^2\mathrm{S}^1\,\omega) = 2[sAsC\,|\,sBsC]^0 \tag{13}$$

(these results follow from a detailed examination, but will not be proved here as they are a direct consequence of a theorem which will be proved in the next part of this series), and (9), it follows that

$$\begin{aligned}&(sA^2\mathrm{S}^1\,sBsC\mathrm{S}^1\,X\mathrm{S}^1\,\omega\,|\,H\,|\,sAsC\mathrm{S}^1\,sB^2\mathrm{S}^1\,Y\mathrm{S}^1\,\omega)\\ &\qquad = -C(X,Y)\,(sA^2\mathrm{S}^1\,sBsC\mathrm{S}^1\,X\mathrm{S}^1\,\omega\,|\,\mathrm{inv}\,|\,sAsC\mathrm{S}^1\,sB^2\mathrm{S}^1\,Y\mathrm{S}^1\,\omega)\\ &\qquad\qquad + 2[sAsC\,|\,sBsC]^0\,(X\,|\,Y).\end{aligned} \tag{14}$$

It may be noted that the following theorem is stated in such general form that it is also applicable to the functions which might be used for molecules. M will be used to denote

$$\sum_{i>j} M_{ij} = \sum_{i>j} (1/r_{ij}).$$

Theorem 3. Let ψ and ψ' be a pair of consistent co-detors. Let the configuration of ψ' contain once a class of elementary functions y, that is, a connected set of eigangs in the case of an atom. It is immaterial whether this occurs in ψ. Let ψ'' be derived from ψ' by replacing every element of y in ψ' by the corresponding elements of another corresponding class z which does not occur either in ψ or ψ'. Then if

$$I' = (M\,\|\,\psi\psi') = \sum_{lmnL} C_{lmnL}\,[x_l x_m\,|\,x_n y]^L + \text{other terms}, \tag{15}$$

it follows that

$$I'' = (M\,\|\,\psi\psi'') = \sum_{lmnL} C_{lmnL}[x_l x_m\,|\,x_n z]^L, \tag{16}$$

and the invariant coefficients are the same for I' and I''.

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

$$\psi = \sum_r q_r j_r, \tag{17}$$

where the typical j has the form $\quad j = w_1(t_1)\,w_2(t_2)\,\ldots.$

From the construction of ψ it is apparent that ψ' and ψ'' can be expanded in exactly corresponding terms with the same numerical coefficients

$$\psi' = \sum_r q'_r j'_r, \quad \psi'' = \sum_r q'_r j''_r. \tag{18}$$

Consider from the total integral I' the contribution given by a particular pair j_r, j'_s and a particular element M, and consider the corresponding contribution to I'' given by the corresponding j_r, j''_s and the same M_{ij}. These are

$$\left(M_{ij} \left\| \begin{matrix} w_1 w_2 & \dots & w_k(t_k) & \dots \\ & \dots & y_m(t_k) & \dots \end{matrix} \right.\right) \tag{19}$$

and the corresponding expression with z replacing y. If neither i nor j is equal to k the contribution to I' does not involve y, although it may depend on y, and so only gives a contribution to other terms. The corresponding contribution to I'' is obviously zero owing to the orthogonality of the z to all other elementary functions. If i or j is equal to k, then corresponding terms are contributed, but with z replacing y in the contributions to I''.

Theorem 4. If X and Y are functions such that all the functions of the following integrals are antisymmetric vector coupled, and if

$$\begin{aligned}(M \,\|\, s_1^2 \mathrm{S}^1 X\omega,\, s_1^2 \mathrm{S}^1 Y\omega) = {} & A[s_1 s_1 \,|\, s_1 s_1]^0 \\ & + \sum_{rs} B_{rs}[s_1 s_1 \,|\, x_r x_s]^0 + \sum_{Lrs} D^L_{rs}[s_1 x_s \,|\, x_r s_1]^L + \text{other terms},\end{aligned} \tag{20}$$

then

$$\begin{aligned}&(M \,\|\, s_1^2 \mathrm{S}^1 X\omega,\, s_1 s_2 \mathrm{S}^1 Y\omega) \\ &\quad = A\sqrt{2}\,[s_1 s_1 \,|\, s_1 s_2]^0 + (1/\sqrt{2}) \sum_{rs} B_{rs}[s_1 s_2 \,|\, x_r x_s]^0 + (1/\sqrt{2}) \sum_{Lrs} D^L_{rs}[s_1 x_s \,|\, x_r s_2]^L.\end{aligned} \tag{21}$$

Proof. If $s_1^2 \mathrm{S}^1$ and $s_1 s_2 \mathrm{S}^1$ are denoted by Z and W, then simple examination shows

$$V^{LS}_{ZWs_1s_2} = (1/\sqrt{2})\, V^{LS}_{ZZs_1s_1},$$

and hence all interaction terms of X, Y with Z, W must have coefficients $(1/\sqrt{2})$ times the case for Z, Z. If there is perfect coincidence between X and Y, then s_1, s_2 interactions are as shown with $A = 1$, but otherwise these are zero. In addition, there are no interactions within X, Y in the second case since there is a non-coincidence in Z, W.

Theorem 5. If

$$(M \,\|\, s_1^2 \mathrm{S}^1 X\omega,\, s_1^2 \mathrm{S}^1 Y\omega) = [s_1 s_1 \,|\, s_1 s_1]^0 + F, \tag{22}$$

where X and Y are such that all complete functions are antisymmetric vector coupled, then

$$(M \,\|\, s_1 s_2 \mathrm{S}^1 X\omega,\, s_1 s_2 \mathrm{S}^1 Y\omega) = [s_1 s_1 \,|\, s_2 s_2]^0 + [s_1 s_2 \,|\, s_2 s_1]^0 + \tfrac{1}{2}[1 + P(s_1^*, s_1 \,|\, s_2^*, s_2)]\, F. \tag{23}$$

Proof. The theorem follows from an exactly parallel examination of V coefficients and s, s interactions to the preceding theorem.

Comment. Using these theorems and those obtained previously all integrals required for the Na^+ calculation may be obtained from the simpler basic integrals already evaluated (part VII). The integrals required fall into three classes: (1) those that vanish in virtue of more than two non-coincidences in their configurations, (2) those that are treated below, and (3) those that may be obtained simply from (2) by the application of theorems 3, 4 and 5.

A complete list of the seventeen co-detors used in the final variational calculations is given in § 7. For convenience, in deriving the formulas below, the notation of that section will be used, (x/y) denoting a function obtained from the 'root function',

$$sA^2\mathrm{S}^1\, sB^2\mathrm{S}^1\, pA^6\mathrm{S}^1\, \omega,$$

by the replacement of x by y and $(x_1/y_1 \| x_2/y_2)$ denoting the usual variational matrix element between the functions (x_1/y_1) and (x_2/y_2). In the case where an x^2 replaces a pA^2 there are three possible methods of coupling corresponding to $x^2\mathrm{S}^1$, $x^2\mathrm{P}^3$ and $x^2\mathrm{D}^1$, and these coupling symbols have been included. For example, $sA^2\mathrm{S}^1\, sB^2\mathrm{S}^1\, pA^4\mathrm{P}^3\, pB^2\mathrm{P}^3\mathrm{S}^1\, \omega$ is denoted by $(pA^2/pB^2\mathrm{P}^3)$. The 'root function' itself is simply denoted by $(/)$.

The derivations of the formulas for the thirty-six integrals between the eight co-detors $(/)$, (sB/sC), (pA/pB), $(pA^2/pB^2\mathrm{S}^1)$, $(pA^2/pB^2\mathrm{P}^3)$, $(pA^2/pB^2\mathrm{D}^1)$, $(pA^2/dA^2\mathrm{S}^1)$, $(pA^2/dA^2\mathrm{P}^3)$ and $(pA^2/dA^2\mathrm{D}^1)$, and of $(sB/sC \| sA/sC)$ and $(sBpA/sCpB \| sAsC)$, are discussed below.

(1) For the integral $(/\|/)$ it is only necessary to evaluate the variant contribution since by theorem 22, part VI, the invariant contribution has the coefficient unity, and by the relation (11) and table 9, part VII, this is given by $(/\,|\,\mathrm{var}\,|\,/) = -1{\cdot}2[pApA\,|\,pApA]^2$.

(2) The invariant coefficient for the integral $(pA/pB \| /)$ is $C(pA^5\mathrm{P}^2 pB\mathrm{S}^1,\ pA^6\mathrm{S}^1)$ by theorem 1, and the variant contribution is $(pA^5\mathrm{P}^2 pB\mathrm{S}^1\, \omega\,|\,\mathrm{var}\,|\,pA^6\mathrm{S}^1)$ by the relation (11). Hence both the invariant coefficient and the variant term may be obtained from table 11, part VII.

(3) For the integral $(pA/pB \| pA/pB)$ it is only necessary to evaluate the variant since the invariant has coefficient unity, and by the relation (11), and table 10, part VII, this is

$$(pA/pB\,|\,\mathrm{var}\,|\,pA/pB) = -0{\cdot}8[pApA\,|\,pApA]^2 - 0{\cdot}4[pApA\,|\,pBpB]^2 + 5[pApB\,|\,pApB]^0 - 0{\cdot}4[pApB\,|\,pApB]^2. \tag{24}$$

(4) The invariant coefficient for the integral $(pA^2/pB^2\mathrm{S}^1 \| /)$ is $C(pA^4\mathrm{S}^1\, pB^2\mathrm{S}^1\, \omega,\ pA^6\mathrm{S}^1)$ by theorem 1, and the variant contribution is $(pA^4\mathrm{S}^1\, pB^2\mathrm{S}^1\, \omega\,|\,\mathrm{var}\,|\,pA^6\mathrm{S}^1)$ by the relation (11). Thus both C and var may be obtained from table 13, part VII.

Formulas for $(pA^2/pB^2\mathrm{P}^3 \| /)$, $(pA^2/pB^2\mathrm{D}^1 \| /)$

and $(pA^2/dA^2\mathrm{S}^1 \| /)$, $(pA^2/dA^2\mathrm{P}^3 \| /)$, $(pA^2/dA^2\mathrm{D}^1 \| /)$

may be obtained in an exactly similar manner.

(5) The invariant coefficient for the integral $(pA^2/pB^2\mathrm{S}^1 \| pA/pB)$ is

$$C(pA^4\mathrm{S}^1\, pB^2\mathrm{S}^1\, \omega,\quad pA^5\mathrm{P}^2\, pB\mathrm{S}^1\, \omega)$$

by theorem 1 and the variant is $(pA^4\mathrm{S}^1\, pB^2\mathrm{S}^1\, \omega\,|\,\mathrm{var}\,|\,pA^5\mathrm{P}^2\, pB\mathrm{S}^1\, \omega)$ by the relation (11) Both C and var may be obtained from table 11, part VII.

Formulas for $(pA^2/pB^2\mathrm{P}^3 \| pA/pB)$, $(pA^2/pB^2\mathrm{D}^1 \| pA/pB)$

and $(pA^2/dA^2\mathrm{S}^1 \| pA/pB)$, $(pA^2/dA^2\mathrm{P}^3 \| pA/pB)$, $(pA^2/dA^2\mathrm{D}^1 \| pA/pB)$

may be obtained in an exactly similar manner.

(6) For the integral $(pA^2/pB^2\mathrm{S}^1\,||\,pA^2/pB^2\mathrm{S}^1)$ it is only necessary to evaluate the variant since the coefficient of the invariant is unity, and by the relation (11) this is

$$(pA^4\mathrm{S}^1\,pB^2\mathrm{S}^1\,\omega\,|\,\mathrm{var}\,|\,pA^4\mathrm{S}^1\,pB^2\mathrm{S}^1\,\omega)$$

which may be obtained from table 10, part VII.

Formulas for $(pA^2/pB^2\mathrm{P}^3\,||\,pA^2/pB^2\mathrm{P}^3)$, $(pA^2/pB^2\mathrm{D}^1\,||\,pA^2/pB^2\mathrm{D}^1)$

and $(pA^2/dA^2\mathrm{S}^1\,||\,pA^2/dA^2\mathrm{S}^1)$, $(pA^2/dA^2\mathrm{P}^3\,||\,pA^2/dA^2\mathrm{P}^3)$, $(pA^2/dA^2\mathrm{D}^1\,||\,pA^2/dA^2\mathrm{D}^1)$

may be obtained in an exactly similar manner.

(7) The invariant coefficient for the integral $(pA^2/pB^2\mathrm{P}^3\,||\,pA^2/pB^2\mathrm{S}^1)$ vanishes by theorem 1 and the result of table 12, part VII. By the relation (11) the variant is

$$(pA^4\mathrm{P}^3\,pB^2\mathrm{P}^3\mathrm{S}^1\,\omega\,||\,pA^4\mathrm{S}^1\,pB^2\mathrm{S}^1\,\omega),$$

and this is given in the same table.

Formulas for $(pA^2/pB^2\mathrm{D}^1\,||\,pA^2/pB^2\mathrm{P}^3)$, $(pA^2/pB^2\mathrm{D}^1\,||\,pA^2/pB^2\mathrm{S}^1)$,

$(pA^2/dA^2\mathrm{D}^1\,||\,pA^2/dA^2\mathrm{P}^3)$, $(pA^2/dA^2\mathrm{D}^1\,||\,pA^2/dA^2\mathrm{S}^1)$, $(pA^2/dA^2\mathrm{P}^3\,||\,pA^2/dA^2\mathrm{S}^1)$

may be obtained in an exactly similar manner.

(8) The integral $(pA^2/dA^2\mathrm{S}^1\,||\,pA^2/pB^2\mathrm{S}^1)$ is, by trivial applications of the general reduction theory when there are two non-coincidences in one part, equal to

$$(pA^4\mathrm{S}^1\,dA^2\mathrm{S}^1\,\omega\,||\,pA^4\mathrm{S}^1\,pB^2\mathrm{S}^1\,\omega)$$

given in table 13, part VII.

The formulas for

$(pA^2/dA^2\mathrm{P}^3\,||\,pA^2/pB^2\mathrm{P}^3)$ and $(pA^2/dA^2\mathrm{D}^1\,||\,pA^2/pB^2\mathrm{D}^1)$

are obtained in an exactly similar manner.

(9) The integral $(pA^2/pB^2\mathrm{P}^3\,||\,pA^2/dA^2\mathrm{S}^1)$ vanishes by theorem 14, part III, and theorem 9, part IV. Likewise the five other similar integrals in which the couplings differ.

(10) The formulas for $(sB/sC\,||\,sA/sC)$ and $(sBpA/sCpB\,||\,sA/sC)$ follow at once from the relation (14) and the results of tables 9 and 11, part VII.

The use of theorems 3, 4 and 5 to obtain all the other integrals required for the Na^+ calculation from the integrals considered above is illustrated by the calculation of $(sB/sC\,||\,/)$, $(sB/sC\,||\,sB/sC)$ and $(sB/sD\,||\,sB/sC)$. The formula for $(sB/sC\,||\,/)$ follows immediately from that for $(/\,||\,/)$ by theorem 4. The formula for $(sB/sC\,||\,sB/sC)$ follows immediately from that for $(/\,||\,/)$ by theorem 5, and that for $(sB/sD\,||\,sB/sC)$ from that for $(sB/sC\,||\,sB/sC)$ by theorem 3.

4. A USEFUL NUMERICAL METHOD FOR THE TREATMENT OF THE TWO-ELECTRON INTEGRALS

A systematic method for evaluating the two-electron integrals has already been developed and is described in part II, § 4. It was, however, thought interesting to examine the advantages of an alternative method, conveniently described as non-dimensional, by using it for the present calculations. The advantage proved to be much greater than was apparent from a preliminary examination, and it appears advisable to use this method for future calculations.

If the radial factors of the elementary orthonormal functions ϕ are denoted by $\bar{\phi}$, then

$$\bar{\phi} = \sum_s X_s^{\phi} r^{n_s} \mathrm{e}^{-\alpha_s r}, \tag{25}$$

and the formula for $[\phi_r \phi_s \mid \phi_t \phi_u]^L$ follows by substitution from (20). It is

$$[\phi_r \phi_s \mid \phi_t \phi_u]^L = \sum_p T_p^{\phi_r \phi_s} \sum_q T_q^{\phi_t \phi_u} (n_p, n_q)^L (\alpha_p, \alpha_q), \tag{26}$$

where $(n_p, n_q)^L (\alpha_p, \alpha_q) = [r^{n_p} \mathrm{e}^{-\alpha_p r} \mid r^{n_q} \mathrm{e}^{-\alpha_q r}]^L$

and
$$T_p^{\phi_r \phi_s} = \sum_{i,j} X_i^{\phi_r} X_j^{\phi_s}, \tag{27}$$

subject to
$$n_i + n_j = n_p,$$
$$\alpha_i + \alpha_j = \alpha_p.$$

The modification, which will be called non-dimensional, consists of defining

$$J(n,m)^L (u,v) = (n,m)^L (u,v) / [\surd\{(n,n)^0 (u,u)\} \surd\{(m,m)^0 (v,v\}] \tag{28}$$

and
$$\overline{T}_r^{\phi_i \phi_j} = T_r^{\phi_i \phi_j} \surd\{(n_r, n_r)^0 (\alpha_r, \alpha_r)\}.$$

It is then apparent that

$$[\phi_r \phi_s \mid \phi_t \phi_u]^L = \sum_p \overline{T}_p^{\phi_r \phi_s} \sum_q \overline{T}_q^{\phi_t \phi_u} J(n_p, n_q)^L (\alpha_p, \alpha_q), \tag{29}$$

and the two-electron integrals were calculated from the $J(n,m)^L (u,v)$ by this relation. The $J(n,m)^L (u,v)$ can be shown to satisfy

$$J(n,m)^L (pu, pv) = J(n,m)^L (u,v), \tag{30}$$

so that for fixed n, m, L the J integrals depend only on the ratio u/v. Obviously

$$J(n,n)^0 (u,u) = 1. \tag{31}$$

Explicit formulas for the J integrals were obtained from their definitions and they were calculated from these, the calculation being probably rather simpler than that of the $(n,m)^L (u,v)$. The advantage of using the non-dimensional $J(n,m)^L (u,v)$ integrals was that for a given L value they were all of the same order of magnitude (every J value lay in the range 1 to about $\frac{1}{10}$), and this both expedited the matrix contractions (see equation (29)) and greatly reduced the chances of error. Since the matrix contractions constituted a major part of the numerical work of the wave-function calculations this was a very important factor. It is interesting to note that it was possible to keep the J tables much more compact than would otherwise have been the case, by using the fact that it was found satisfactory to work with sets of α's (see equation (25)) and hence of the u's and v's, which were in the ratio of small integers. The J values used thus corresponded to four small integral arguments and were tabulated accordingly.

5. The solution of the Ritz equations; the root function

A method for the solution of the Ritz equations

$$\sum_s H_{rs} Y_s = EY_r, \tag{32}$$

using as a variational function a linear combination, $\Sigma Y_r \Phi_r$, of co-detors, Φ_r, has been described in part II, § 5. The method is applicable when

$$H_{rr} - H_{11} \gg H_{rs} \quad (r \neq s), \tag{33}$$

and the rapidity of convergence starting with a solution $Y_r = (1, 0, 0, \ldots)$ will be great if

$$Y_1 \gg Y_r \quad (r \neq 1). \tag{34}$$

The conditions (33) and (34) can generally be fulfilled by choosing the co-detor Φ_1 such that it gives an approximate minimum to

$$E_1 \equiv (\Phi_1 \,|\, H \,|\, \Phi_1), \tag{35}$$

and Φ_1 is then called a root function and E_1 is called its energy. In practice the configuration of Φ_1 was taken to correspond to no electronic interaction and the elementary radial functions chosen to obtain a minimum of (35).

When a suitable root function had been obtained the matrix elements H_{rs} of equation (32) were calculated. Theoretically, at any stage of the calculation all independent co-detors Φ_r with the same symmetry as Φ_1 which could be constructed from the elementary radial functions at that stage should have been included in equation (32). In practice, however, large numbers of the Φ's were omitted from these equations since it was often the case that their inclusion gave a negligible contribution to the energy, and on the energy criterion they were excluded. It can be shown that generally a fairly good estimate of the extra contribution to the energy brought about by the inclusion of Φ_r is

$$-(H_{1r})^2/(H_{rr} - H_{11}), \tag{36}$$

and in practice this was evaluated first, and if it was very small Φ_r was not included in the solution of the equations. The Ritz equations (32) were solved using the method of part II, § 5. When (as sometimes happened) not both $H_{rr} - H_{11}$ and $H_{ss} - H_{11}$ were greater than a few times $|H_{rs}|$, for some pair (r, s), the procedure is very slowly convergent or even divergent. In such cases the procedure was modified by determining formulas for the δY's by the solution of the small sets of simultaneous equations given by retaining only the larger H_{rs} coefficients followed by some empirical adjustment when necessary. With this modification the procedure was rapidly convergent.

6. The stretching transformation

In the absence of electronic interaction the total wave function reduces to a single co-detor whose elementary functions only depend on the nuclear charge as a scale factor. This suggested using the same set of primary functions (with scale factors in the ratio 9 : 10 : 11) for the F^-, Ne and Na^+ calculations respectively. This method of choice was found to be satisfactory and, because of the following theorem, made possible a great saving of labour.

Theorem. If the primary elementary functions are of the form $r^{n_s}\,e^{-k\alpha_s r}$ ($s = 1, 2, \ldots$), where k is a constant, and orthonormal functions ϕ'_t be constructed from the functions $r^{n_s}\,e^{-\alpha_s r}$, then the normalized multiples, ϕ, of $\phi'(kr)$,

$$\phi(r) = \phi'(kr)/(\phi'(kr) \mid \phi'(kr)) \tag{37}$$

are orthonormal combinations of the primary functions. The one- and two-electron integrals of ϕ are immediately obtained from those of ϕ' by the following relations:

$$\left.\begin{aligned}[\phi_s \mid \phi_t] &= [\phi'_s \mid \phi'_t],\\ [\phi_s \mid V \mid \phi_t] &= k[\phi'_s \mid V \mid \phi'_t],\\ [\phi_s \mid K \mid \phi_t] &= k^2[\phi'_s \mid K \mid \phi'_t],\\ [\phi_s\phi_t \mid \phi_u\phi_v]^L &= k[\phi'_s\phi'_t \mid \phi'_u\phi'_v]^L.\end{aligned}\right\} \tag{38}$$

ϕ is said to be 'stretched' from ϕ' by a stretching (or scale) factor k.

Comment. It follows at once that the whole wave-function calculation may be carried out in terms of the integrals of the ϕ', and that the Ritz variational equation (part II, § 5) may be written

$$\sum_s \{Z[(k/Z)\,K'_{rs} - V'_{rs}] + M'_{rs}\}\,Y_s = (E/k)\,Y_r, \tag{39}$$

where K', V' and M' are the matrix elements (see § 2) of the co-detors constructed from the orthonormal functions ϕ'. Obviously the calculation in terms of the ϕ' involves no more labour than the direct calculation in terms of ϕ. The advantage of using the 'un-stretched' primary functions $r^{n_s}\,e^{-\alpha_s r}$ is that since it is found satisfactory to use the same functions with different values of k for different atoms, only one set of integrals (those corresponding to $r^{n_s}\,e^{-\alpha_s r}$) need be evaluated for these atoms.

This 'stretching' procedure was used in the present calculations. A set of (n_s, α_s) values $(0, 5)$, $(1, 1)$, ..., was taken and the k values $\frac{9}{5}$, $\frac{10}{5}$ and $\frac{11}{5}$ for F^-, Ne and Na^+ respectively, were used. With these values of the stretching factor the first exponential corresponds to a $1s$ function for a single electron on each of the respective nuclei. Though the same (n_s, α_s) values were used it was not found desirable to use the same orthonormal combinations for all three calculations. The same orthonormal functions were used for F^- and Ne, and those for Na^+ were related to these by a simple linear transformation. This point will be discussed further in § 7.

7. The different numerical trials and the final wave-function calculation

At the outset of the wave-function calculations it was decided to concentrate on the calculation for the sodium ion, Na^+, since this was the only ion for which the ground state energy was available (Fock & Petraschen 1934), and thus the only one which could be readily compared with previous calculations.

As a first step to the ground-state wave function for Na^+ a number of trials for those radial functions which would give a satisfactory root function, $sA^2S^1\,sB^2S^1\,pA^6S^1\,\omega$ (see § 5), were made. The first three trials will not be described in any details as they did not give satisfactory root functions.

Trial one. The radial parts of the elementary eigangs were chosen to be hydrogen-like combinations of e^{-6r}, $r\,e^{-3r}$, e^{-3r}, $r^2\,e^{-2r}$, $r\,e^{-2r}$, e^{-2r} (with a stretching factor $k = \frac{11}{6}$, see § 6) together with other orthonormal combinations necessary for the completeness of the set. With these functions the solution of the Ritz equations by the method of numerical successive approximations (see § 5) was only very slowly convergent. To obtain a solution new combinations of the radial functions were chosen for which the convergence to the solution of the equations was more rapid. Though the new combinations gave an estimated value of the ground state energy near the value given by Fock & Petraschen it was decided not to proceed with this choice of radial functions. This was because it was found that any increase in the number of such functions would entail a very large amount of work and it was conjectured that the same value of the energy might be obtained with fewer functions, which would lighten both the work of improvements and the adaptation to ions with more electrons.

Trial two. For this trial the radial parts of the elementary eigangs were chosen to be orthonormal linear combinations of e^{-6r}, e^{-12r}, $r\,e^{-2r}$, $r\,e^{-3r}$ and $r^2\,e^{-2r}$ (with a stretching factor $k = \frac{11}{6}$). The root-function energy was higher than the Fock & Petraschen value, and the difference between them was rather large. The inclusion of other co-detors, Φ_r, formed from the elementary eigangs did not compensate for this. For the reason given in trial one it was thought better to make a fresh choice of radial functions rather than continue with the trial.

Trial three. A number of different orthonormal linear combinations of e^{-12r}, $r\,e^{-2r}$ and $r\,e^{-6r}$, were taken as the radial parts of the elementary eigangs and the corresponding root-function energies evaluated. This involved much less work than the preceding trials. The lowest root-function energy was higher than the Fock-Petraschen value and the difference between them was rather large. The inclusion of other co-detors was dropped in favour of a fresh trial.

Trial four. For this trial some radial functions obtained from Brown's work on the Hartree wave function for Ne were used. Brown (1934) fitted the Hartree functions by linear combinations of functions approximating to e^{-5kr}, $r\,e^{-kr}$, $r\,e^{-2kr}$, where k is a constant, and these functions with $k = \frac{11}{5}$ were used in this trial. Linear combinations sa, ab, etc., of the form

$$\sum_{n,\alpha} C(n,\alpha)\, r^n\, e^{-\alpha r} \tag{40}$$

with the numerical values of the coefficients $C(n,\alpha)$ given in table 1 were used as the radial functions for the orthonormal eigangs sA, sB, sC, pA and pB. The coefficients were chosen to satisfy the orthonormality condition exactly and so that sA, sB and pA approximated to the stretched Brown functions. Using the elementary eigangs sA, sB and pA with radial factors sa, sb and pa respectively, the root-function energy was calculated as follows: The one-electron integrals by the method described in part II, § 3, and the two-electron integrals by the method described in § 4. The root-function energy $E_1 = (\Phi_1|H|\Phi_1)$, where $\Phi_1 = sA^2\mathrm{S}^1\,sB^2\mathrm{S}^1\,pA^6\mathrm{S}^1\,\omega$, was then calculated by direct substitution for the one- and two-electron integrals in the formula for this integral obtained in § 3. The result was $-161{\cdot}015$ atomic units of energy, and since the Fock-Petraschen result was $-161{\cdot}8$ atomic units of energy, the root function was considered satisfactory. Having obtained a reasonably good

Table 1. The coefficients $C(n, \alpha)$

n, α	sa	sb	sc	sd	se
0, 5	22·3606798	−4·98395647	−9·431006505	−22·037941	11·82407477
1, 1	—	0·821993820	−1·584902631	1·577072790	−11·79318802
1, 2	—	2·465981461	10·48417666	−28·3959101	53·7275742
1, 3	—	—	—	73·5469757	−76·4568205
2, 1	—	—	—	—	2·813695776

n, α	pa	pb	pc	pd	da
1, 1	0·656024532	−1·60168918	1·4694271	3·82862908	0·0
1, 2	3·28012266	9·22527187	−24·198840	122·049338	0·0
1, 3	—	—	54·952045	−165·936268	0·0
2, 2	—	—	—	67·0473215	4·77027835

root function the calculation was extended to include eigangs sC and pB with radial factors sc and pb respectively. The Ritz equations, in which were included other co-detors with S^1 symmetry which could be constructed from the eigangs sA, sB, sC, pA and pB, were solved. The method of solution was that described in part II, § 5, with the modification indicated in § 5. The matrix elements H_{rs} were evaluated in the same manner as the root-function energy, H_{11}, using the formulas obtained in § 3 and other formulas for integrals involving co-detors which were not included in the final calculation. The energy, E, was still higher than the value given by Fock & Petraschen and it was decided to extend the calculation. To the original primary functions were added the functions $r\,e^{-3r}$, $r^2\,e^{-r}$, $r^2\,e^{-2r}$ and radial factors sd, se, pc, pd, da for corresponding eigangs sD, sE, pC, pD, dA (orthogonal to the previous eigangs) were constructed. The radial factors sd, se, etc., are given in table 1. The calculation was then repeated including the new eigangs. The final value of the total energy, E, was $-161{\cdot}803$ atomic units of energy and the corresponding (un-normalized) solution of the Ritz equations of the form

$$\Psi' = \Phi_1 + a\Phi_a + b\Phi_b + c\Phi_c + \ldots,$$

where Φ_1 is the root function $sA^2S^1\,sB^2S^1\,pA^6S^1\,\omega$ and

$$\Phi_a = sA^2S^1\,sBsCS^1\,pA^6S^1\,\omega,$$

$$\Phi_b = sA^2S^1\,sB^2S^1\,pA^5P^2\,pBS^1\,\omega,$$

and $a \simeq 0{\cdot}23$, $b \simeq 0{\cdot}09$ and $a, b \gg c, d, \ldots$. It was decided to change the radial factors of sB and sC, and pA and pB, the aim being to include the energy contributions for Φ_a and Φ_b in the root function. It was hoped that this would reduce the number of co-detors, Φ_r, required to obtain a good approximation to the accurate energy, and thus considerably reduce the number of matrix elements, H_{rs}, to be calculated. New radial factors sb', sc', pa' and pb' were obtained by the linear transformations of the original factors sb, sc, pa and pb:

$$\left.\begin{aligned} sb' &= \surd(1-u^2)\,sb + u\,sc, \\ sc' &= -u\,sb + \surd(1-u^2)\,sc, \end{aligned}\right\} \tag{41}$$

$$\left.\begin{aligned} pa' &= \surd(1-v^2)\,pa + v\,pb, \\ pb' &= -v\,pa + \surd(1-v^2)\,pb, \end{aligned}\right\} \tag{42}$$

where $u = 0{\cdot}1579905$ and $v = 0{\cdot}0349786$. The values of u and v were determined to minimize the root-function energy. Actually it can be shown that a good choice of these is given by

$\surd 2\,u = a$ and $\surd 6\,v = b$, and they were determined from these equations. The one- and two-electron integrals for the new eigangs (i.e. the eigangs with radial factors *sa*, *sb′*, *sc′*, *sd*, etc.) were calculated from the integrals of the original eigangs by a simple transformation, thus saving a considerable amount of labour. The matrix elements, H_{rs}, for the new eigangs were calculated and the Ritz equations solved. The final value for the total energy, E, was about 0·08, lower than the Fock-Petraschen result and the corresponding wave function is that given in table 2. The root function and total energy are also given in this table. The table gives the coefficients Y_r occurring in the expansion of the un-normalized wave function, $\Sigma Y_r \Phi_r$. $1/\sum\limits_r Y_r^2$ is given (to six significant figures to provide a check that errors have not been made in transcription), at the foot of the column Y_r. The seventeen co-detors, Φ_r, used in this final Na⁺ calculation are shown, using the following notations, in the first column. Every co-detor is denoted by a symbol (x/y), the co-detor corresponding to (x/y) being determined by the following relations:

$$(/) = \text{the root function} = sA^2\mathrm{S}^1\, sB^2\mathrm{S}^1\, pA^6\mathrm{S}^1\,\omega,$$

where ω is the antisymmetry operator necessary to make the function preceding it normalized and antisymmetric:

$$(sB/x) = sA^2\mathrm{S}^1\, sBx\mathrm{S}^1\, pA^6\mathrm{S}^1\,\omega,$$

and similarly for (sA/x),

$$(pA/x) = sA^2\mathrm{S}^1\, sB^2\mathrm{S}^1\, pA^5\mathrm{P}^2\, x\mathrm{S}^1\,\omega,$$

$$(pA^2/x^2\theta) = sA^2\mathrm{S}^1\, sB^2\mathrm{S}^1\, pA^4\theta pB^2\theta\mathrm{S}^1\,\omega,$$

where $\theta = \mathrm{S}^1$, P^3 or D^1,

$$(sBpA/sCpB) = sA^2\mathrm{S}^1\, sBsC\mathrm{S}^1\, pA^5\mathrm{P}^2\, pB\mathrm{S}^1\,\omega.$$

TABLE 2. THE COEFFICIENTS Y_r FOR THE UN-NORMALIZED WAVE FUNCTIONS

	Na⁺	Ne	F⁻
$sA^2\mathrm{S}^1 sB^2\mathrm{S}^1 pA^6\mathrm{S}^1\mathrm{S}^1$	1·0	1·0	1·0
(sB/sC)	0·018	0·162	0·067
(sB/sD)	−0·112	−0·094	−0·068
(sB/sE)	−0·013	−0·001	0·017
(sA/sC)	0·033	0·037	0·043
(sA/sD)	0·034	0·036	0·038
(sA/sE)	−0·006	−0·006	−0·007
(pA/pB)	0·057	−0·075	−0·285
(pA/pC)	0·022	0·070	0·119
(pA/pD)	−0·042	−0·004	0·038
$(pA^2/pB^2\mathrm{S}^1)$	0·044	0·044	0·038
$(pA^2/pB^2\mathrm{P}^3)$	0·043	0·062	0·034
$(pA^2/pB^2\mathrm{D}^1)$	−0·061	−0·069	−0·052
$(pA^2/dA^2\mathrm{S}^1)$	−0·038	−0·040	−0·042
$(pA^2/dA^2\mathrm{P}^3)$	−0·052	−0·054	−0·057
$(pA^2/dA^2\mathrm{D}^1)$	0·041	0·043	0·045
$(sBpA/sCpB)$	−0·054	−0·065	−0·071
$1/\sum\limits_r Y_r^2$	0·964259	0·935057	0·887345
root-function energy (atomic units)	−161·2236	−128·1430	−98·9174
total energy (atomic units)	−161·8784	−128·6920	−99·5279

It was considered very interesting to examine if satisfactory wave functions for F⁻ and Ne could be obtained using the radial functions (orbitals) *sa*, *sb′*, *sc′*, etc., used in the final Na⁺ calculation, with stretching factors $\frac{9}{5}$ and $\frac{10}{5}$ respectively, (see § 6). Using the method of § 6 the calculations were relatively short. However, these orbitals were not found satisfactory because some of the Y's in the expansions $\sum Y_r \Phi_r$, for the wave functions were rather large and a transformation, of the type used for the Na$^+$ calculation, to reduce these large Y's was considered. Fortunately the orbitals *sa*, *sb*, *sc*, etc., used for the Na$^+$ calculation in trial four (i.e. those given in table 1), were found to satisfy this requirement, and it was therefore not necessary to perform the transformation explicitly. Here again, the calculations were performed using the method of § 6.

The values of Y_r occurring in the expansions, $\Sigma Y_r \Phi_r$, for the resulting wave functions using these orbitals are given in table 2. The root function and total energies are also given. In this table it should be noted that the elementary eigangs *sA*, *sB*, *sC*, ..., from which the co-detors Φ_r are constructed have the unstretched orbitals *sa*, *sb'*, *sc'*, *sd*, *se*, *pa'*, *pb'*, *pc*, *pd* and *da* for the Na$^+$ wave function and *sa*, *sb*, *sc*, *sd*, *se*, *pa*, *pb*, *pc*, *pd* and *da* for the F$^-$ and Ne calculation. Because no fresh integrals had to be calculated for the F$^-$ and Ne calculations the labour required for these was only a fraction of that required for the Na$^+$ calculation.

The experimental energy for Na$^+$ is $-162{\cdot}126$ a.u. (see Morse, Young & Haurwitz 1935). Most of the discrepancy between the experimental and calculated values will be due to the spin-orbit interaction, which would require a long calculation to evaluate and so it is not possible to use the experimental energy as a criterion of accuracy of the wave function.

8. Discussion

The chief significance of these calculations is that they are the first calculations by a convergent method for systems containing ten electrons. The previous most complicated case examined by such a method was the beryllium atom with four electrons. The experience gained during the course of the calculations suggests that the method is practicable for a number of systems appreciably more complicated.

It is a very valuable characteristic of the method that a large amount of the data accumulated in the present calculations will be of use for future calculations. For example, all the formulas for the Schrödinger integrals are of permanent value since they may be used in any other calculations for Ne-like atoms with different orbitals. Actually they have a wider application than this owing to the occurrence of closed shells, s^2S^1, p^6S^1, in the lower states of more complicated atoms. The evaluation of the Schrödinger integrals for these states will be considerably simplified by use of the integrals already calculated. Further, the J integrals already calculated will probably be used in any future calculation by the present method in which integral values of n and α, in the unstretched primary functions, $r^n e^{-\alpha r}$, are used.

The previous most accurate wave function for which the calculated energy is available is the wave function for Na$^+$ calculated by the Hartree-Fock method by Fock & Petraschen (1934). However, this cannot reliably be compared with the present result since the arithmetical accuracy, apart from the fundamental theoretical approximation, is of a completely lower order. In that calculation the kinetic energy contribution to the total energy is twice the latter in magnitude and is in effect the integral of numerically differentiated functions, and since the numerical functions were only obtained to four significant figures the possible arithmetical error appears larger than the differences concerned in such comparisons. The actual integrals used in the present calculation were evaluated to seven significant figures from explicit formulas. In addition, Hartree & Hartree (1948) have found small errors in this previous calculation but do not give a corrected energy. In view of these uncertainties it is difficult to estimate which digits of the Fock-Petraschen result of $-161{\cdot}8$ are really established by their calculation, although it appears that the present result of $-161{\cdot}88$ is established to all these digits. The use of this previous result as a guide in the various trials reported above should be considered as a best expedient in the absence of other data, and it is the opinion of the authors that the results do suggest that the true energy for the Fock-Petraschen calculation should be somewhat higher in the absolute sense. On the other hand, these trials should not be considered just as attempts to improve the particular energies and wave functions concerned, they have provided very valuable experience in the organization of such converging calculations, and would make any repetition or extension much briefer. This is probably of more permanent value than the particular data. In view of the above considerations and the fact that the present calculations for the first time include electronic correlation for Na^+, Ne, F^-, it appears that the wave functions given in table 2 are the most accurate available for these ions.

The wave functions obtained correspond to a variational calculation with a finite number of terms, but the process used is such that it can be extended without any fresh type of analysis to any number of terms when it will converge to the accurate solution of the many electron Schrödinger equation.

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