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ELECTRONIC WAVE FUNCTIONS

XI. A CALCULATION OF EIGHT VARIATIONAL WAVE FUNCTIONS FOR Cl, Cl⁻, S AND S⁻

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CONTENTS

The variational co-detor method has been applied to calculate wave functions and energies for the P^2 and S^2 states of Cl, the S^1 state of Cl^-, the P^3, D^1, S^1 and P^3_0 states of S and the P^2 state of S^-. This is the first application of the method to atoms of the second chemical period, and is thus an application to considerably more complicated circumstances than have been previously examined. Except for the wave functions of the P^2 state of Cl and the S^1 state of Cl^- there are no records of any previous approximations of comparable accuracy to these wave functions, and no comparable predictions for any of the energy values. The introduction of relativistic corrections has been investigated and incorporated in this calculation. It was also found possible to adapt several sections of the calculation to the automatic calculating machine, the EDSAC, which has performed a considerable amount of the computation.

1. Introduction

The only method known at present for calculating atomic wave functions and their energies to unlimited accuracy is the co-detor variational method. This method has previously been applied only to atoms of the first chemical period, and the calculations required considerable effort both in theoretical analysis and in computation. Here some corresponding calculations for atoms of the second chemical period are reported. In these calculations some new developments have been made so that expenditure of effort has only been about the same or less than that required for the calculations for the first period. To report these developments it is convenient to assume the general theory with the notation and nomenclature as specified in part X. Also, the numerical evaluation and the checking of the H_{rs} matrices have been performed by using the methods described there, and no further description of this part of the calculation will be given.

The first new aspect which needed examination was the evaluation of the projective reduction formulae. Although the formulae derived for the atoms of the first chemical period are also used for the atoms of the second chemical period, it is necessary to have a completely new range of these, which may be regarded as corresponding to integrals in which both the $2s$, $2p$ and the $3s$, $3p$ shells are involved. These have been evaluated for the whole range of the $3p$ to $3p^6$ period in accordance with the general theory of parts III to VI.

The results of these necessary for the present calculations will be assumed here, and the whole scheme of calculation reported on a later occasion. It may be noted that considerations of the labour involved in projective reduction calculations for atoms of the second chemical period to the present degree of approximation are no longer of much importance, since the complete set of coefficients, which will also be used in calculations for atoms of the third or higher periods with incomplete *s*, *p* shells, has now been found.

Secondly, since the EDSAC, the automatic electronic calculating machine built by Wilkes, Renwick and others (1949), was very kindly put at our disposal soon after these calculations were begun, it was considered desirable to construct programmes for carrying out some of the laborious parts of the calculation by means of this machine. These have been completely effective and may be regarded as practically indispensible for future calculations on complicated atoms.

Thirdly, the relativistic corrections to Schrödinger's equation for these atoms become comparable with the present numerical accuracy and it was considered informative to investigate the magnitude of these corrections and to develop a method for including them, to the first order, in this type of calculation.

The calculation of the relativistic effects which is in effect a modification of the general theory, will be examined first in § 2, and then the EDSAC automatic computation procedures will be described in § 3. Other detailed aspects of the numerical work will be considered in § 4, and the resulting wave functions will be given in § 5. Finally, it is interesting (§ 6) to review what deductions can be made from the present experience with regard to the application of similar methods to other atoms and to molecules.

2. Relativistic corrections

At present the exact relativistic wave equation for a system of many electrons is not known, but the equation given by Breit (1929, 1930, 1932), which is based on the exact Dirac equation (1927) for a single electron, and the modified Schrödinger equation derived as an approximation to it, are generally accepted as accurate to the first relativistic order. It has been assumed that the accuracy of this modified Schrödinger equation is sufficient for the present investigation, and the extra terms in it which appear to be comparable with the present standard of accuracy of the calculation of the wave functions, have been evaluated.

It appears that the corrections to the Schrödinger Hamiltonian, which influence the energy and wave functions of atoms most, are the single-electron operators corresponding to mass change and the special *s* electron effect. Explicitly these are

$$R = \sum_i (\pi\rho_i(0) - (\nabla_i^2)^2)\frac{a^2}{2}, \tag{1}$$

where $\rho_i(0)$ is the charge density at the nucleus expressed as a function of the co-ordinates of the ith electron, and $1/a$ is the velocity of light in atomic units, that is, $a \simeq \frac{1}{137}$.

Since these are single-electron terms it is possible to compare the effect of them on the energy of a wave function with the exact relativistic energy obtained from the Dirac equation for a single electron. For this, consider a single electron in the (1*s*) state of a hydrogen-like ion with nuclear charge Z. Let E be the energy of the Schrödinger

Hamiltonian H, and $E+\Delta E_1$ be the energy of the perturbed Hamiltonian $H+R$. By treating the term R as a small perturbation and expanding the perturbed wave function in terms of the (ns) H-like unperturbed wave functions, then by the standard method one obtains the result

$$\Delta E_1 = -\tfrac{1}{8}a^2Z^4 - 0{\cdot}029a^4Z^6 + O(a^6Z^8). \tag{2}$$

The exact value of the energy of the electron $E+\Delta E_2$ was proved by Dirac to be given by

$$E+\Delta E_2 = a^{-2}\left(1+\frac{a^2Z^2}{1-a^2Z^2}\right)^{-\frac{1}{2}} - a^{-2}.$$

Hence

$$\Delta E_2 = -\tfrac{1}{8}a^2Z^4 - \tfrac{1}{16}a^4Z^6 + O(a^6Z^8). \tag{3}$$

Thus it is seen that the main terms in ΔE_1 and ΔE_2 are the same. In the third column of table 1 are given some of the values of ΔE_1 which can be used to estimate whether, according to the accuracy expected in the calculation, any relativistic corrections should be included, and in the fourth column are given some of the values of $\Delta E_1 - \Delta E_2$ which indicate the reliability of the procedure of allowing for the relativistic effects by modifying the Schrödinger Hamiltonian with the term R.

TABLE 1. THE RELATIVISTIC CORRECTIONS TO THE ENERGY OF A ($1s$) ELECTRON AS CALCULATED BY THE APPROXIMATE BREIT FORMULA (ΔE_1) AND BY THE EXACT DIRAC FORMULA (ΔE_2)

Z	E	ΔE_1	$\Delta E_1-\Delta E_2$
6	− 18	−0·008 6	0
7	− 24·5	−0·016 0	0
8	− 32	−0·027 3	0
9	− 40·5	−0·043 7	0
10	− 50	−0·066 7	0·000 1
12	− 72	−0·138 4	0·000 3
14	− 98	−0·256 5	0·000 7
16	−128	−0·437 9	0·001 6
18	−162	−0·701 9	0·003 2
20	−200	−1·070 9	0·006 1
25	−312·5	−2·621 7	0·023 2
30	−450	−5·454 6	0·069 3
35	−612·5	−9·994 2	0·174 8

However, in addition to the correction to the energy of the electron, it is important to test the change in the shape of the wave function caused by the corrections. This can be estimated for a H-like ion by using an approximate wave function $\sqrt{(u^3/\pi)}\,e^{-ur}$ for the ground state and determining the best value of u for the Hamiltonian $H+R$ by the variational method.

$$H+R = -\tfrac{1}{2}\nabla^2 - Z/r + \tfrac{1}{2}a^2\pi\rho - \tfrac{1}{8}a^2(\nabla^2)^2 \tag{4}$$

and

$$(\psi\,|\,H+R\,|\,\psi) = \tfrac{1}{2}u^2 - Zu + \tfrac{1}{2}a^2Zu^3 - \tfrac{5}{8}a^2u^4$$

is the energy of the trial wave function. The best value of u is given by

$$u - Z + \tfrac{3}{2}a^2Zu^2 - \tfrac{5}{2}a^2u^3 = 0,$$

which gives approximately

$$u = Z(1+a^2Z^2) + O(a^4Z^5), \tag{5}$$

particular values of which are given in table 2.

Table 2. The best parameter values for wave functions of the form $\sqrt{(u^3/\pi)}\,\mathrm{e}^{-ur}$ for H-like ions allowing for relativistic effects

Z	u	Z	u
6	6·012	16	16·218
7	7·018	18	18·311
8	8·027	20	20·426
9	9·039	25	25·833
10	10·053	30	31·439
12	12·092	35	37·284
14	14·146		

Since the correction to the value of $Z = 17$ for chlorine is about 0·3 and is thus about the same as the effect of the He-like repulsion for this Z, which is one of the essential effects which the poly-detor method is used to treat quantitatively; and since the corresponding energy lowering of two 1*s* electrons is about one atomic unit and so greater than other errors of the calculation, it was decided to include the relativistic corrections in the calculations of the atomic wave functions reported in this paper. The matrix elements of R were only calculated for the elements involving the (1*s*) and the (1*s*′) functions since the matrix elements of R involving the other *s* functions are very much smaller. The (1*s*′) function is used to correct the position of the (1*s*) shell and allow for radial correlation in this shell.

The formulae for the matrix elements of R can be deduced by elementary methods and are as follows:

$$(r^m\,\mathrm{e}^{-ur}\,|\,\pi\rho\,|\,r^n\,\mathrm{e}^{-vr}) = \begin{cases} \frac{1}{4}Z & \text{if } m=n=0,\\ 0 & \text{otherwise;}\end{cases} \tag{6}$$

$$\begin{aligned}(r^m\,\mathrm{e}^{-ur}\,|\,(\nabla^2)^2\,|\,r^n\,\mathrm{e}^{-vr})\\ = m(m+1)\,n(n+1)\,T(m+n-4,u+v)-2(m+1)\,(n+1)\,(mv+nu)\,T(m+n-3,u+v)\\ +[m(m+1)\,v^2+n(n+1)\,u^2-4(m+1)\,(n+1)\,uv]\,T(m+n-2,u+v)\\ -2[(m+1)\,v+(n+1)\,u]\,uv\,T(m+n-1,u+v)+u^2v^2\,T(m+n,u+v),\end{aligned} \tag{7}$$

where
$$T(x,y) = x!/y^{x+1}. \tag{8}$$

3. The computations performed by the EDSAC

In addition to the theoretical aspects of the present calculation the opportunity was taken to work out automatic computation procedures which enabled some of the longest sections of computation to be performed on the EDSAC. The present calculation would have been just practicable without these methods, but their use saved considerable labour and they are of considerable importance, since other calculations which would otherwise be prohibitively laborious will be quite feasible by their use.

With a desk machine any calculation has to be resolved into a sequence of basic arithmetical operations, and with an automatic machine this resolution has to be performed in much greater detail. For example, with a desk machine explicit instructions would not have to be given for any intermediate results to be written on paper, but with an automatic machine there would have to be an explicit order which would specify the location where a particular result would remain until required later. It is this sequence of orders, each corresponding to a small basic step in the calculation, which constitutes the programme for that calculation. The basic operations which are performed by the EDSAC have been given by Wilkes (1949), and with this set of orders it is possible to construct a programme for any numerical calculation however complicated.

There are, however, two important limitations of automatic computation machines such as the EDSAC, which have to be considered when any programme is being constructed. The first is the limited storage. This storage consists of a certain number of locations, in which are stored the orders of the programme, one to each location, and also the numerical data of the calculation, as numbers of about ten decimal places each in two locations. Although the number of available storage locations has been increased, at the time when this calculation was performed the number of locations was only 512, and this significantly influenced the programmes which were used in the calculation.

Secondly, unless special provision is made in the programme, all the numerical data must be less than unity in modulus. There are a few general ways in which this problem can be overcome, such as working with numbers stored in floating decimal form, that is, to specify a number by two quantites a and p the value of the number being $a10^p$, where a is less than unity in modulus and p is an integer, positive or negative. However, very often in any particular calculation there is a particular method which enables the EDSAC to complete the calculation quicker than if some general method were used.

It is mainly these two general problems which make the task of constructing a programme for most calculations quite complicated. If such a programme were going to be used only once, in spite of the fact that the EDSAC performs the calculation much more quickly than could be done with a desk machine, in many cases it would be doubtful if it were worth while constructing the programme. However, in addition to the speed of the EDSAC, there is a second very important advantage: when a programme has once been constructed it is punched on tape, and this tape and copies of it can be used for any number of similar calculations with different numerical quantities, thus saving very much time. Thus, although the EDSAC was very useful in the calculation of atomic wave functions reported in this paper, it will be even more effective in future calculations of this type.

The first part of the calculation to be programmed, which had previously been the longest part of the calculation, was the calculation of all the electrostatic integrals $[\phi_p\phi_q\,|\,\phi_r\phi_s]^k$, where ϕ_p are the orthonormal single-electron functions which are used in the calculation. This is performed in two parts, first the calculation of all the elementary integrals $[\eta_A\eta_B\,|\,\eta_C\eta_D]^k$, where the functions η_A have just a single exponential term in their radial factors, and then the necessary matrix multiplication corresponding to the linear combinations of functions η_A which form the functions ϕ_p. The special programme described below was constructed for the elementary integrals, and a programme constructed by Mr L. A. G. Dresel was used for the matrix multiplication.

The required integrals can be written in the form

$$\begin{aligned} J_{uv}(m,n)^k &= [r^m\,\mathrm{e}^{-ur}\,|\,r^n\,\mathrm{e}^{-vr}]^k \\ &= U(m+1-k,n+2+k,u,v)+U(n+1-k,m+2+k,v,u), \end{aligned} \tag{9}$$

where

$$\begin{aligned} U(A,B,u,v) &= \int_0^\infty \mathrm{d}r_1\int_0^{r_1}\mathrm{d}r_2\,r_1^A r_2^B\,\mathrm{e}^{-ur_1-vr_2} \\ &= \left(-\frac{\partial}{\partial u}\right)^A\left(-\frac{\partial}{\partial v}\right)^B\frac{1}{u(u+v)}. \end{aligned} \tag{10}$$

However, the numerical magnitude of these integrals varies over a very large range, which is very inconvenient, especially for use with the EDSAC. Therefore certain multiples of the integrals, which are all of the order of magnitude unity, are calculated and allowance is made for the additional factors in the stage of the matrix multiplication. Thus the actual integrals which are used in the calculation are

$$\bar{J}_{uv}(m,n)^k = C_n C_m u^{m+\frac{5}{2}} v^{n+\frac{5}{2}} J_{uv}(m,n)^k, \tag{11}$$

where

$$C_n = \{J_{11}(n,n)^0\}^{-\frac{1}{2}}. \tag{12}$$

These $\bar{J}$ integrals are all less than or equal to unity, and are conveniently called non-dimensional since they only depend on the ratio u/v.

An explicit formula is given for the quantities $U(A,B,u,v)$ in equation (14), part II, but instead of using this explicitly, it is more convenient to use a recurrence relation for certain intermediate quantities g_r^{aB},

$$g_r^{(a+1),B} = (a+2-r)\,g_r^{aB} + (B+r-1)\,u g_{r-1}^{a,B}/(u+v) \quad (r = 1, \ldots, a+2;\ a = 0, \ldots, A-1), \tag{13}$$

in terms of which the final value can be expressed by

$$U(A,B,u,v) = \sum_{r=1}^{A+1} g_r^{AB}. \tag{14}$$

The recurrence relation is started with the single term g_1^{0B}, which is a suitable multiple of $\left(-\frac{\partial}{\partial v}\right)^B \frac{1}{u(u+v)}$, and the application of the recurrence relation (13) corresponds to the differentiation with respect to u in (10).

In order that all the intermediate numbers occurring in the calculation should be less than unity any integer p used in the calculation is replaced by $\frac{1}{16}p$. It can easily be seen that if all the coefficients in (13) are replaced by $\frac{1}{16}$th of their true value then the final result will be much smaller than the correct one, and so if one continued to work with fractions correct to just ten decimal places one would not have very many significant figures in the result. Thus in order to obtain the results with the required accuracy of nine significant decimal places, subroutines were constructed which enabled the arithmetic to be performed to twenty decimal places.

The present programme, applicable for integral values of u and v less than 32 and values of n and m less than 7, calculates the integrals in sets, in each of which the parameters n, m, u and v take specified values, and k takes all values such that $0 \leqslant k \leqslant n, m$. It is convenient to calculate the integrals in such sets, and check them by another programme which calculates, theoretically independently, the sum of the integrals in each set. To evaluate a set of integrals it is only necessary to punch four tape symbols corresponding to the specified values of n, m, u and v; and, up to the present, the average time taken to evaluate such a set has been about 20 s. This can be compared with 1 h which would be required on a desk calculating machine, assuming that the coefficients of the power series had been evaluated previously. The present calculation required about 400 new $\bar{J}$ integrals, for which the time saved by automatic computation is considerable.

4. THE CHOICE OF FUNCTIONS USED IN THE CALCULATION

As was stated in part X, there is not at present any systematic method of choosing the initial single-electron functions from which the wave function is formed, although there is a method of testing the quality of the initial choice fairly early in the calculation and of examining how this may be improved if necessary. It was by this method that the single-electron functions given in table 3 were obtained, these being a second choice after the first choice was found to be unsatisfactory.

Table 3. Values of the coefficients, X_p^s, of the normalized exponential terms in the single-electron functions ϕ_s

$$\phi_s = \sum_p X_p^s \{(r^{m_p}\,\mathrm{e}^{-u_p r} \,|\, r^{m_p}\,\mathrm{e}^{-u_p r})\}^{-\frac{1}{2}}\, r^{m_p}\,\mathrm{e}^{-u_p r}$$

ϕ_s $r^m\,\mathrm{e}^{-ur}$	$(1s)$	$(2s) = (2p)$	$(3s)$
e^{-8r}	1·024 513 8	0·0	0·074 817 0
e^{-7r}	0·037 551 5	0·0	0·002 742 3
$r\,\mathrm{e}^{-3r}$	−0·357 029 6	1·0	−0·254 736 5
$r^2\,\mathrm{e}^{-r}$	0·0	0·0	1·028 406 6
	$(1s')$	$(2s')$	$(3s')$
e^{-8r}	−16·370 033 3	0·532 068 4	0·211 720 4
e^{-7r}	17·661 009 1	0·019 501 9	0·007 760 2
$r\,\mathrm{e}^{-3r}$	−5·139 088 0	−2·837 459 4	−1·378 616 6
$r^2\,\mathrm{e}^{-r}$	−1·589 378 9	−0·477 340 1	−3·835 376 8
$r^2\,\mathrm{e}^{-3r}$	4·144 318 2	3·021 430 4	2·007 955 5
$r^3\,\mathrm{e}^{-r}$	1·221 741 2	0·0	3·641 768 7
	$(3p)$	$(2p')$	$(3p')$
$r\,\mathrm{e}^{-3r}$	−0·243 637 5	−2·565 671 8	−0·214 048 2
$r^2\,\mathrm{e}^{-r}$	0·786 118 5	−1·664 124 5	−3·449 787 8
$r^2\,\mathrm{e}^{-3r}$	0·052 292 7	3·100 882 4	0·745 205 5
$r^3\,\mathrm{e}^{-r}$	0·236 819 4	1·177 739 4	3·374 835 0
	$(1p')$	$(2d')$	$(3d')$
$r\,\mathrm{e}^{-3r}$	−0·364 401 9	0·0	0·0
$r^2\,\mathrm{e}^{-r}$	0·074 914 0	−0·214 484 8	1·0
$r\,\mathrm{e}^{-12r}$	1·061 233 6	0·0	0·0
$r^2\,\mathrm{e}^{-4r}$	0·0	1·022 743 2	0·0

The choice of the original set of single-electron functions was made as follows. An approximate estimate of the effective Coulomb field under which each electron moves can be obtained by the rules given by Slater (1930). The results of this led to the use of e^{-8r}, $r\,\mathrm{e}^{-3r}$ and $r^2\,\mathrm{e}^{-r}$ for the main contributions to the radial factors of the functions representing the (1*s*), (2*s*) and (2*p*), and (3*s*) and (3*p*) shells respectively. In order to allow for better fitting of the two outer shells, the additional terms $r^2\,\mathrm{e}^{-3r}$ and $r^3\,\mathrm{e}^{-r}$ were introduced, since the use of $r^{n+1}\,\mathrm{e}^{-ur}$ has approximately the same effect as a change in the value of u in $r^n\,\mathrm{e}^{-ur}$. Because of the previous experience of calculations for He-like ions, e^{-7r} was used to allow the form of the (1*s*) shell to be adjusted. Normalized orthogonal linear combinations of these single terms were found by the direct method, known as the Schmidt process, applied to these functions taken in the order $r\,\mathrm{e}^{-3r}$, $r^2\,\mathrm{e}^{-r}$, e^{-8r}, $r^2\,\mathrm{e}^{-3r}$, $r^3\,\mathrm{e}^{-r}$ and e^{-7r}. With the functions in this order it was possible to use a common radial factor for the 2*s* and 2*p* functions, another for the (3*s*) and (3*p*) functions, and another for an *s* and a *p* replacement. This was thought to be very desirable when the calculation was planned, since it was intended that all the computing would be done on a desk calculating machine, and this would have saved very much time in the matrix multiplication for calculating the electrostatic integrals between the orthonormal functions, but it would have been of much less value with the automatic computation.

The root functions were tested by finding the approximate contributions of the co-detors formed by single replacements in the root functions, and it was found that the (3*p*) function was not very satisfactory because the contribution of the co-detor formed by replacing a $(3p)$ function by the $(3p')$ function was more than 30 %. Hence the $(3p)$ function was modified by adding a suitable multiple of the $(3p')$ function, and a corresponding alteration made in the replacement function to keep it orthogonal to the new $(3p)$ function. With these alterations made, the p functions of the root functions and their replacement functions as given in table 4 were obtained. In this test of the original functions the $(2s)$ and $(3s)$ functions had appeared to be quite satisfactory, but in a subsidiary calculation of a He-like ion allowing for relativistic corrections the $(1s)$ shell was fitted better with $e^{-8r}+0{\cdot}03\,e^{-7r}$ than with e^{-8r}. Thus the final set of s functions as given in table 3 were obtained by applying the Schmidt process to the functions $r\,e^{-3r}$, $e^{-8r}+0{\cdot}03\,e^{-7r}$, $r^2\,e^{-r}$, $r^2\,e^{-3r}$, $r^3\,e^{-r}$ and e^{-7r}, taken in this order.

The only other single-electron functions to be introduced were to allow for angular correlation in the $(1s)$, $(2p)$ and $(3p)$ shells, and the functions chosen for this were $r\,e^{-12r}$, $r^2\,e^{-4r}$ and $r^2\,e^{-r}$ respectively for similar reasons to those given in part VIII. The radial factor of the $(1p')$ function to allow for angular correlation in the $(1s)$ shell was chosen to depend mainly on $r\,e^{-12r}$, since empirical tests show that to lower as much as possible the energy of a $(1s)$ shell depending on the factor e^{-Zr}, a p function with a radial factor $r\,e^{-1{\cdot}5Zr}$ should be used. Although the $(1p')$ function was made orthogonal to the $(2p)$ and the $(3p)$ functions it was not considered worth while to make it orthogonal to the other p replacement functions, since the extra complication involved in the calculation of some of the elements of the variational matrices was quite insignificant. Finally, the d functions to allow for angular correlation in the $(2p)$ and $(3p)$ shells were chosen to depend on the radial factors $r^2\,e^{-4r}$ and $r^2\,e^{-r}$ respectively, since these factors are approximately the same as the radial factors of the $(2p)$ and $(3p)$ functions. Also these two d functions were normalized and made orthogonal to each other.

A stretching factor was applied to all of these single-electron functions in the same way as was described in part VIII. The values of the stretching factors were 2, 2, $(\frac{17}{8})$ and $(\frac{17}{8})$ for S, S^-, Cl and Cl^- respectively.

The co-detors for the variational calculation were built up from these single-electron functions and were chosen as described in part X. The empirical criterion used in the present calculation was to omit the co-detors for which H^2_{r1}/H_{rr}, the approximate estimate of the energy lowering, was less than 0·005 atomic unit. The actual co-detors examined were chosen in accordance with the approximate physical significance as discussed in part X and comprised chiefly those obtained by single replacements in the root function to allow the form of a shell orbital to be adjusted, and those obtained by double replacements corresponding to radial or angular repulsive correlations or to interaction of configurations.

5. Results and discussion

In table 4 are given the coefficients of the co-detors in each of the wave functions, designated by the configuration of the outer electrons occurring in the root function. The magnitude of each wave function is adjusted so that the coefficient of the root function is 1, that is, the wave function is not normalized.

The actual vector coupling system for each separate co-detor has not been given explicitly, since this merely seems to obscure the relation to the root function. Instead, each set of co-detors is labelled by what substitutions are made in the root function to obtain that particular set. Thus, for example, the set of co-detors labelled by $(3p)/(3p')$ in the wave function of the ground state of Cl are $(1s)^2\,(2s)^2\,(2p)^6\,(3s)^2\,(3p)^4\,\theta(3p')\,\mathrm{P}^2$, where $\theta = \mathrm{S}^1$, P^3 and D^1. In those sets of co-detors where there is more than one possible vector coupling system to give the same overall final coupling, all the possible co-detors have been included in that set, and these are ordered according to the alphabetic system. If (L_1, S_1) is the first variable pair of eigang values occurring in each co-detor, (L_2, S_2) the second pair, and so on, then the co-detors are arranged so that the sets $\{(L_1, S_1)\,(L_2, S_2)\,\ldots S_N\}$ are in ascending order, regarding L_1 as the most significant symbol. For example, the set of co-detors labelled $(3p)^2/(3d')^2$ in the wave function of the ground state of Cl are arranged in the following order:

$$p^3\mathrm{S}^4d^2\mathrm{P}^3\mathrm{P}^2,\quad p^3\mathrm{P}^2d^2\mathrm{S}^1\mathrm{P}^2,\quad p^3\mathrm{P}^2d^2\mathrm{P}^3\mathrm{P}^2,\quad p^3\mathrm{P}^2d^2\mathrm{D}^1\mathrm{P}^2,\quad p^3\mathrm{D}^2d^2\mathrm{P}^3\mathrm{P}^2\quad\text{and}\quad p^3\mathrm{D}^2d^2\mathrm{D}^1\mathrm{P}^2.$$

TABLE 4. COEFFICIENTS Y_r FOR WAVE FUNCTIONS IN THE FORM $\Sigma Y_r \Phi_r$

atom …	S	S	S	S
root function …	$(3s)^2\,(3p)^4\,\mathrm{P}^3$	$(3s)^2\,(3p)^4\,\mathrm{D}^1$	$(3s)^2\,(3p)^4\,\mathrm{S}^1$	$(3s)\,(3p)^5\,\mathrm{P}^3_0$
energy …	−397·012	−396·954	−396·875	−396·595
Φ_r				
$(\ )/(\ )$	1·0	1·0	1·0	1·0
$(1s)/(1s')$	−0·005 0	−0·005 0	−0·005 0	−0·005 0
$(1s)/(2s')$	−0·083 7	−0·083 7	−0·083 6	−0·084 0
$(1s)/(3s')$	−0·014 2	−0·014 2	−0·014 4	−0·013 8
$(2s)/(2s')$	0·151 6	0·151 6	0·151 3	0·152 2
$(2s)/(3s')$	0·017 2	0·017 2	0·017 8	0·016 5
$(3s)/(2s')$	−0·017 1	−0·017 0	−0·016 8	−0·009 0
$(3s)/(3s')$	−0·047 1	−0·047 2	−0·047 7	−0·040 2
$(2p)/(3p')$	−0·143 0	−0·143 1	−0·143 2	−0·142 6
$(2p)/(2p')$	0·001 0	0·001 0	0·001 0	0·001 3
$(3p)/(3p')$	0·035 1	0·023 6	0·059 8	−0·006 3
	−0·019 1	0·048 4	—	−0·052 6
	0·030 1	—	—	0·022 1
$(2p)^2/(2p')^2$	0·013 9	0·013 9	0·013 9	0·013 9
	0·020 4	0·020 4	0·020 4	0·020 5
	−0·021 9	−0·021 9	−0·021 9	−0·022 0
$(2s)\ (2p)/(2s')\ (2p')$	−0·013 6	−0·013 6	−0·013 2	−0·013 6
$(3p)^2/(3d')^2$	0·019 5	−0·021 8	−0·097 6	−0·044 9
	0·051 4	−0·059 2	0·059 1	−0·070 7
	−0·047 9	−0·049 0	0·056 1	0·039 1
	0·055 8	0·062 1	—	0·031 2
	0·043 8	—	—	0·047 9
	—	—	—	−0·065 8
$(2p)/(3p)$	−0·072 0	0·073 4	−0·075 4	−0·049 9
$(2p)^2/(2d')^2$	−0·023 5	−0·023 5	−0·023 5	−0·023 6
	−0·032 2	−0·032 2	−0·032 1	−0·032 2
	0·025 1	0·025 1	0·025 0	0·025 1
$(3s)/(3d')$	0·063 0	−0·097 5	—	−0·039 8
	−0·075 7	—	—	—
$(3s)^2/(3p)^2$	—	—	−0·096 9	—
$(1s)^2/(1s')^2$	−0·003 7	−0·003 7	−0·003 7	−0·003 7
$(1s)^2/(1p')^2$	0·006 5	0·006 5	0·006 5	0·006 5
$(3p^2)/(3s)\ (3d')$	—	—	—	0·073 8
	—	—	—	0·116 5

TABLE 4 (*cont.*)

atom …	Cl^-	Cl	Cl	S^-
root function …	$(3s)^2\ (3p)^6\ S^2$	$(3s)^2\ (3p)^5\ P^2$	$(3s)\ (3p)^6\ S^2$	$(3s)^2\ (3p)^5\ P^2$
energy …	−458·917	−458·901	−458·388	−396·934
Φ_r				
(1)	1·0	1·0	1·0	1·0
$(1s)/(1s')$	−0·007 9	−0·007 9	−0·007 9	−0·005 1
$(1s)/(2s')$	−0·076 5	−0·075 7	−0·076 1	−0·084 5
$(1s)/(3s')$	−0·015 8	−0·016 6	−0·015 9	−0·013 2
$(2s)/(2s')$	0·135 7	0·134 0	0·134 9	0·153 3
$(2s)/(3s')$	0·021 7	0·023 6	0·022 1	0·015 2
$(3s)/(2s')$	−0·003 6	0·018 9	0·015 3	−0·038 8
$(3s)/(3s')$	−0·053 9	−0·093 8	−0·070 2	−0·007 2
$(2p)/(3p')$	−0·113 5	−0·107 4	−0·106 1	−0·150 8
$(2p)/(2p')$	−0·038 6	−0·040 0	−0·040 2	0·002 6
$(3p)/(3p')$	0·072 6	0·006 3	−0·005 9	−0·027 7
	—	−0·000 9	—	−0·102 4
	—	−0·005 7	—	0·070 1
$(2p)^2/(2p')^2$	0·013 0	0·012 9	0·012 9	0·013 9
	0·018 7	0·018 6	0·018 6	0·020 5
	−0·020 3	−0·020 2	−0·020 2	−0·022 0
$(2s)\ (2p)/(2s')\ (2p')$	−0·016 7	−0·016 7	−0·016 8	−0·013 7
$(3p)^2/(3d')^2$	−0·080 9	−0·048 5	−0·084 7	−0·045 2
	−0·097 6	−0·072 3	−0·089 7	−0·066 5
	0·086 1	0·041 7	0·085 9	0·038 8
	—	0·033 1	—	0·030 7
	—	0·054 0	—	0·050 2
	—	−0·070 8	—	−0·064 9
$(2p)/(3p)$	—	−0·036 7	—	−0·052 5
$(2p)^2/(2d')^2$	−0·022 5	−0·022 4	−0·022 5	−0·023 5
	−0·030 8	−0·030 8	−0·030 8	−0·032 2
	0·023 9	0·023 9	0·023 9	0·025 1
$(3s)/(3d')$	—	−0·079 1	—	−0·073 7
$(3s)^2/(3p)^2$	—	—	—	—
$(1s)^2/(1s')^2$	−0·003 6	−0·003 6	−0·003 6	−0·003 7
$(1s)^2/(1p')^2$	0·006 1	0·006 1	0·006 1	0·006 5
$(3p)^2/(3s)\ (3d')$	—	—	0·188 3	—

There is one exception to the rule of including all the possible vector coupling systems, and this is concerned with the co-detors $(3s)/(3d')$. In every case in which there remains one $(3s)$ function to be coupled with the $(3d')$ function, this coupling is D^3 and not D^1. This other coupling possibility is not included because the contributions of such co-detors with a D^1 coupling are very much smaller than those with a D^3 coupling.

The only known reliable single test which can be applied to any wave function is to compare the total energy of the wave function with the corresponding experimental energy or the energy of a previously calculated wave function for the same state, using the well-known minimum property of the energy. Unfortunately, it is not possible to apply this test to the wave functions given in table 4, because the total experimental energies of the atoms are not known, and there have not been any previously calculated values of these energies. The only previous approximations to any of these wave functions are some for the ground states of Cl and Cl^- obtained by self-consistent field methods (see Hartree, Kronig & Petersen (1934) and Hartree & Hartree (1936)), but the energies of these wave functions have not been calculated. Thus, the only possible tests which can be applied immediately to the wave functions are those depending on the difference of the energies of the various wave functions, comparing these with the experimental differences. The results of this comparison are given in table 5.

TABLE 5

wave functions	energy differences calculated	energy differences experimental
$Cl(P^2)-Cl^-(S^1)$	0·016	0·144
$Cl(S^2)-Cl(P^2)$	0·513	—
$S(P^3)-S^-(P^2)$	−0·078	—
$S(D^1)-S(P^3)$	0·058	0·043
$S(S^1)-S(P^3)$	0·136	0·102
$S(P^3_0)-S(P^3)$	0·407	0·332

Although the electron affinity of Cl has the correct sign, it is very small, and this suggests that the negative value for the electron affinity of S, which implies that the ion S^- is not stable, is unreliable. It is probable that the main errors in these values of the electron affinities lie in the wave functions of the ground states of the negative ions, and that to improve these significantly one would have to introduce extra single-electron functions to adjust the orbitals of the outer electrons.

The calculated difference between the S^2 state and the ground state of Cl indicates that the S^2 state is just in the spectral continuum of the atom, since the ionization potential of Cl is 0·485 atomic unit. However, it is generally found that variational wave functions of excited states are less accurate than wave functions of the ground states, as is shown here by the predicted energy differences between the various states of S. Thus one would expect that the true value of the energy difference between the S^2 state and the ground state of Cl would be less than 0·513 and probably less than 0·485, in which case this level would occur, in the discrete spectrum of Cl. This level has not, however, been observed.

The ratio of the differences of the energies of the lowest three states of S can also be compared with the theoretical ratio which one would obtain by any method such as the self-consistent field method in which the approximate wave function is given by a single co-detor. The values for single co-detors can be easily evaluated from the theory of vector coupling, as shown by Condon & Shortley (1935). The comparison given in table 6 shows the increased accuracy of the wave functions formed from the several co-detors.

TABLE 6. VALUES OF THE RATIO $(D^1-P^3):(S^1-P^3)$ OF THE ENERGY DIFFERENCES OF THE THREE LOWEST STATES OF SULPHUR

experimental value	0·422
theoretical value from the wave functions in the form $\Sigma Y_r \Phi_r$	0·427
theoretical value from wave functions in the form of single co-detors	0·400

6. CONCLUSIONS

The direct result of this investigation is to provide eight wave functions, each of which is the most accurate known for the particular stationary state. For six of these states there have been no comparable functions, and for none of these states has there been a comparable previous energy prediction. In the present type of calculation the total energy is found in the process of calculating the wave function, and it is considered that these values will be very useful for comparing the accuracy of future calculations of wave-function approximations. In addition, the form of these wave functions is probably the most suitable, of any at present available, for the prediction of atomic physical properties.

The general intermediate information found in this investigation should also be of appreciable value in the further use of converging methods of calculation for other states in the second and higher chemical periods. The investigation has been performed on a broad basis and should provide considerable guidance in choice of the elementary functions and of the linear combinations for other stationary states for calculations of increased accuracy for those considered here. The relativistic effects have only been introduced as explicit corrections, but it appears that this will be sufficient for practical standards of accuracy for the near future.

Finally, assessed from a more general point of view, this investigation contributes to the general development of practical converging methods of calculation of atomic and molecular wave functions and the physical properties dependent on these. It is desirable in each particular investigation that some of the many difficulties of the general problem be resolved so that these may be treated by stereotyped procedures in subsequent investigations. The adaption of the calculation of the elementary integrals and of the integrals of the orthonormal linear combinations to the EDSAC, and also the general systematic procedures developed for the large arrays of numbers are all advances of this nature. In particular they should reduce significantly the necessary labour for subsequent investigations such as on the (3*d*) shell of the next chemical period and on simple molecules, both of which present considerable difficulties.

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