In conclusion the author wishes to acknowledge his indebtedness to Professor J. A. Bearden, under whose direction this work was done, for his continued interest and many valuable suggestions, to Professor James Franck for the original suggestion of the problem, and to Dr. D. R. Inglis for advice in the preparation of this manuscript.

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A Method for Improved Calculation of Energies of Two-Electron Configurations from Hartree Functions

Application to $2p^2$ Terms in O III

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A generalization of the method of the self-consistent field for two-electron configurations previously given by the author has now been simplified and improved in two ways. Firstly, it is now assumed that the radial functions are identical with the Hartree functions (or with simpler approximations to these), so that a considerable saving in labor results. Secondly, the core electrons are taken account of more accurately than in the original method. The final results are in general only valid if the valence electrons are equivalent or if the difference in their azimuthal quantum numbers exceeds two; they do not involve a great deal of computation once the Hartree functions are known. Numerical calculations have been made for the normal state of helium (as a test of the method) and for the $2p^2$ terms of O III. The improvement obtained with the present method, while not great, is significant; in particular, the separation ratio for the O III terms is markedly improved.

1. INTRODUCTION

In a recent paper,[1] a generalization of the method of the self-consistent field (s.c.f.) was given, applicable to the case of two-electron configurations in Russell-Saunders coupling, the core electrons being taken into account through a possible screening of the Coulomb field acting on the valence electrons.[2]

The generalization consists essentially in assuming for the wave function the form

$$\psi=\psi_0\cdot X(x), \qquad (1)$$

where ψ_0 is a function of the form usually assumed in the s.c.f. method when the correct symmetry properties of the wave function are taken into account, and contains the two radial functions, while $X(x)$ is an adjustable function of $x=\cos(\mathbf{r}_1, \mathbf{r}_2)$. The variational method is then applied, and yields differential equations for the two radial functions analogous to those of the s.c.f., together with a third equation for the function X. The assumption (1) is perhaps the most general one that can be made without introducing complications which would make the calculations intractable in many cases.

As developed in I, however, the method has two disadvantages. In the first place, the labor involved in carrying through numerical calculations would be considerable, particularly when exchange terms are taken into account. Secondly—and this is the more serious objection—the wave function (1) does not automatically satisfy the condition of being orthogonal to the wave functions of lower levels which have the same symmetry characteristics.[3] Since the effect of the

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[1] A. F. Stevenson, Proc. Roy. Soc. **A160**, 588 (1937), referred to hereafter as I. The following correction may be noted: in Eq. (2), the sign in front of each of the square brackets should be $-$ instead of $+$. What is really a special case of the method had been previously used by Breit, Phys. Rev. **36**, 383 (1930).

[2] The extension to the case where the core electrons are taken more accurately into account was also briefly indicated, but was not worked through in any detail.

[3] The orthogonality condition is automatically satisfied for levels with different symmetry characteristics on account of the transformation properties of the wave functions. The same nonorthogonality situation may arise in the s.c.f. method (with any number of electrons) if there are lower levels for which the electrons have the same azimuthal quantum numbers as in the configuration considered, since the corresponding radial functions will

core electrons is replaced by a given central field acting on the valence electrons, there will often be a number of lower "virtual" levels of the same symmetry characteristics in which the valence electrons are in lower orbits, even though such configurations would violate the Pauli principle if the core electrons were more properly taken into account. Consequently, the method would lead to very misleading results in some cases.

As regards the first disadvantage, a considerable simplification results if the radial functions are not regarded as being arbitrary as in I, but are assumed to be identical with the s.c.f. functions,[4] and it is probable that the resulting loss in accuracy is slight. Such a simplification is made in the present paper. Further, an extension of the method is given which takes proper account of the core electrons, so that the orthogonality difficulty mentioned above does not arise—at least so long as there are no lower states, with the same symmetry characteristics, of the atom as a whole.

It will be found that if the valence electrons are equivalent (the most important case), or if the difference in their azimuthal quantum numbers exceeds two, the final form of the results is comparatively simple, and requires (in addition to some straightforward algebraical work) only the calculation of certain integrals involving the s.c.f. radial functions, so that, when once these functions are known, the labor required is not very great. The method may thus be regarded as one for making more accurate calculations of energies from the s.c.f. functions than are provided by the usual method.

Numerical calculations have been carried through for the normal state of helium (as a try-out of the method), and for the $2p^2$ terms of O III, for which the s.c.f. (without exchange) has been worked out by Hartree and Black.[5] While the improvement obtained over the s.c.f. result is not great, it is nevertheless significant, and appears to be roughly of the same order of magnitude as the improvement obtained by including exchange terms in the s.c.f. equations.

2. The "Two-Electron" Method

We shall first work out the case where the same assumption is made as in I regarding the core electrons—i.e., we take them into account only by a modification of the central field—but where the radial functions are regarded as being already known. We may refer to this as the "two-electron" method. Although, as discussed above, this may lead to erroneous results, it may nevertheless be valid in certain cases, and the results form, as we shall see, a check on the more complicated calculations of Section 4.

We denote the configuration quantum numbers of the two electrons by (n_1l_1) and (n_2l_2) and their radial functions by $P_1(r)$, $P_2(r)$.[6] We make the assumption (1), where ψ_0 takes proper account of exchange, etc. The energy, to be minimized, is

$$E=\int\psi^*H\psi d\tau\Big/\int|\psi|^2d\tau.$$

The method of handling such integrals (coordinate system to be adopted, etc.) has been fully discussed in I, and we shall here give only the final result. Although the general case can be handled without difficulty, the results simplify considerably if we assume *either* (1) $l_1=l_2$, *or* (2) $|l_1-l_2|>2$ and $X=$linear function of x. These include the cases considered in the more complete theory of Section 4.

We then find, measuring the energy in atomic units (instead of rydbergs as in I),

$$E=C+\int XL(X)dx\Big/\int f(x)X^2dx, \qquad (2)$$

where

$$L(X)=-A\frac{d}{dx}\left[(1-x^2)f(x)\frac{dX}{dx}\right]+\phi(x)X. \qquad (3)$$

The integrals with respect to x are taken, in (2) and throughout this section, from -1 to $+1$. C is

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not be accurately orthogonal on account of the difference in central fields. For instance, some of the calculations of Wilson and Lindsay on doubly excited states of helium (Phys. Rev. **47**, 681; **48**, 536 (1935)) would seem to be subject to doubt for this reason.

[4] It is immaterial for our purpose whether these functions are obtained by a strict application of the s.c.f. method (with or without exchange), or in some simpler manner. Naturally, the more accurate the functions are, the better.

[5] D. R. Hartree and M. M. Black, Proc. Roy. Soc. **A139**, 311 (1933). The coupling for this case appears to be sufficiently near to Russell-Saunders, though the interva rule is not very well satisfied for the ^3P multiplet.

[6] We follow Hartree in writing $P(r)/r$ for the radial part of the wave function. We suppose these functions normalized.

a constant depending only on the radial functions, and need not be given explicitly, while

$$A=(1/2)\int_0^\infty (P_1^2+P_2^2)/r^2dr. \qquad (4)$$

Further,

$$\phi(x)=f(x)\sum_{n=0}^{\infty} F_nP_n(x)+g(x)\sum_{n=0}^{\infty} G_nP_n(x), \qquad (5)$$

where F_n, G_n are Slater's integrals,[7]

$$F_n=\int\int_0^\infty [P_1(r_1)P_2(r_2)]^2 r_<^n/r_>^{n+1}dr_1dr_2,$$

$$G_n=\int\int_0^\infty P_1(r_1)P_2(r_2)P_2(r_1) \times P_1(r_2)r_<^n/r_>^{n+1}dr_1dr_2, \qquad (6)$$

and $f(x)$, $g(x)$ are certain polynomials (of which $f(x)$ is always even, while $g(x)$ can be put equal to zero for equivalent electrons), whose explicit form need not be given for the moment.

Now if X be put equal to a constant, the energy must reduce to the s.c.f. energy E_0. Hence, from (2),

$$E_0=C+E', \quad E'=\int\phi(x)dx\Big/\int f(x)dx. \qquad (7)$$

E' gives the part of E_0 containing the Coulomb and exchange integrals F, G of (6). Thus from (2) and (7) we have $E=E_0+\Delta E$, where ΔE, the correction to the s.c.f. energy, is given by

$$\Delta E=\int XL(X)dx\Big/\int f(x)X^2dx-E'. \qquad (8)$$

The polynomials $f(x)$, $g(x)$ may be found most simply as follows: let

$$f(x)=\sum_n f_nP_n(x), \quad g(x)=\sum_n g_nP_n(x), \qquad (9)$$

where the f's and g's are constants, of which we may arbitrarily put $f_0=1$ since $f(x)$ is undetermined to a constant factor. Then from (7), (5), (9),

$$E'=\sum_n (f_nF_n+g_nG_n)/(2n+1). \qquad (10)$$

Comparing (10) with the expression for E' in terms of the F's and G's as found by the usual methods,[8] we then immediately have the values of the constants f_n, g_n, and hence, from (9), the polynomials $f(x)$, $g(x)$.

On varying the function X and minimizing E, we see from (2) that X (provided it is not restricted to be a linear function) satisfies the differential equation

$$[L-\lambda f(x)]X=0,$$

where $\lambda=\Delta E+E'$. However, it is not necessary to actually solve this equation, for X will be a slowly-varying function which will be well approximated by a polynomial, say

$$X=\sum_i a_ix^i \qquad (11)$$

and we may then use the Ritz method. This leads to the determinantal equation

$$|L_{ij}-\lambda f_{ij}|=0 \qquad (12)$$

for λ, where

$$L_{ij}=\int x^iL(x^j)dx, \quad f_{ij}=\int x^{i+j}f(x)dx.$$

Quite a small number of terms will suffice in (11), and it then becomes necessary to calculate only a few of the F, G integrals of (6). In fact, we shall confine ourselves later on to the case where X is a *linear* function of x. It can then be shown that (12) becomes (in a notation used for subsequent convenience)

$$\begin{vmatrix} -\Delta E & H_{01} \\ H_{01} & H_{11}'-N_{11}\Delta E \end{vmatrix}=0, \qquad (13)$$

where

$$H_{01}=\int x\phi(x)dx/f(x)dx,$$

$$N_{11}=\int x^2f(x)dx\Big/\int f(x)dx, \qquad (14)$$

$$H_{11}'=A\int(1-x^2)f(x)dr\Big/\int f(x)dx.$$

In H_{11}' certain comparatively small terms depending on the F's and G's have been neglected;

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[7] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge, 1935), 177. These integrals are there denoted by F^n, G^n. We shall refer to this book as "C.S."

[8] C.S., Chapter 7.

this is justifiable since ΔE is small, so that it is only necessary to have an approximate value of H_{11}'. If ΔE^2 is neglected, (13) gives simply

$$\Delta E = -H_{01}^2/H_{11}'. \tag{15}$$

3. Application to Normal State of Helium

As a test of the efficacy of the method of the preceding section, we consider the simplest possible case, namely the normal state of helium, for which (8) or (12) are valid without restricting X to be a linear function. It will not, of course, be expected that results comparable in accuracy with those of Hylleraas in his well-known work on helium will be reached. We have in this case

$$f(x)=1, \quad \phi(x)=\sum_{n=0}^{\infty} F_n P_n(x), \quad E'=F_0.$$

Using (12), and confining ourselves to three terms of (11), we find

$$L_{00}=2F_0, \quad L_{01}=\frac{2}{3}F_1, \quad L_{02}=\frac{2}{3}F_0+\frac{4}{15}F_2,$$

$$L_{11}=\frac{4}{3}A+L_{02}, \quad L_{12}=\frac{2}{5}F_1+\frac{4}{35}F_3,$$

$$L_{22}=\frac{16}{15}A+\frac{2}{3}F_0+\frac{8}{35}F_2+\frac{16}{315}F_4,$$

$$f_{00}=2, \quad f_{01}=f_{12}=0, \quad f_{11}=f_{02}=\frac{2}{3}, \quad f_{22}=\frac{2}{5}.$$

Since we are here only interested in the order of magnitude of the results, we simplify the calculation of the radial integrals by using the approximate (un-normalized) function

$$P(r)=re^{-(27/16)r}$$

rather than the accurate s.c.f. function; the results will not differ much. We then find

$$A=8/27, \quad F_0=5/8, \quad F_1=3/8,$$
$$F_2=0.2605, \quad F_3=0.1973, \quad F_4=0.1580.$$

Application of (12) then gives (atomic units):

with 2-term function for X: $\Delta E=-0.0115$,
with 3-term function for X: $\Delta E=-0.0125$.

Taking the 3-term value for ΔE, we then have the following values for the ionization potential of helium in rydbergs:

s.c.f. = 1.723, corrected = 1.748,
experimental = 1.807.

The correction thus accounts for rather less than one-third of the discrepancy between the s.c.f. and experimental values. It is seen that very little improvement is obtained by taking a 3-term rather than a 2-term function for X.

4. The Generalized Method

We now generalize the method of Section 2 so as to take account more properly of the core electrons, but confine ourselves to the case where X is a linear function of x. We denote the valence electrons by 1, 2 and the core electrons by $3, \cdots, N$, and use the usual notation for quantum numbers, etc. In the "two-electron" method, our assumption (1) is now equivalent to

$$\psi=\psi_0+c\psi_1, \tag{16}$$

where $\psi_0(1, 2)$ is the s.c.f. function (more strictly, one of a *set* of such functions belonging to the given level), c is an adjustable constant, and

$$\psi_1(1, 2)=\cos(\mathbf{r}_1, \mathbf{r}_2)\psi_0(1, 2).$$

Let now U_0 denote the s.c.f. function for the whole atom. Then we know that U_0 is a linear combination of determinantal wave functions u_0 of the form

$$u_0=\frac{1}{N!}\begin{vmatrix} u(\alpha_1, 1) & \cdots & u(\alpha_N, 1) \\ \cdot & \cdot\ \cdot\ \cdot & \cdot \\ u(\alpha_1, N) & \cdots & u(\alpha_N, N) \end{vmatrix} \tag{17}$$

in which α_1 stands for the four quantum numbers $(n_1 l_1 m_1 s_1)$ etc., and where, in the usual notation

$$u(\alpha, \mathbf{r})=\frac{1}{r}P_{nl}(r)Y_{lm}(\theta, \phi)\delta(s, \sigma). \tag{18}$$

(s, σ denote, respectively, spin quantum number and spin variable, Y_{lm} a surface harmonic; we suppose all functions normalized.)

Consider now the function

$$u_1=u_1'+u_1''+u_1''', \tag{19}$$

where

$$\begin{aligned}
u_1'&=\frac{1}{N!}\begin{vmatrix} u(\alpha_1,1)\cos\theta_1 & u(\alpha_2,1)\cos\theta_1 & u(\alpha_3,1) & \cdots & u(\alpha_N,1)\\ \cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot & \cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot & \cdot\;\cdot\;\cdot & \cdot & \cdot\;\cdot\;\cdot\\ u(\alpha_1,N)\cos\theta_N & u(\alpha_2,N)\cos\theta_N & u(\alpha_3,N) & \cdots & u(\alpha_N,N)\end{vmatrix}\\
u_1''&=\frac{1}{N!}\begin{vmatrix} u(\alpha_1,1)\sin\theta_1\cos\phi_1 & u(\alpha_2,1)\sin\theta_1\cos\phi_1 & u(\alpha_3,1) & \cdots & u(\alpha_N,1)\\ \cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot & \cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot & \cdot\;\cdot\;\cdot & \cdot & \cdot\;\cdot\;\cdot\\ u(\alpha_1,N)\sin\theta_N\cos\phi_N & u(\alpha_2,N)\sin\theta_N\cos\phi_N & u(\alpha_3,N) & \cdots & u(\alpha_N,N)\end{vmatrix}\\
u_1'''&=\frac{1}{N!}\begin{vmatrix} u(\alpha_1,1)\sin\theta_1\sin\phi_1 & u(\alpha_2,1)\sin\theta_1\sin\phi_1 & u(\alpha_3,1) & \cdots & u(\alpha_N,1)\\ \cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot & \cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot & \cdot\;\cdot\;\cdot & \cdot & \cdot\;\cdot\;\cdot\\ u(\alpha_1,N)\sin\theta_N\sin\phi_N & u(\alpha_2,N)\sin\theta_N\sin\phi_N & u(\alpha_3,N) & \cdots & u(\alpha_N,N)\end{vmatrix}
\end{aligned}\qquad(20)$$

and let U_1 denote the *same* linear combination of the functions u_1 of (19) that U_0 is of the functions u_0 of (17). Then a suitable assumption for the wave function is, analogously to (16),

$$\psi=U_0+cU_1. \qquad (16')$$

For, since

$$\cos(\mathbf{r}_1,\mathbf{r}_2)=\cos\theta_1\cos\theta_2+\sin\theta_1\cos\phi_1\times\sin\theta_2\cos\phi_2+\sin\theta_1\sin\phi_1\sin\theta_2\sin\phi_2,$$

we see that U_1 reduces to our previous ψ_1 if $N=2$. Further, if the determinants (20) be expanded by Laplace's rule from the first two columns, it can be seen that, when the proper linear combinations for the function U_1 are taken, the set U_1 transforms in the correct way under rotations and reflections. Also evidently U_1 is antisymmetrical in all electrons. Thus (16′), with (17), (19), (20), satisfies all requirements as to symmetry properties and is the required generalization.

Minimizing the energy with respect to c with (16′), we see that E is given by

$$\begin{vmatrix} H_{00}-EN_{00} & H_{01}\\ H_{01} & H_{11}-EN_{11}\end{vmatrix}=0, \qquad (21)$$

where

$$H_{ij}=\int U_i^*HU_jd\tau,\quad N_{ij}=\int U_i^*U_jd\tau.$$

To calculate H_{ij}, N_{ij} we need only find these matrix elements with respect to the functions u_0, u_1 of (17), (19), and then use the diagonal sum rule in the familiar way.[9] We shall therefore calculate

$$H_{ij}=\int u_i^*Hu_jd\tau,\quad N_{ij}=\int u_i^*u_jd\tau,$$

and understand that it is really linear combinations of such quantities which are implied. We now use the formulae[10]

$$\begin{aligned}
Y_{lm}\cos\theta&=aY_{l+1,\,m}+bY_{l-1,\,m}\\
Y_{lm}\sin\theta\cos\phi&=cY_{l+1,\,m}+dY_{l+1,\,m-1}\\
&\quad+eY_{l-1,\,m+1}+fY_{l-1,\,m-1}\\
Y_{lm}\sin\theta\sin\phi&=i(-cY_{l+1,\,m+1}+dY_{l+1,\,m-1}\\
&\quad-eY_{l-1,\,m+1}+fY_{l-1,\,m-1}),
\end{aligned}\qquad(22)$$

where

$$\begin{aligned}
a=a(l,m)&=\left[\frac{(l-m+1)(l+m+1)}{(2l+1)(2l+3)}\right]^{\frac{1}{2}},\\
b&=\left[\frac{l^2-m^2}{4l^2-1}\right]^{\frac{1}{2}},\\
c&=-\frac{1}{2}\left[\frac{(l+m+1)(l+m+2)}{(2l+1)(2l+3)}\right]^{\frac{1}{2}},\\
d&=\frac{1}{2}\left[\frac{(l-m+1)(l-m+2)}{(2l+1)(2l+3)}\right]^{\frac{1}{2}},\\
e&=\frac{1}{2}\left[\frac{(l-m)(l-m-1)}{4l^2-1}\right]^{\frac{1}{2}},\\
f&=-\frac{1}{2}\left[\frac{(l+m)(l+m-1)}{4l^2-1}\right]^{\frac{1}{2}}.
\end{aligned}\qquad(23)$$

It is then possible to express u_1 as a sum of 12 determinants containing one-electron functions of the type (17). To save space, we write (17),

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[9] See, e.g., C.S., 191 *et seq.* We use the term "diagonal sum rule" in a somewhat more general sense than usual, namely: if ϕ_1, ϕ_2, $\cdots$ and χ_1, χ_2, $\cdots$ are any two sets of the same number of functions, and if ϕ_1', ϕ_2', $\cdots$ and χ_1', χ_2', $\cdots$ are the sets obtained from these by the *same* unitary transformation, then

$$\Sigma_i\int\phi_i^*H\chi_id\tau=\Sigma_i\int\phi_i'^*H\chi_i'd\tau.$$

[10] These follow at once from C.S., 53, formula (21), on using $\cos\phi=(e^{i\phi}+e^{-i\phi})/2$ etc. A particular definition of Y_{lm} for negative m is implied.

with the help of (18), as follows:

$$u_0=(l_1,\, m_1;\, l_2,\, m_2),$$

that is, all four quantum numbers of the core electrons and the n, s quantum numbers of the valence electrons are regarded as being always equal to those in (17), and we only allow for the possibility of the l, m quantum numbers of the valence electrons varying. With this convention, and using (20), (22), (23) we can now write (19) in the form

$$u_1=\sum_{k=1}^{12}\gamma_k u_1^{(k)}, \tag{24}$$

where

$$\begin{aligned}
&\gamma_1=a_1a_2, &&\gamma_2=b_1b_2, &&\gamma_3=a_1b_2,\\
&\gamma_4=a_2b_1, &&\gamma_5=2c_1d_2, &&\gamma_6=2c_2d_1,\\
&\gamma_7=2c_1f_2, &&\gamma_8=2c_2f_1, &&\gamma_9=2d_1e_2,\\
&\gamma_{10}=2d_2e_1, &&\gamma_{11}=2e_1f_2, &&\gamma_{12}=2e_2f_1
\end{aligned} \tag{25}$$

$$(a_1=a(l_1,\, m_1)\text{ etc.})$$

and

$$\begin{aligned}
u_1^{(1)}&=(l_1+1,\, m_1;\, l_2+1,\, m_2),\\
u_1^{(2)}&=(l_1-1,\, m_1;\, l_2-1,\, m_2),\\
u_1^{(3)}&=(l_1+1,\, m_1;\, l_2-1,\, m_2),\\
u_1^{(4)}&=(l_1-1,\, m_1;\, l_2+1,\, m_2),\\
u_1^{(5)}&=(l_1+1,\, m_1+1;\, l_2+1,\, m_2-1),\\
u_1^{(6)}&=(l_1+1,\, m_1-1;\, l_2+1,\, m_2+1),\\
u_1^{(7)}&=(l_1+1,\, m_1+1;\, l_2-1,\, m_2-1),\\
u_1^{(8)}&=(l_1-1,\, m_1-1;\, l_2+1,\, m_2+1),\\
u_1^{(9)}&=(l_1+1,\, m_1-1;\, l_2-1,\, m_2+1),\\
u_1^{(10)}&=(l_1-1,\, m_1+1;\, l_2+1,\, m_2-1),\\
u_1^{(11)}&=(l_1-1,\, m_1+1;\, l_2-1,\, m_2-1),\\
u_1^{(12)}&=(l_1-1,\, m_1-1;\, l_2-1,\, m_2+1).
\end{aligned} \tag{26}$$

For clarity, we give the extended form of $u_1^{(1)}$ for instance: $u_1^{(1)}$ is the same as the function u_0 of (17), except that now

$$\begin{aligned}
u(\alpha_1,\, \mathbf{r})&=\frac{1}{r}P_{n_1l_1}(r)\,Y_{l_1+1,\, m_1}(\theta,\, \phi)\,\delta(s_1,\, \sigma),\\
u(\alpha_2,\, \mathbf{r})&=\frac{1}{r}P_{n_2l_2}(r)\,Y_{l_2+1,\, m_2}(\theta,\, \phi)\,\delta(s_2,\, \sigma).
\end{aligned} \tag{27}$$

Each of the $u_1^{(k)}$ is of the usual form of determinantal wave function; but for facility in calculating matrix elements, it is necessary that the one-electron functions of which the determinant is composed be mutually orthogonal. This is not so in general, the function $P_{n_1l_1}(r)$ in (27), for instance, not being orthogonal to the other radial functions which have azimuthal quantum number (l_1+1). However, we can, without altering the value of the determinant, add to $P_{n_1l_1}(r)$ and $P_{n_2l_2}(r)$ multiples of the radial functions of quantum numbers $l_1\pm1$, $l_2\pm1$ so that all the one-electron functions are mutually orthogonal (cf., for instance, Hartree and Black).[5] We shall suppose this done, and shall write P_{nl}^+, P_{nl}^- for the radial functions which have thus been made orthogonal to all other radial functions having azimuthal quantum numbers $l+1$, $l-1$ respectively, so that in (27), e.g., we would have $P_{n_1l_1}^+(r)$ instead of $P_{n_1l_1}(r)$. We must remember, however, that the functions P_{nl}^+, P_{nl}^- are not normalized.

For convenient calculation it is further necessary that the one-electron functions composing a given $u_1^{(k)}$ be either orthogonal or identical with those composing u_0 and the remaining $u_1^{(k)}$. An examination of (26) shows that this is always the case *either if the electrons are equivalent or if* $|l_1-l_2|>2$. Since the calculations would be very complicated unless the orthogonality conditions are satisfied, we shall restrict ourselves to these two cases.[11] If $|l_1-l_2|>2$, the functions u_0, $u_1^{(1)}$, $\cdots$, $u_1^{(12)}$ are mutually orthogonal; but in the equivalent electron case, we must note that:[12]

(a) if $s_1=s_2$, $m_1=m_2+1$, then

$$u_1^{(1)}=-u_1^{(6)},\quad u_1^{(2)}=-u_1^{(12)},$$
$$u_1^{(3)}=-u_1^{(8)},\quad u_1^{(4)}=-u_1^{(9)}.$$

(b) if $s_1=s_2$, $m_1=m_2+2$, then

$$u_1^{(6)}=u_1^{(12)}=0.$$

We can now calculate our matrix elements with the formulae given in C.S., 196 *et seq.*, the only difference being that the functions P_{nl}^+, P_{nl}^- are not necessarily normalized. In calculating H_{11}

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[11] The formulae to be given are still valid in certain other cases; we shall not detail these.

[12] The cases $s_1=s_2$, $m_2=m_1-1$ and $s_1=s_2$, $m_2=m_1-2$ are also exceptional, but these need not be dealt with separately, since we can always suppose $m_1\geqslant m_2$.

we shall simplify by regarding each electron as moving in the same (screened) central field and disregarding interaction: this is justifiable (cf. the discussion following (14)). The results are then as follows:

$$H_{00}=E_0,$$

$$\begin{aligned}H_{01}=\sum_{k=1}^{12}\sum_{j}\gamma_k[&c^j(l_1m_1,l_1{}^km_1{}^k)c^j(l_2{}^km_2{}^k,l_2m_2)\\&\times F_j(n_1l_1{}^k,\,n_2l_2{}^k)-\delta(s_1,\,s_2)\\&\times c^j(l_1m_1,\,l_2{}^km_2{}^k)c^j(l_1{}^km_1{}^k,\,l_2m_2)\\&\qquad\qquad\times G_j(n_1l_1{}^k,\,n_2l_2{}^k)],\end{aligned}$$

$$H_{11}=N_{11}E_0+H_{11}',$$

where (28)

$$\begin{aligned}H_{11}'=&(l_1+1)(B_1N_2{}^++B_2N_2{}^-)A(n_1l_1{}^+)\\&-l_1(B_3N_2{}^++B_4N_2{}^-)A(n_1l_1{}^-)\\&+(l_2+1)(B_1N_1{}^++B_3N_1{}^-)A(n_2l_2{}^+)\\&-l_2(B_2N_1{}^++B_4N_1{}^-)A(n_2l_2{}^-),\end{aligned}$$

$$N_{00}=1,\quad N_{01}=0,$$

$$\begin{aligned}N_{11}=&B_1N_1{}^+N_2{}^++B_2N_1{}^+N_2{}^-\\&+B_3N_1{}^-N_2{}^++B_4N_1{}^-N_2{}^-,\end{aligned}$$

where

$$B_1=\gamma_1{}^2+\gamma_5{}^2+\gamma_6{}^2,\quad B_2=\gamma_3{}^2+\gamma_7{}^2+\gamma_9{}^2,$$

$$B_3=\gamma_4{}^2+\gamma_8{}^2+\gamma_{10}{}^2,\quad B_4=\gamma_2{}^2+\gamma_{11}{}^2+\gamma_{12}{}^2.$$

We use $l_1{}^k$ for $l_1\pm1$, etc., depending on the l, m values in the particular $u_1{}^{(k)}$ which goes with γ_k according to (24) and (26). The c^j are integrals of the product of three tesseral harmonics and are identical with the constants denoted thus in C.S., 175, formula (6). They are tabulated in C.S., 178, 179. The A, F, G are radial integrals analogous to those of (4) and (6), namely, with k denoting + or − according as $l_1{}^k=l_1\pm1$, $l_2{}^k=l_2\pm1$,

$$A(nl^k)=\int_0^\infty P_{nl}(r)P_{nl^k}(r)/r^2dr,$$

$$\begin{aligned}F_j(n_1l_1{}^k,\,n_2l_2{}^k)=&\int\int_0^\infty P_{n_1l_1}(r_1)P_{n_2l_2}(r_2)\\&\times P_{n_1l_1{}^k}(r_1)P_{n_2l_2{}^k}(r_2)r_<{}^j/r_>{}^{j+1}dr_1dr_2,\end{aligned}$$

$$\begin{aligned}G_j(n_1l_1{}^k,\,n_2l_2{}^k)=&\int\int_0^\infty P_{n_1l_1}(r_1)P_{n_2l_2}(r_2)\\&\times P_{n_2l_2{}^k}(r_1)P_{n_1l_1{}^k}(r_2)r_<{}^j/r_>{}^{j+1}dr_1dr_2.\end{aligned}$$

Finally, the N's are normalizing factors:

$$N_1{}^+=N(n_1l_1{}^+)=\int_0^\infty[P_{n_1l_1{}^+}(r)]^2dr,\text{ etc.}$$

All these formulae hold for the case of equivalent electrons (when $F_j=G_j$), except that they must be modified in the exceptional cases (a), (b) mentioned above as follows:

Case (a):—To B_1, B_4, B_2+B_3 we must add $-2\gamma_1\gamma_6$, $-2\gamma_2\gamma_{12}$, $-2(\gamma_3\gamma_8+\gamma_4\gamma_9)$, respectively (only the sum B_2+B_3 occurs in the case of equivalent electrons).

Case (b):—Put $\gamma_6=\gamma_{12}=0$.

Putting $E=E_0+\Delta E$, (21) now takes precisely the form (13), with the meanings of H_{01}, H_{11}', N_{11} given in (28). Moreover, since the final results involve only the radial functions of the valence electrons, except for the "orthogonality" modification, we see that if this modification be disregarded—i.e. if we put $P_{nl}{}^+=P_{nl}{}^-=P_{nl}$—the H_{01}, H_{11}', N_{11} of (28) must reduce precisely to those of (14) obtained by the "two-electron" method. This forms a useful check on the work, since the integrals in (14) are easily calculated.

5. Application to $2p^2$ Terms in O III

The configuration is $1s^22s^22p^2$ and the terms ^1S, ^3P, ^1D. Application of the formulae of the preceding section, together with the diagonal sum rule, leads to the following results:

$$\begin{aligned}H_{01}(^1S)=&\frac{4}{15}F_1(2p,\,2p)\\&+\frac{1}{3}F_1(2p^-,\,2p^-)+\frac{6}{35}F_3(2p,\,2p),\end{aligned}$$

$$H_{01}(^3P)=\frac{1}{5}F_1(2p,\,2p)-\frac{3}{35}F_3(2p,\,2p),$$

$$\begin{aligned}H_{01}(^1D)=&\frac{7}{75}F_1(2p,\,2p)\\&+\frac{4}{15}F_1(2p,\,2p^-)+\frac{3}{175}F_3(2p,\,2p),\end{aligned}$$

$$\begin{aligned}H_{11}'=&[4B_1+2(B_2+B_3)N(2p^-)]A(2p)\\&-[(B_2+B_3)+2B_4N(2p^-)]A(2p^-),\end{aligned}$$

$$N_{11}=B_1+(B_2+B_3)N(2p^-)+B_4[N(2p^-)]^2,$$

TABLE I.

	S.C.F.	CORRECTED	OBSERVED
^3P:	-1.988	-1.992	-2.025
	0.099	0.099	0.091
^1D:	-1.889	-1.893	-1.934
	0.148	0.134	0.105
^1S:	-1.741	-1.759	-1.829
$\frac{^1S-{}^1D}{^1D-{}^3P}$:	1.5	1.35	1.15

where, for

$$^1S:\quad B_1=\frac{4}{15},\quad B_2+B_3=0,\quad B_4=\frac{1}{3},$$

$$^3P:\quad B_1=\frac{1}{5},\quad B_2+B_3=0,\quad B_4=0,$$

$$^1D:\quad B_1=\frac{7}{75},\quad B_2+B_3=\frac{4}{15},\quad B_4=0.$$

$P_{2p}^-(r)$ denotes the $2p$-function made orthogonal to both the $1s$ and $2s$ functions in the manner explained;[13] $P_{2p}^+(r)$ is identical with $P_{2p}(r)$ since there are no d electrons.

Numerical integration with the functions of Hartree and Black[5] yields the approximate values:

$$F_1(2p,2p)=0.575,\quad F_1(2p,2p^-)=0.002,$$
$$F_1(2p^-,2p^-)=0.000_6,\quad F_3(2p,2p)=0.317,$$
$$A(2p)=2.27_5,\quad A(2p^-)=-0.068,$$
$$N(2p^-)=0.005,$$

whence, for ^1S, ^3P, ^1D, respectively:

$$H_{01}=0.208,\ 0.088,\ 0.059,$$
$$H_{11}'=2.43,\ 1.82,\ 0.873_5,$$
$$N_{11}=0.267,\ 0.200,\ 0.0947.$$

Hence from (13) (or (15), which is sufficiently accurate),

$$\Delta E(^1S)=-0.018,\quad \Delta E(^3P)=-0.004,$$
$$\Delta E(^1D)=-0.004.$$

This leads to the results in Table I, with energies in atomic units and measured from the normal state of O IV as zero.

The improvement in energy values relative to the O IV ground state is small, but it must be remembered that the energy of the O IV ground state used by Hartree and Black is itself the result of an s.c.f. calculation. The results become more significant if we consider the separations between the ^3P, ^1D, ^1S terms, also shown above. It is then seen that the good agreement between the calculated (s.c.f.) and observed $^1D-{}^3P$ separation is left unaltered, while the calculated $^1S-{}^1D$ separation is noticeably improved, about $\frac{1}{3}$ of the discrepancy between theory and observation being accounted for.[14] The improvement in the separation ratio $(^1S-{}^1D)/(^1D-{}^3P)$ is of particular interest (somewhat less than one-half the discrepancy being accounted for), since the s.c.f. theory leads to a value 1.5 for this ratio for p^2 terms independently of the radial functions, this value not being in good agreement with experiment in most cases.[15]

Thus the method of this paper, where applicable, seems—judging by the results worked out here—to afford a worthwhile improvement over the ordinary s.c.f. method, and to indicate that theory would be in complete agreement with experiment if the mathematical difficulties could be surmounted.

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[13] The $1s$ and $2s$ functions must also be made orthogonal to each other as explained by Hartree and Black, reference 5.

[14] Hartree and Black estimate that the probable error of their calculated results is "rather smaller" than 0.007, so that it is really only the correction for the ^1S which is significant. This does not invalidate the above comparison.

[15] C.S., 198. It may be remarked, however, that the value 1.5 would not be obtained if the s.c.f. *with exchange* were used.