Self-Consistent Field, Including Exchange and Superposition of Configurations, with Some Results for Oxygen

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SELF-CONSISTENT FIELD, INCLUDING EXCHANGE AND SUPERPOSITION OF CONFIGURATIONS, WITH SOME RESULTS FOR OXYGEN

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1. Introduction

The calculation of approximate wave functions for the normal configurations of the ions O^{+++}, O^{++}, O^{+}, and neutral O, and the calculation of energy values from the wave functions, was carried out some years ago by Hartree and Black (1933). In this work, the one-electron radial wave functions were calculated by the method of the self-consistent field without exchange, but exchange terms were included in the calculation of the energy from these radial wave functions. In the energy calculations, the same radial wave functions were taken for each of the spectral terms arising from a single configuration;* consequently the ratios between the calculated intermultiplet separations were exactly those given by Slater's (1929) theory of complex spectra.† The ratios between the observed intermultiplet separations, however, depart considerably from these theoretical values (for example, we have for O^{++}

$$({}^1D-{}^1S)/({}^3P-{}^1D),\ \text{calc. } 3:2,\ \text{obs. } 1{\cdot}04:1),$$

although the energies of the individual terms, and particularly the intermultiplet separation between the lower terms, show quite a good agreement with the observed values.

Approximate calculations by Levy (1934) showed that when exchange terms were included, as in Fock's (1930) equations, the resulting differences between the wave functions for the different spectral terms would not be nearly large enough to account for the observed deviations of the ratios of intermultiplet separations from the ratios given by Slater's theory. This made it appear likely that these deviations are due to appreciable matrix components between the normal configuration and some excited configurations, so that the wave functions for the lowest states include appreciable multiples of the wave functions for higher configurations superposed on that for the normal configuration, a situation which we will describe by the term "superposition

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* Strictly, the departure from spherical symmetry in the charge distribution of an incomplete ($2p$) group would give rise to small differences between the radial wave functions for different spectral terms arising from a single configuration, even when only terms in the equations arising from Coulomb interactions are taken into account, and those arising from exchange interactions are omitted. But these differences are of the same order as those due to exchange and are smaller than the main effect of exchange, so there seems no significance in including them so long as exchange terms are excluded.

† See also Condon and Shortley (1935, chaps. 6, 7). For the comparison of ratios of intermultiplet separations, observed and calculated from Slater's theory, see Condon and Shortley (1935, chap. 7, § 5).

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of configurations". [Condon and Shortley (1935) use the term "configuration interaction" for this situation, and its effects on spectral terms and lines are often referred to as "perturbations". But as the terms "interaction" and "perturbation" are both used in different senses from these in atomic mechanics, there seems to be a danger of confusion in their use in this sense. Hence we have preferred to coin the term "superposition of configurations" rather than use "configuration interaction".]

An estimate by Hartree and Swirles (1937) of the magnitude of the effect of superposition of configurations on the energy values, using the wave functions of Hartree and Black, seemed, however, to show that this effect would be about twice too large to account for the observed intermultiplet separations. The position seemed not altogether satisfactory, and with the development in the meantime of practical methods of evaluating solutions of Fock's equations, it seemed desirable to carry out calculations for oxygen, and to revise the calculation of energy values using the resulting wave functions.

When working with any approximation to the structure of an atom in which the wave function for the whole atom is built up from one-electron wave functions, there are two steps in the calculation of energy values at which approximation is involved, first in the way in which the one-electron wave functions are determined, and secondly in the way in which the wave function for the whole atom is taken as built up out of them. In the work of Levy and of Hartree and Swirles, the improved approximation resulting from the inclusion of effects of exchange and of the superposition of configurations was introduced in the second step only. Their inclusion in this step is the more important, since the radial wave functions given by any reasonable approximation will probably not be very greatly different from the best possible wave functions, and by the variation principle the energy value is not sensitive to small variations in the wave functions. But the intermultiplet separations are rather a refinement of the theory; as will be seen from the discussion of results, the second decimal in the ratio of intermultiplet separations involves the fifth significant figure in the calculated energy values. It seemed worth while, therefore, to find whether the use of the best obtainable wave functions would greatly improve the agreement with the experimental energy values and particularly with the ratios of observed intermultiplet separations.

The solution of Fock's equations for the self-consistent field with exchange but without superposition of configurations was carried out for O^{+++}, O^{++}, O^{+}, neutral O, and O^{-}. It is possible also to include terms arising from superposition of configurations, as well as those arising from exchange, in the equations for the one-electron wave functions, though the solution of the resulting equations is much more lengthy than the solution of Fock's equations. However, to see the effect on the wave functions, and on the energy calculated from them, it was decided to attempt the solution of these equations in one case at least, and O^{+} was chosen since only one of the spectral terms arising from the normal configuration appeared likely to be seriously affected by the superposition of higher configurations.

It was found that although the coefficient of the wave function for the higher configuration was quite large (about 0·2), the one-electron wave functions calculated from the generalized Fock equations, including exchange and superposition of the higher configuration, differed surprisingly little from those calculated from the solution of Fock's equations, including exchange only. Also the results of the calculation of energy values showed the discrepancy already shown by the estimates of Hartree and Swirles; the effect of the superposition of configurations, as far as we have taken it, is nearly twice as much as is required to account for the observed deviation from Slater's ratios of intermultiplet separations.

The small effect on the one-electron wave functions, and the small improvement in the energy values, resulting from the use of the generalized Fock equations for O^+ including superposition of configurations, seemed not enough to justify the carrying out of the extensive calculations which would be needed to obtain the solutions of the similar equations for the other states of ionization of oxygen.

2. Generalization of fock's equations to include superposition of configurations

We will consider in particular the normal configuration $(1s)^2\,(2s)^2\,(2p)^q$, which we will call "configuration A", of an atom of atomic number N. The general argument, and general forms of the results, will apply to any incomplete 8-shell outside closed groups, but it is simpler and shorter to present the argument for a particular case.

Superposition of configurations can only occur if the two configurations have the same parity (Σl odd or even), and the terms arising from the two configurations must (in Russell-Saunders coupling) have the same L and the same S.* The only configuration of the same parity as the normal configuration which does not involve a change of principal quantum number is $(1s)^2\,(2p)^{q+2}$, which we will call configuration B. This involves the excitation of two electrons; other configurations, involving the excitation of one electron with change of principal quantum number, namely $(1s)^2\,(2s)\,(2p)^q\,(3s)$ and $(1s)^2\,(2s)^2\,(2p)^{q-1}\,(3p)$, may lie not much higher in energy, but the spatial extension of their wave functions will be greater; their overlap with configuration A, and hence the extent to which they are superposed on it, will probably be less than that of configuration B. Further, their inclusion would increase not only the complexity but the number of equations to be solved, and, as a first step at any rate, it seemed best to consider configurations A and B only.

Let Ψ_A be the normalized wave function, including exchange, for an (L, S) term arising from configuration A, and Ψ_B be that for the same (L, S) term arising from configuration B; these will be taken as sums of determinants of one-electron wave functions of central-field type,† and they will necessarily be orthogonal.

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* See Condon and Shortley (1935), chap. 15, § 1 (p. 366).

† For example, see Hartree and Swirles (1937).

By "superposition of configurations" we mean that we take the linear combination

$$\Psi = (\Psi_A + \mu\Psi_B)/(1+\mu^2)^{\frac{1}{2}} \tag{1}$$

as an approximation to the wave function of the whole atom, where μ is a parameter whose value is to be determined by the variation principle. It does not seem necessary to use the same radial wave functions in Ψ_A and Ψ_B, but it seems doubtful if there would be any significance in not doing so; also the already large amount of work involved in evaluating a solution of the equations including superposition of configurations would be greatly increased if different $(2p)$ wave functions were taken in Ψ_A and Ψ_B. So we have been content with the approximation in which the radial wave functions in Ψ_B are taken as the same as those in Ψ_A.

For Ψ given by (1), the energy integral

$$E = \int \Psi^* H \Psi \, d\tau \Big/ \int \Psi^* \Psi \, d\tau$$

is given by $$(1+\mu^2)\,E = H_{AA} + \mu(H_{AB} + H_{BA}) + \mu^2 H_{BB},$$

where $H_{AB} = \int \Psi_A^* H \Psi_B \, d\tau$, etc. Writing E_A, E_B for the energy integrals for configurations A, B alone, respectively, and E_{AB} for the real part of H_{AB}, this becomes

$$(1+\mu^2)\,E = E_A + 2\mu E_{AB} + \mu^2 E_B. \tag{2}$$

TABLE I. COEFFICIENTS IN ENERGY FORMULAE, FOR WAVE FUNCTION

$$\Psi = (\Psi_A + \mu\Psi_B)/(1+\mu^2)^{\frac{1}{2}},$$

where Ψ_A is wave function for configuration $(1s)^2\,(2s)^2\,(2p)^q$,
Ψ_B is wave function for configuration $(1s)^2\,(2p)^{q+2}$.

Integral	E_A	E_{AB}	E_B	$(1+\mu^2)\,E$
$I(2s)$	2	0	2	$2(1+\mu^2)$
$I(2s)$	2	0	0	2
$I(2p)$	q	0	$q+2$	$q+(q+2)\,\mu^2$
$F_0(1s, 1s)$	1	0	1	$1+\mu^2$
$F_0(1s, 2s)$	4	0	0	4
$F_0(1s, 2p)$	$2q$	0	$2(q+2)$	$2[q+(q+2)\,\mu^2]$
$F_0(2s, 2s)$	1	0	0	1
$F_0(2s, 2p)$	$2q$	0	0	$2q$
$F_0(2p, 2p)$	$\frac{1}{2}q(q-1)$	0	$\frac{1}{2}(q+2)\,(q+1)$	$\frac{1}{2}[q(q-1)+(q+2)\,(q+1)\,\mu^2]$
$F_2(2p, 2p)$	β_A	0	β_B	$\beta_A+\beta_B\mu^2$
$G_0(1s, 2s)$	-2	0	0	-2
$G_1(1s, 2p)$	$-\frac{1}{3}q$	0	$-\frac{1}{3}(q+2)$	$-\frac{1}{3}[q+(q+2)\,\mu^2]$
$G_1(2s, 2p)$	$-\frac{1}{3}q$	γ	0	$-\frac{1}{3}q+2\gamma\mu$

Values of β_A, β_B, γ

q	6	5	4			3			2			1
Term	^{1}S	^{2}P	^{3}P	^{1}D	^{1}S	^{4}S	^{2}D	^{2}P	^{3}P	^{1}D	^{1}S	^{2}P
β_A	$-\frac{6}{5}$	$-\frac{4}{5}$	$-\frac{3}{5}$	$-\frac{9}{25}$	0	$-\frac{3}{5}$	$-\frac{6}{25}$	0	$-\frac{1}{5}$	$\frac{1}{25}$	$\frac{2}{5}$	0
β_B	—	—	—	—	$-\frac{6}{5}$	—	—	$\frac{4}{5}$	$-\frac{3}{5}$	$-\frac{9}{25}$	0	0
γ	0	0	0	0	$\frac{1}{3}\sqrt{3}$	0	0	$\frac{1}{3}\sqrt{2}$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{3}\sqrt{2}$

Written out in full, the expression of $(1+\mu^2)\,E$ consists of multiples of the integrals of the type

$$I(nl) = -\tfrac{1}{2}\int P(nl\,|\,r)\left[\frac{d^2}{dr^2}+\frac{2N}{r}-\frac{l(l+1)}{r^2}\right]P(nl\,|\,r)\,dr, \tag{3}$$

$$F_k(nl,n'l') = \iint P^2(nl\,|\,r)\,P^2(n'l'\,|\,r')\,\frac{r_a^k}{r_b^{k+1}}\,dr\,dr', \tag{4}$$

$$G_k(nl,n'l') = \iint P(nl\,|\,r)\,P(n'l'\,|\,r)\,P(nl\,|\,r')\,P(n'l'\,|\,r')\,\frac{r_a^k}{r_b^{k+1}}\,dr\,dr' \tag{5}$$

(r_a being the smaller and r_b the larger of r and r'), with coefficients given by Table I. In this table the coefficients in the columns E_A and E_B and the values of β have been found by Slater's method,* and the values of γ are taken from the paper by Hartree and Swirles (1937).

The value of this expression for E has to be stationary for independent variations of the radial wave functions P and of the parameter μ. Formal differentiation with respect to $P(2s)$ and $P(2p)$ respectively, using the expressions (7)–(10) of D. R. and W. Hartree (1936 *b*), gives equations for these functions, namely,

$$\left[\frac{d^2}{dr^2}+\frac{2}{r}\{N-2Y_0(1s,1s)-Y_0(2s,2s)-qY_0(2p,2p)\}-\epsilon_{2s,2s}\right]P(2s)$$
$$+\frac{2Y_0(1s,2s)}{r}P(1s)+\tfrac{1}{3}(q-6\gamma\mu)\,\frac{Y_1(2s,2p)}{r}P(2p) = 0, \tag{6}$$

$$\left[\frac{d^2}{dr^2}+\frac{2}{r}\left\{N-2Y_0(1s,1s)-\frac{2q}{q+(q+2)\,\mu^2}Y_0(2s,2s)-\frac{q(q-1)+(q+2)\,(q+1)\,\mu^2}{q+(q+2)\,\mu^2}Y_0(2p,2p)\right.\right.$$
$$\left.\left.-\frac{2(\beta_A+\beta_B\,\mu^2)}{q+(q+2)\,\mu^2}Y_2(2p,2p)\right\}-\frac{2}{r^2}-\epsilon_{2p,2p}\right]P(2p)$$
$$+\frac{2}{3}\,\frac{Y_1(1s,2p)}{r}P(1s)+\frac{2}{3}\,\frac{q-6\gamma\mu}{q+(q+2)\,\mu^2}\,\frac{Y_1(2s,2p)}{r}P(2s) = 0. \tag{7}$$

From the condition that the value of E must also be stationary for variations of μ, we obtain from (2)

$$\mu = (E-E_A)/E_{AB},$$

or, eliminating E between this result and (2),

$$\mu/(1-\mu^2) = -E_{AB}/(E_B-E_A). \tag{8}$$

Equations (6)–(8) form a generalization of Fock's equations to include terms (those in μ) arising from the superposition of configurations A and B.

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* See Slater (1929); Condon and Shortley (1935), chaps. 6, 7.

The method of solving these equations is first to estimate a value of μ, and solve (6) and (7) using this value; then to calculate the right-hand side of (8) from the solution, and hence to obtain a "final" value of μ. The estimate of μ is altered by trial and error until the final value so obtained agrees with it. This requires a complete solution of the extended Fock's equations (6) and (7) for each trial value of μ, so that the work involved in a single solution of the equations including superposition of configurations is as much as in several solutions of Fock's equations including exchange only. Fortunately the radial wave functions P and the final value of μ are not very sensitive to the estimate of μ, and the process of approximation to the correct value of μ is quite rapidly convergent. Even so, the amount of work involved is considerable.

If the superposition of other configurations, such as

$$(1s)^2\,(2s)\,(2p)^q\,(3s) \quad \text{or} \quad (1s)^2\,(2s)^2\,(2p)^{q-1}\,(3p),$$

were taken into account, both the form of the equations and the process of deriving them would be more complicated, there would also be more equations (one extra for each new radial wave function such as $(3s)$ or $(3p)$, and possibly more, since it might then be desirable to take different $(2s)$ or $(2p)$ wave functions for the different configurations), and there would be further conditions of the form (8) to be satisfied; and the numerical work might be too formidable to be practicable.

3. Energy formulae

In calculating energies, it is usually convenient to make use of the equations satisfied by the radial functions P to eliminate some of the integrals from the energy formula, and this is the case here. The values of E_A and E_B are wanted in two contexts, both in the calculation of E from (2), and in the calculation of the "final" value of μ from (8).

To a sufficient approximation, the variations of the $(1s)$ wave function can be neglected; this is certainly an amply good enough approximation as far as intermultiplet separations are concerned, and even between different states of ionization the differences are small and, by the variation principle, the contribution to the energy from the $(1s)^2$ group is insensitive to small variations of the $(1s)$ wave functions from that of O^{+6}. Then we can consider the energy of the $(2s)$ $(2p)$ shell due to its interaction with the O^{+6} core and its internal interactions only; and on substituting for d^2P/dr^2 in $I(2s)$ and $I(2p)$ from (6), (7) we get the energies expressed as the sum of multiples of integrals and of the ϵ parameters with coefficients given in Table II.

Here the column headed $E_A(\mu = 0)$ refers to the energy expression without superposition of configurations; the other columns give the coefficients in the respective expressions when the terms arising from the superposition of configurations are included both in the equations from which the wave functions are calculated, and in the energy formula (1); they do not apply if such terms are only included in the latter formula.

TABLE II. COEFFICIENTS IN ENERGY FORMULAE AFTER SUBSTITUTION FOR d^2P/dt^2 IN $I(2s)$ AND $I(2p)$

	Coefficient in				
Integral	E_A ($\mu=0$)	E_A	E_B	E_B-E_A	$(1+\mu^2)E$ $=E_A+2\mu E_{AB}+\mu^2E_B$
$F_0(2s, 2s)$	-1	-1	0	$+1$	-1
$F_0(2s, 2p)$	$-2q$	$-\dfrac{2q^2}{q+(q+2)\mu^2}$	$-\dfrac{2q(q+2)}{q+(q+2)\mu^2}$	$-\dfrac{4q}{q+(q+2)\mu^2}$	$-2q$
$F_0(2p, 2p)$	$-\frac{1}{2}q(q-1)$	$-\frac{1}{2}q(q-1)-\dfrac{2q(q+2)\mu^2}{q+(q+2)\mu^2}$	$-\frac{1}{2}(q+1)(q+2)+\dfrac{2q(q+2)}{q+(q+2)\mu^2}$	$\dfrac{3q-(q+2)\mu^2}{q+(q+2)\mu^2}$	$-\frac{1}{2}[q(q-1)+(q+1)(q+2)\mu^2]$
$F_2(2p, 2p)$	$-\beta_A$	$\beta_A-\dfrac{2q(\beta_A+\beta_B\mu^2)}{q+(q+2)\mu^2}$	$\beta_B-\dfrac{2(q+2)(\beta_A+\beta_B\mu^2)}{q+(q+2)\mu^2}$	$\beta_B-\beta_A-\dfrac{4(\beta_A+\beta_B\mu^2)}{q+(q+2)\mu^2}$	$-[\beta_A+\beta_B\mu^2]$
$G_1(2s, 2p)$	$\frac{1}{3}q$	$-2\gamma\mu+\dfrac{q(q-6\gamma\mu)}{3[q+(q+2)\mu^2]}$	$\dfrac{(q+2)(q-6\gamma\mu)}{3[q+(q+2)\mu^2]}$	$2\gamma\mu+\dfrac{2(q-6\gamma\mu)}{3[q+(q+2)\mu^2]}$	$\frac{1}{3}q-2\gamma\mu$
$\epsilon_{2s,2s}$	-1	-1	0	1	-1
$\epsilon_{2p,2p}$	$-\frac{1}{2}q$	$-\frac{1}{2}q$	$-\frac{1}{2}(q+2)$	-1	$-\frac{1}{2}[q+(q+2)\mu^2]$

The small number of integrals involved in Table II, compared with the number in Table I, shows the practical advantage of working with the modified energy formulae given by the substitution for d^2P/dr^2 in the integrals.

It should be noted that, from the way in which the coefficients in the formula for $E_B - E_A$ in Table II were obtained, it follows that in calculating the "final" value of μ from (8), using this formula for $E_B - E_A$, it is correct to use the *estimated* value of μ in calculating these coefficients, rather than any better approximation to the "final" value.

4. PROCEDURE

The procedure used for solving both the Fock equations with exchange only, and the generalized Fock equations (6), (7) for each estimate of μ, was very similar to that used for the (2*s*) (2*p*)^{3}P excited state of Be (see D. R. and W. Hartree (1936*a*)). There were two main modifications based on the experience of work subsequent to that on Be; first, the present work was done throughout with the equations for normalized wave functions, the values of P/r^{l+1} at $r = 0$ being adjusted by trial so that the solutions when found were normalized, and secondly, that the work was started from estimates of the P's not of Z_k's.

As already explained, when the superposition of configurations is taken into account, this solution of (6), (7) has to be carried out for a number of trial values of μ, until relation (8) is satisfied by the solution.

For each stage of ionization the solution of Fock's equations with exchange only was carried out first for the highest and for the lowest of the three spectral terms arising from the normal configuration. Then radial wave functions P were interpolated, linearly in β, for the intermediate term, and these estimates were always found to be adequate (cf. Table I). For all but O^+, the work was done to three decimals in P over the main part of the range, but for O^+ it was improved to four decimals, as the three-decimal results did not seem likely to be accurate enough to show conclusively the effect of superposition of configurations.

A rather thorough attempt was made to obtain a solution for O^{--}, but without success; it seems rather well established that, to the accuracy of this approximation to the structure of a many-electron atom, the O^{--} ion cannot exist in the free state.

As already mentioned, the only solution of the generalized Fock equations, including the superposition of configurations, was done for O^+, for which the terms in E and in the equations are given by putting $q = 3$ in Tables I, II and equations (6), (7). The normal configuration gives ^{4}S, ^{2}D and ^{2}P terms, of which only the last, the highest, is subject to the superposition of the $(2p)^5$ configuration. The value of μ, estimated from (8) using values of E_A, E_B calculated from the results of the solution of Fock's equations was $-0{\cdot}18$; four approximations were made, and the result of the final approximation was $-0{\cdot}202$ (the minus sign is of no significance, it depends on the convention of sign adopted for the radial wave functions).

5. Results. Wave functions

The results for O^+ are given in Table III, and those for the other states of ionization in Table IV.

For O^+ all three normalized radial wave functions, namely ($1s$), ($2s$) and ($2p$), are tabulated for the lowest term (^4S, $\beta = -\frac{3}{5}$) arising from the normal configuration, the ($2s$) and ($2p$) wave functions being given to the full four decimals retained in the calculations. For the other terms (^2D, $\beta = -\frac{6}{25}$ and ^2P, $\beta = 0$, the latter calculated without superposition of configurations) the differences ΔP from the wave functions for the lowest term, namely,

$$\Delta P = P_N\ (\text{upper term}) - P_N\ (\text{lower term}) \tag{9}$$

are tabulated in units of the fourth decimal, to show how very small is the departure, over this range, of the normalized wave function P_N from a linear dependence on β. If P_N were exactly linear in β, the numbers in the columns headed $\Delta\beta = \frac{9}{25}$ would be 0·6 of those in the corresponding columns headed $\Delta\beta = \frac{3}{5}$; actually the maximum departure is hardly a unit in the fourth decimal for $P(2s)$ and 2 in the fourth decimal for $P(2p)$, and this is hardly outside the range of possible effect of accumulation of rounding off errors in the integration. The values of the Lagrange parameter $\epsilon_{nl,\,nl}$ show a corresponding linear dependence on β.

For the upper state (^2P, $\beta = 0$) the normalized radial wave functions P_N themselves, calculated without superposition of configurations (columns headed $\mu = 0$), are also tabulated, for comparison with the values calculated including the terms in the equations arising from superposition of configurations (columns headed $\mu = -0{\cdot}202$), and the differences $\Delta' P$ arising from the effect of superposition of configurations are given. These differences are small, less than 0·4 % of the maximum $|P|$ for both wave functions; they would hardly have been established with certainty by calculations to three decimals, since in the third decimal they would be hardly greater than the possible effect of accumulation of rounding off errors in the numerical integration.

The results for other states of ionization are tabulated in a more compact form, and to three decimals only, in Table IV. The wave functions P_N are given in full for the lowest term only; for O^{++} and O neutral, for which the normal configuration gives three terms, the difference ΔP from the lowest term (cf. (9)) are given for the upper term only, for the intermediate term they can be taken as proportional to β in all cases. This is justified by the comparison of the four-decimal results for O^+, and had been established by solution of the equations for the intermediate terms for the other states of ionization, before these four-decimal results for O^+ were calculated.

The effect of superposition of configurations on the wave functions for O^+ and on the energy (cf. § 6) was considered too small to justify the extensive calculations which would be required to obtain the corresponding effects for the other states of ionization; for O^{++} all three terms ^3P, ^1D and ^1S are affected, and there seemed no object in carrying out the calculation for one of these and not for the others.

TABLE III. O$^+$ NORMALIZED RADIAL WAVE FUNCTIONS

	Without superposition of configurations							^{2}P term, $\beta = 0$					
								Without superposition of configurations		With superposition of configurations			
	^{4}S term, $\beta = -3/5$			^{2}D term, $\Delta\beta = 9/25$		^{2}P term, $\Delta\beta = 3/5$		$\mu = 0$		$\mu = -0{\cdot}202$		$\Delta'\mu = -0{\cdot}202$	
Table of P_N/r^{l+1} and $\Delta P_N/r^{l+1}$													
r	$P(1s)/r$	$P(2s)/r$	$P(2p)/r^2$	$\Delta P(2s)/r$	$\Delta P(2p)/r^2$	$\Delta P(2s)/r$	$\Delta P(2p)/r^2$	$P(2s)/r$	$P(2p)/r^2$	$P(2s)/r$	$P(2p)/r^2$	$\Delta' P(2s)/r$	$\Delta' P(2p)/r^2$
0·00	43·17	10·20$_5$	16·34	3	−13	4$_5$	−21$_5$	10·25	16·12$_5$	10·31$_5$	16·09$_5$	6$_5$	−3
0·01	39·86	9·41$_5$	15·70$_5$	3	−12$_5$	4$_5$	−20$_5$	9·46	15·50	9·52	15·47	6	−3
0·02	36·80	8·68	15·10	2$_5$	−12$_5$	4	−20	8·72	14·90	8·77$_5$	14·87	5$_5$	−3
0·03	33·99	7·99	14·52	2$_5$	−12$_5$	4	−19	8·03	14·33	8·08	14·30	5	−3
Table of P_N and ΔP_N													
	$P(1s)$	$P(2s)$	$P(2p)$	$\Delta P(2s)$	$\Delta P(2p)$	$\Delta P(2s)$	$\Delta P(2p)$	$P(2s)$	$P(2p)$	$P(2s)$	$P(2p)$	$\Delta' P(2s)$	$\Delta' P(2p)$
0·00	0	0	0					0	0	0	0		
0·01	0·398$_5$	0·0942	0·0015$_5$	2$_5$		4		0·0946	0·0015$_5$	0·0952	0·0015$_5$	6	
0·02	0·736	0·1737	0·0060$_5$	4	−0$_5$	7	−1	0·1744	0·0059$_5$	0·1754$_5$	0·0059$_5$	10$_5$	
0·03	1·020	0·2398	0·0130$_5$	6	−1	10	−1$_5$	0·2408	0·0129	0·2423	0·0128$_5$	15	−0$_5$
0·04	1·256	0·2939	0·0223$_5$	8	−2	13	−3	0·2952	0·0220$_5$	0·2970	0·0220	18	−0$_5$
0·06	1·609	0·3710	0·0466	10	−4	16	−7	0·3726	0·0459$_5$	0·3749	0·0459	23	−0$_5$
0·08	1·834	0·4133	0·0769	10	−7	17	−11	0·4150	0·0758	0·4176	0·0757	26	−1
0·10	1·962	0·4277	0·1117	11	−10	18	−16	0·4295	0·1101	0·4322	0·1100	27	−1
0·12	2·015	0·4199	0·1497	11	−13	17	−21	0·4216	0·1476	0·4243	0·1474	27	−2
0·14	2·015	0·3947	0·1900	9	−16	15	−27	0·3962	0·1873	0·3988	0·1870	26	−3
0·16	1·974	0·3559	0·2316	8	−20	13	−33	0·3572	0·2283	0·3596	0·2280	24	−3
0·18	1·905	0·3068	0·2739	6	−24	10	−40	0·3078	0·2699	0·3100	0·2696	22	−3
0·20	1·818	0·2500	0·3164	4	−28	7	−47	0·2507	0·3117	0·2526	0·3114	19	−3
0·25	1·555	+0·0876	0·4204	0	−39	0	−64	+0·0876	0·4140	+0·0887	0·4136	11	−4
0·30	1·281	−0·0852	0·5177	−5	−51	−8	−83	−0·0860	0·5094	−0·0858	0·5091	+2	−3
0·35	1·028	−0·2533	0·6053	−10	−62	−17	−102	−0·2550	0·5951	−0·2555	0·5949	−5	−2
0·40	0·810	−0·4080	0·6818	−14	−72	−24	−118	−0·4104	0·6700	−0·4116	0·6700	−12	0
0·45	0·630	−0·5447	0·7469	−17	−82	−30	−135	−0·5477	0·7334	−0·5495	0·7337	−18	+3
0·50	0·485	−0·6614	0·8004	−20	−90	−34	−148	−0·6648	0·7856	−0·6672	0·7863	−24	7

0·6	0·280	−0·8354	0·8755	−22	−100	−37	−165	−0·8391	0·8590	−0·8420	0·8603	−29	13
0·7	0·159	−0·9382	0·9137	−21	−103	−36	−170	−0·9418	0·8967	−0·9448	0·8985	−30	18
0·8	0·089	−0·9842	0·9224	−17	−98	−28	−162	−0·9870	0·9062	−0·9899	0·9084	−29	22
0·9	0·050	−0·9875	0·9087	−13	−85	−21	−142	−0·9896	0·8945	−0·9919	0·8968	−23	23
1·0	0·028	−0·9608	0·8787	−7	−67	−11	−113	−0·9619	0·8674	−0·9635	0·8696	−16	22
1·1	0·015$_5$	−0·9140	0·8375	−1	−45	−1	−77	−0·9141	0·8298	−0·9150	0·8317	−9	19
1·2	0·008$_5$	−0·8548	0·7891	+4	−22	+7	−38	−0·8541	0·7853	−0·8541	0·7867	0	14
1·4	0·002$_5$	−0·7203	0·6822	12	+26	20	+40	−0·7183	0·6862	−0·7169	0·6866	+14	+4
1·6	0·001	−0·5861	0·5743	17	68	28	110	−0·5833	0·5853	−0·5807	0·5846	26	−7
1·8		−0·4654	0·4744	19	99	31	161	−0·4623	0·4905	−0·4590	0·4888	33	−17
2·0		−0·3629	0·3860	19	119	31	196	−0·3598	0·4056	−0·3562	0·4032	36	−24
2·2		−0·2791	0·3105	17	128	29	212	−0·2762	0·3317	−0·2726	0·3289	36	−28
2·4		−0·2123	0·2474	15	130	26	216	−0·2097	0·2690	−0·2063	0·2659	34	−31
2·6		−0·1600	0·1955	13	126	22	211	−0·1578	0·2166	−0·1547	0·2134	31	−32
2·8		−0·1196	0·1535	10	117	17	197	−0·1179	0·1732	−0·1151	0·1701	28	−31
3·0		−0·0889	0·1198	9	106	15	180	−0·0874	0·1378	−0·0851	0·1349	23	−29
3·2		−0·0657	0·0931	7	94	12	160	−0·0645	0·1091	−0·0626	0·1065	19	−26
3·4		−0·0484	0·0720	6	82	10	140	−0·0474	0·0860	−0·0458	0·0837	16	−23
3·6		−0·0354	0·0555	4	70	7	120	−0·0347	0·0675	−0·0334	0·0655	13	−20
3·8		−0·0258	0·0426	3	60	5	103	−0·0253	0·0529	−0·0243	0·0511	10	−18
4·0		−0·0188	0·0326	2$_5$	51	4	87	−0·0184	0·0413	−0·0176	0·0398	8	−15
4·5		−0·0084	0·0166	0$_5$	31	1	53	−0·0083	0·0219	−0·0078	0·0210	5	−9
5·0		−0·0037	0·0083	0$_5$	20	0$_5$	32	−0·0036$_5$	0·0115	−0·0034	0·0110	2$_5$	−5
5·5		−0·0016$_5$	0·0042		12		18	−0·0016$_5$	0·0060	−0·0015	0·0057	1$_5$	−3
6·0		−0·0007$_5$	0·0021		7		10$_5$	−0·0007$_5$	0·0031$_5$	−0·0006$_5$	0·0029$_5$	1	−2
6·5		−0·0003$_5$	0·0010$_5$		4		5$_5$	−0·0003$_5$	0·0016	−0·0003	0·0015	0$_5$	−1
7·0		−0·0001$_5$	0·0005		2$_5$		3	−0·0001$_5$	0·0008	−0·0001$_5$	0·0007$_5$		−0$_5$
7·5		−0·0000$_5$	0·0003		1		1	−0·0000$_5$	0·0004	−0·0000$_5$	0·0004		
8·0			0·0001$_5$		0$_5$		0$_5$		0·0002		0·0002		
8·5			0·0000$_5$				0$_5$		0·0001		0·0001		
9·0			0·0000$_5$						0·0000$_5$		0·0000$_5$		
				$\Delta\epsilon$	$\Delta\epsilon$	$\Delta\epsilon$	$\Delta\epsilon$					$\Delta'\epsilon$	$\Delta'\epsilon$
$\epsilon_{nl,nl}$	42·7	3·603	2·653$_5$	+30	−165	+50$_5$	−272	3·653$_5$	2·381$_5$	3·743	2·425	89$_5$	43$_5$

TABLE IV. NORMALIZED RADIAL WAVE FUNCTIONS FOR O^{+++}, O^{++}, O NEUTRAL, AND O^{-}

	O^{+++}			O^{++}					O neutral					O^{-}		
	^{2}P term, $\beta = 0$			^{2}P term, $\beta = -1/5$			^{1}S term, $\Delta\beta = 3/5$		^{2}P term, $\beta = -3/5$			$\Delta\beta = 3/5$		^{2}P term, $\beta = -4/5$		
	Table of P_N/r^{l+1} and $\Delta P_N/r^{l+1}$															
r	$P(1s)/r$	$P(2s)/r$	$P(2p)/r^2$	$P(1s)/r$	$P(2s)/r$	$P(2p)/r^2$	$\Delta P(2s)/r$	$\Delta P(2p)/r^2$	$P(1s)/r$	$P(2s)/r$	$P(2p)/r^2$	$\Delta P(2s)/r$	$\Delta P(2p)/r^2$	$P(1s)/r$	$P(2s)/r$	$P(2p)/r^2$
0·00	43·24	11·33	19·81	43·20	10·74	18·01	6	−39	43·16	9·77$_5$	14·63	7	−15	43·15	9·51	13·12
0·01	39·92	10·45	19·04	39·89	9·91	17·31	5$_5$	−38	39·85	9·02	14·06	6$_5$	−15	39·84	8·77$_5$	12·61
0·02	36·86	9·63	18·30	36·83	9·13$_5$	16·64	5	−36	36·80	8·31$_5$	13·52	6	−14	36·79	8·09	12·12
0·03	34·05	8·87	17·60	34·02	8·41	16·01	4$_5$	−35	33·99	7·65$_5$	13·00	5$_5$	−14	33·98	7·45	11·66

Table of P_N and ΔP_N

	$P(1s)$	$P(2s)$	$P(2p)$	$P(1s)$	$P(2s)$	$P(2p)$	$\Delta P(2s)$	$\Delta P(2p)$	$P(1s)$	$P(2s)$	$P(2p)$	$\Delta P(2s)$	$\Delta P(2p)$	$P(1s)$	$P(2s)$	$P(2p)$
0·00	0	0	0	0	0	0			0	0	0			0	0	0
0·01	0·399	0·104$_5$	0·002	0·399	0·099	0·001$_5$	0$_5$		0·398$_5$	0·090	0·001$_5$	1		0·398$_5$	0·088	0·001
0·02	0·737	0·192$_5$	0·007$_5$	0·737	0·182$_5$	0·006$_5$	1		0·736	0·166	0·005$_5$	1$_5$		0·736	0·162	0·005
0·03	1·021	0·266	0·016	1·020	0·252	0·014$_5$	1$_5$		1·020	0·230	0·011$_5$	1$_5$		1·020	0·223	0·010$_5$
0·04	1·258	0·326	0·027	1·257	0·309	0·024$_5$	2	− 0$_5$	1·256	0·282	0·020	2		1·256	0·274	0·018
0·06	1·612	0·411	0·056$_5$	1·610	0·390	0·051$_5$	2$_5$	− 1	1·609	0·355	0·042	2$_5$	− 0$_5$	1·609	0·346	0·037$_5$
0·08	1·837	0·458	0·093	1·835	0·435	0·084$_5$	2$_5$	− 1$_5$	1·833	0·396	0·069	2$_5$	− 1	1·833	0·385	0·061$_5$
0·10	1·965	0·473	0·135	1·963	0·449	0·123	3	− 2$_5$	1·961	0·410	0·100	3	− 1$_5$	1·960	0·399	0·090
0·12	2·018	0·464	0·181	2·016	0·441	0·165	3	− 3$_5$	2·015	0·403	0·134	2$_5$	− 1$_5$	2·014	0·392	0·120
0·14	2·018	0·435	0·230	2·016	0·414	0·209	2$_5$	− 4$_5$	2·015	0·379	0·170	2$_5$	− 2	2·014	0·369	0·153
0·16	1·977	0·391	0·280	1·975	0·373	0·255	2$_5$	− 6	1·974	0·342	0·208	2$_5$	− 2$_5$	1·974	0·333	0·186
0·18	1·908	0·335	0·331	1·906	0·321	0·301	2$_5$	− 7	1·905	0·295	0·246	2	− 3	1·905	0·287	0·220
0·20	1·819	0·270	0·381	1·818	0·260	0·348	2	− 8$_5$	1·818	0·241	0·284	1$_5$	− 3$_5$	1·818	0·235	0·254
0·25	1·555	+0·087	0·505	1·555	+0·088	0·462	1$_5$	−11$_5$	1·555	+0·086	0·377	+0$_5$	− 5	1·555	+0·084	0·339
0·30	1·280	−0·107	0·619	1·281	−0·095	0·567	+0$_5$	−14	1·281	−0·079	0·465	−1	− 6	1·281	−0·076	0·418
0·35	1·026	−0·295	0·720	1·027	−0·272	0·662	−0$_5$	−17$_5$	1·028	−0·240	0·544	−2	− 7$_5$	1·029	−0·232	0·489
0·40	0·807	−0·467	0·806	0·809	−0·435	0·743	−1	−20	0·811	−0·388	0·614	−3	− 9	0·811	−0·376	0·553
0·45	0·626	−0·618	0·876	0·628	−0·579	0·811	−1$_5$	−22	0·631	−0·519	0·674	−4	−10$_5$	0·631	−0·504	0·607
0·50	0·481	−0·745	0·931	0·483	−0·701	0·866	−2	−24	0·486	−0·632	0·724	−4$_5$	−12	0·486	−0·613	0·653

0·6	0·276	−0·928	0·999	0·278	−0·879	0·939	−2$_5$	−26	0·281	−0·800	0·797	−5	−13$_5$	0·282	−0·779	0·722
0·7	0·155	−1·027	1·019	0·157	−0·981	0·970	−2$_5$	−25$_5$	0·160	−0·902	0·839	−5	−14	0·161	−0·880	0·763
0·8	0·086	−1·058	1·002	0·088	−1·021	0·967	−2	−22$_5$	0·090	−0·951	0·855	−5	−14	0·091	−0·929	0·782
0·9	0·047	−1·041	0·959	0·049	−1·016	0·940	−1$_5$	−17$_5$	0·050$_5$	−0·960	0·852	−4	−13	0·051	−0·940	0·785
1·0	0·026	−0·990	0·899	0·027	−0·978	0·896	−1	−11$_5$	0·028$_5$	−0·941	0·835	−2$_5$	−12	0·028$_5$	−0·924	0·776
1·1	0·014	−0·919	0·828	0·015	−0·921	0·840	0	− 4$_5$	0·016	−0·902	0·808	−1$_5$	−10$_5$	0·016	−0·890	0·759
1·2	0·007$_5$	−0·837	0·752	0·008	−0·851	0·778	+0$_5$	+ 2$_5$	0·009	−0·851	0·774	0	− 7$_5$	0·009	−0·843	0·735
1·4	0·002	−0·664	0·600	0·002$_5$	−0·697	0·648	1	14	0·003	−0·732	0·696	+2	− 3	0·003	−0·734	0·678
1·6	0·000$_5$	−0·505	0·463	0·000$_5$	−0·549	0·523	1$_5$	23$_5$	0·001	−0·610	0·613	3$_5$	+ 2	0·001	−0·621	0·616
1·8		−0·372	0·348		−0·421	0·413	1$_5$	29$_5$		−0·499	0·533	4$_5$	6$_5$		−0·517	0·555
2·0		−0·268	0·257		−0·316	0·320	1$_5$	32		−0·401	0·459	5	10$_5$		−0·424	0·497
2·2		−0·189	0·186		−0·233	0·244	1	32$_5$		−0·319	0·391	4$_5$	13$_5$		−0·346	0·444
2·4		−0·132	0·133		−0·170	0·185	1	30		−0·252	0·332	4$_5$	15$_5$		−0·281	0·396
2·6		−0·091	0·094		−0·123	0·138	1	27		−0·198	0·280	4	17		−0·227	0·352
2·8		−0·061	0·066		−0·088	0·102	0$_5$	24		−0·154	0·236	3$_5$	17$_5$		−0·183	0·314
3·0		−0·041	0·046		−0·062	0·075$_5$	0$_5$	20$_5$		−0·120	0·198	3	17$_5$		−0·147	0·279
3·2		−0·028	0·031$_5$		−0·044	0·055	0$_5$	17$_5$		−0·093	0·165	2$_5$	17$_5$		−0·118	0·249
3·4		−0·018	0·021$_5$		−0·031	0·040	0$_5$	14$_5$		−0·071	0·138	2	17		−0·095	0·222
3·6		−0·012	0·014$_5$		−0·021$_5$	0·029	0$_5$	11		−0·055	0·115	1$_5$	16		−0·077	0·198
3·8		−0·008	0·010		−0·015	0·021$_5$		8$_5$		−0·042	0·095	1	15		−0·062	0·177
4·0		−0·005$_5$	0·007		−0·010	0·015$_5$		7		−0·032$_5$	0·079	1	13$_5$		−0·049$_5$	0·158
4·5		−0·002	0·002$_5$		−0·004	0·007		3		−0·016$_5$	0·049	0$_5$	11		−0·028$_5$	0·119
5·0		−0·000$_5$	0·001		−0·001$_5$	0·003		2		−0·008$_5$	0·030	0$_5$	8$_5$		−0·016$_5$	0·090
5·5			0·000$_5$		−0·000$_5$	0·001		1		−0·004$_5$	0·018$_5$	0$_5$	6$_5$		−0·009$_5$	0·068$_5$
6·0						0·000$_5$		0$_5$		−0·002$_5$	0·011		5		−0·005$_5$	0·052
6·5								0$_5$		−0·001	0·007		3$_5$		−0·003	0·039$_5$
7·0										−0·000$_5$	0·004		2$_5$		−0·001$_5$	0·030$_5$
8											0·001$_5$		1$_5$		−0·000$_5$	0·018
9											0·000$_5$		1			0·010$_5$
10													0$_5$			0·006$_5$
11																0·004
12																0·002$_5$
13																0·001$_5$
14																0·001
15																0·000$_5$
							$\Delta\epsilon$	$\Delta\epsilon$				$\Delta\epsilon$	$\Delta\epsilon$			
$\epsilon_{nl, nl}$	46·7	6·49	5·72	44·6	4·96	4·09	+0·04	−0·48	41·5	2·48$_1$	1·26$_2$	+ ·06$_8$	−·15$_1$	40·4	1·624	0·259

6. RESULTS. ENERGIES

In calculating energy values, using the expression for the energy in which the coefficients are given by Table II, we require the values of various F and G integrals, and the diagonal Lagrange parameters ϵ for the $(2s)$ and $(2p)$ wave functions. Values of these integrals and parameters, calculated from the wave functions discussed in § 5 are given in Table V, and the energy values calculated from them, with some other values for comparison, are given in Tables VI and VII.

TABLE V. OXYGEN. F AND G INTEGRALS AND ϵ PARAMETERS

	O^{+++}	O^{++}		O^{+}				O		O^{-}
						$(\mu=0)$	$(\mu=-0{\cdot}202)$			
	^2P	^3P	^1S	^4S	^2D	^2P	^2P	^3P	^1S	^2P
β	0	$-1/5$	$2/5$	$-3/5$	$-6/25$	0	0	$-3/5$	0	$-4/5$
$F_0(2s, 2s)$	0·920	0·876	0·878	0·8336	0·8356	0·8369	0·8401	0·797	0·802	0·771
$F_0(2s, 2p)$	0·954	0·898	0·884	0·8401	0·8348	0·8308	0·8340	0·773	0·766	0·705
$F_0(2p, 2p)$	1·004	0·930	0·897	0·8530	0·8398	0·8309	0·8333	0·754	0·736	0·651
$F_2(2p, 2p)$	0·473	0·434	0·413	0·3908	0·3828	0·3776	0·3793	0·336	0·325	0·278
$G_1(2s, 2p)$	0·579	0·548	0·540	0·5176	0·5120	0·5090	0·5109	0·472	0·465	0·421
$\epsilon_{2s,2s}$	$6{\cdot}48_5$	4·96	5·00	3·603	3·633	$3{\cdot}653_5$	3·743	$2{\cdot}48_1$	$2{\cdot}54_9$	1·625
$\epsilon_{2p,2p}$	5·72	4·09	3·61	$2{\cdot}653_5$	$2{\cdot}488_5$	$2{\cdot}381_5$	2·425	$1{\cdot}26_2$	$1{\cdot}10_9$	0·259

We will consider the results for O^+ first, as this is the ion for which full calculations, including the effect of superposition of configurations on the radial wave functions, were carried out, and also because for this ion the calculations were carried to a greater numerical accuracy. Four decimals are given in the values of the F and G integrals, but as in the calculation of E some of these integrals occur with a coefficient 6, the fourth decimal has no significance in the values of E, which are given to three decimals, of which the last is not reliable to a unit.

TABLE VI. O^+ ENERGIES

	Calculated total energy of $(2s)$ $(2p)$ shell					Observed $E(O^+)$
	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)	$-E(O^{++}, {}^3P)$
^4S, $\beta=-3/5$	$-15{\cdot}265$	$-15{\cdot}265$	$-15{\cdot}265$			$-1{\cdot}290$
^2D, $\beta=-6/25$	$-15{\cdot}126$	$-15{\cdot}126$	$-15{\cdot}126$			$-1{\cdot}167$
^2P, $\beta=0$	$-15{\cdot}031$	$-15{\cdot}073$	$-15{\cdot}077$			$-1{\cdot}105$
$^2D-{}^4S$	0·139	0·139	0·139	0·129	0·129	0·123
$^2P-{}^2D$	0·095	0·053	0·049	0·087	0·046	0·062
$^2P-{}^4S$	0·234	0·192	0·188	0·216	0·175	0·185
$\dfrac{^2P-{}^2D}{^2D-{}^4S}$	0·68	0·38	0·35	0·67	0·35	0·50

Methods of calculation

(*a*) Including exchange but not superposition of configurations, either in calculation of radial wave functions or in energy formula.

(*b*) Wave functions calculated with exchange, superposition of configurations included in energy formula *only*.

(*c*) Exchange and superposition of configurations included both in calculation of radial wave functions and in energy formula.

(*d*), (*e*) Corresponding to (*a*), (*b*) but with wave functions calculated without exchange.

Total energy values E for the $(2s)$ $(2p)$ shell, calculated in three different ways, are given in Table VI. Those in column (*c*) are to be regarded as the most accurate, as both exchange and superposition of configurations have been included in the calculation both of the radial wave functions and of the energy from those wave functions. The energy values in columns (*a*) and (*b*) have been calculated from the wave functions obtained by the solution of Fock's equations with exchange but without the superposition of configurations, which has also been omitted in the energy formula in obtaining the results in column (*a*), but included, in the energy formula *only*, in obtaining the results in column (*b*).

The inclusion of superposition of configurations in the calculation of the energy values in column (*b*), and in the corresponding energy values for the other states of ionization which will be considered later, requires the solution of the equation

$$(E_A - E)\,(E_B - E) = (E_{AB})^2 \tag{10}$$

(see Hartree and Swirles 1937, equation (4)). An approximation to the root near E_A is

$$E_A - (E_{AB})^2/(E_B - E_A) \tag{11}$$

(Hartree and Swirles 1937, formula (6)), but it is easy to find the root more accurately by writing (10) in the form

$$E = E_A - (E_{AB})^2/[(E_B - E_A) + (E_A - E)], \tag{12}$$

and using an iterative method, which converges very rapidly for the values of $E_B - E_A$ and E_{AB} concerned. An expression for $E_B - E_A$, convenient for use in this context, is given by putting $\mu = 0$ in the column headed $E_B - E_A$ in Table II. Since $E_A - E$ is positive, (12) shows that the use of the first approximation (11) gives an overestimate of $E - E_A$; the degree of this overestimate, in the case of O^+ ^2P, is ·002 which is just appreciable to the accuracy of the results in Table VI.

Comparison of columns (*b*) and (*c*) shows that the full integration of the extended Fock equations, including the effect of the superposition of configurations as well as the effect of exchange, gives a final energy lower by only 0·004, or 1 part in 4000, than the value obtained by neglecting the difference between the radial wave functions calculated with and without the terms expressing the effect of superposition of configurations. The smallness of this improvement in the energy values is, of course, related to the minimal property of the wave functions calculated from the integration of the extended Fock equations, and to the small differences between the wave functions calculated with and without the superposition of configurations. As pointed out in § 5, those differences are less than 1 in 200 of the maximum $|P|$, and it is not surprising that the relative energy difference is of the order of the square of this relative difference in the wave functions. As already mentioned, this improvement in the energy values was regarded as not sufficient to justify the calculation of wave functions with superposition of configurations for the other states of ionization. At the same time, the very close agreement between the energy values for the ^2P state in columns (*b*) and (*c*) justifies the use of (12) as giving an adequate approximation to the contribution to the energy from the effect of the superposition of the higher configuration considered, and a similar method has been used for estimating these contributions for the other states of ionization.

In columns (*d*) and (*e*) of Table VI are given intermultiplet separations calculated using the wave functions without exchange and (*d*) without, (*e*) with, the inclusion of superposition of configurations in the energy calculations. They are quoted from Hartree and Black (1933) and Hartree and Swirles (1937) respectively.*

The last column of the table gives the observed energy values reckoned from the normal state of O^{++}. Accurate total energy values for the $(2s)$ $(2p)$ shell cannot be given on account of the lack of a well determined ionization energy for O^{+++}.†

Comparison of the observed intermultiplet separations with those calculated shows that whereas for the original results of Hartree and Black (column (*d*)) the calculated separation between the lower two terms, ${}^2D-{}^4S$, is about right and the upper term (${}^2P$) a good deal too high, and, as shown by column (*e*) and noted by Hartree and Swirles, the effect of the superposition of configurations was to over-correct the upper term, now the extreme term separation ${}^2P-{}^4S$ is about right, and the intermediate ${}^2D$ is relatively too high.

As far as the ratio of the intermultiplet separations is concerned, the last line of the table shows that the final result of the present calculations (column (*c*)) is very much the same as that obtained by the rougher approximation of Hartree and Swirles (column (*e*)). The simple Slater theory (1929) gives a value 2/3 for the ratio $({}^2P-{}^2D)/({}^2D-{}^4S)$, the observed value for O^+ is 0·51, whereas the best calculated value is 0·37. Thus the effect of superposition of configurations, as far as we have taken it, over-corrects the value given by the simple Slater theory by a factor of nearly 2.

The residual differences between the calculated intermultiplet separations in column (*c*) and the observed separations in column (*e*) are presumably due to the combined effect of the superposition of other configurations such as $(2s)$ $(2p)^3$ $(3s)$ and $(2s)^2$ $(2p)^2$ $(3p)$, which together give a number of terms of the same parity, L, and S as the normal configuration, and of the dependence of the wave function for the whole atom on the mutual distances r_{ij} between the individual electrons. It does not seem possible to take either of these into account without a great deal of additional elaboration both in the algebraical and in the numerical work.

Table VII gives values for the total energy of the $(2s)$ $(2p)$ group calculated from wave functions obtained by the solution of Fock's equations including exchange only, and (*a*) without, (*b*) with, the inclusion of the effect of superposition of configurations in the energy formula. The results (*b*), where they differ from the corresponding results (*a*), were calculated from (12).

Except for O^+ the third decimal in the calculated results is hardly significant. For

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* In these papers, the ionization energy of the ${}^4S$ term is given as 1·301, and the ${}^2D-{}^4S$ separation correspondingly as 0·134. We are indebted to Dr C. W. Ufford for pointing out the error.

† See Bacher and Goudsmit 1932, Table O IV, p. 343.

O^{+++} and O^{++} the third decimal in the ϵ values is not established by the three decimal calculations of the radial wave functions, and for neutral O and O^- some of the *F* integrals, which are only accurate to three decimals, are multiplied by 8 or 10. A third decimal has been retained throughout Table VII, however, as it is significant in some of the differences between entries in the table, for example in the differences between columns (*b*) and (*c*).

TABLE VII. TOTAL AND IONIZATION ENERGIES

		Total energies of (2*s*) (2*p*) shell		Ionization energies			
		(*a*)	(*b*)	(*a*)	(*b*)	(*c*)	Observed
O^{+++}	^2P	−11·980	−12·036				
O^{++}	^3P	−13·996	−14·021	2·016$_{109}$	1·985$_{109}$	1·988$_{99}$	2·025$_{91}$
	^1D	−13·887	−13·912	1·907$_{163}$	1·886$_{105}$	1·889$_{148}$	1·934$_{105}$
	^1S	−13·724	−13·837	1·744	1·781	1·741	1·829
O^+	^4S	−15·265	−15·265	1·269$_{139}$	1·244$_{139}$	1·258$_{129}$	1·290$_{123}$
	^2D	−15·126	−15·126	1·130$_{95}$	1·105$_{53}$	1·129$_{87}$	1·167$_{62}$
	^2P	−15·031	−15·073	1·035	1·052	1·042	1·105
O	^3P	−15·679	−15·679	0·414$_{76}$	0·414$_{76}$	0·416$_{73}$	0·500$_{72}$
	^1D	−15·603	−15·603	0·338$_{113}$	0·338$_{86}$	0·343$_{109}$	0·428$_{81}$
	^1S	−15·490	−15·517	0·225	0·252	0·234	0·347
O^-	^2P	−15·698	−15·698	0·019	0·019		0·08

(*a*) Calculated including exchange but not superposition of configurations.

(*b*) Calculated including exchange in evaluation of wave functions and energies, and superposition of configurations in evaluation of energies *only*.

(*c*) Calculated from wave functions evaluated without exchange (see Hartree and Black 1933, Table V).

Values of the ionization energies corresponding to the various values of the total energy are also given, and, for comparison, those originally calculated by Hartree and Black (column (*c*)) and the observed values.‡ It will be noted that although (presumably) the better wave functions give a lower value of the *total* energy, several of the calculated *ionization* energies in column (*b*) show rather worse agreement with the observed values than those in column (*c*). But where the normal configuration gives three terms, the uppermost is always brought into better agreement with the observed term.

The result for O^- shows that, to the accuracy of these calculations, O^- is not only a possible structure but is energetically stable. Further, the differences between the calculated and observed ionization energies for the other states of ionization leave little doubt that a more accurate calculation, if it could be carried out, would give a higher positive value of the ionization energy of O^- in general agreement with Lozier's (1934) experimental value, though a rather higher value, perhaps between 0·12 and 0·15, might be expected.

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‡ The value for O^- is that quoted by Massey (1938, chap. 1, § 4·21) from the work of Lozier (1934).

The intermultiplet separations for neutral oxygen in column (*b*) show a fairly good agreement with the observed values. For the other states of ionization the agreement is better than that shown by those in column (*c*) but not to any very marked extent, so that the present calculations have not provided a complete quantitative account of the deviations from Slater's values for the ratios of these separations.

Another point in this connexion, which remains unexplained, is the close agreement of the ratios of the intermultiplet separations with Slater's values in the case of sulphur. The $(3s)$ $(3p)$ shell of sulphur, in each state of ionization, would be expected to have very much the same properties, qualitatively and roughly quantitatively, as the $(2s)$ $(2p)$ shell in the corresponding state of ionization of oxygen, and it seems surprising that the effects of superposition of configuration should not be comparable with those in oxygen.

7. Summary

In the simplest approximation to the structure of a many electron atom, each term is regarded as arising from a single configuration of one-electron wave functions. When, to this approximation, two or more configurations give terms of the same parity, L, and S, not greatly different in energy, an appreciably better approximation may be obtained by taking, as the wave function for each term, a linear combination of the wave functions for the various configurations. The term "superposition of configurations" is used to denote the use of such linear combinations.

The effect of this superposition of configurations can be taken into account in the calculation of energy values only, or in the determination of the one-electron wave functions also. The latter requires an extension of Fock's equations, and in the present paper this extension is worked out for the superposition of the $(np)^{q+2}$ configuration on the normal $(ns)^2 (np)^q$ configuration of atoms with an incomplete 8-shell. The solution of these equations involves a set of calculations, each of which is similar to a complete solution of Fock's equations, for a set of trial values of a parameter expressing the relative amplitudes of the wave functions for the two configurations.

For O^+, the normal configuration $(2s)^2 (2p)^3$ gives ^4S, ^2D, and ^2P terms, of which only the highest (^2P) is subject to the superposition of the $(2p)^5$ configuration. A full solution of the extended equations has been worked out for this case. The effect of superposition of configurations on the radial wave functions is found to be small, less than 1 in 200 of their greatest values, and the consequent effect on the total energy of the $(2s)$ $(2p)$ shell very small, about 1 in 4000. This small improvement of the energy value did not seem to justify the solution of the extended equation for other states of ionization, and for these solutions of the ordinaryFock equations only have been evaluated, though superposition of configurations has been taken into account in calculating energy values.

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