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Analytic Wave Functions. II. Atoms with 1*s*, 2*s*, 2*p*, 3*s*, and 3*p* Electrons*

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The variation program for the computation of atomic wave functions which has been developed and programed for the IBM-704 electronic data processing machine is detailed. This calculation has been set up so as to be able to handle atoms having any combination of 1*s*, 2*s*, 2*p*, 3*s*, and 3*p* electrons. One example of the program is provided by a calculation of the wave functions for aluminum for all degrees of ionization. Another example is provided by a calculation of the fourteen configurations for oxygen having the electron distribution $(1s)^2(2s)^2(2p)^3(3p)$. Finally, the three ^3P wave functions thus obtained are combined by means of the configuration interaction.

I. INTRODUCTION

IN a previous paper[1] we have described the analytic radial orbitals selected by us to represent *s* and *p* electrons having principal quantum numbers one through three. For those electrons having principal quantum numbers one and two, we found it a reasonable procedure to write out the expressions for the bare nuclear field, Coulomb, and exchange integrals in closed form. The subsequent machine calculation which concerns itself primarily with the variation of the total atomic energy made up of these closed form integrals leads to the best analytic wave functions for these representations. This was described in some detail in the previous paper. We also remarked there that the tremendous addition in complexity with an increase to three of the principle quantum number in these energy integrals requires a somewhat different mathematical technique. The difference is one of detail, however, for in principle, the treatment remains a variational one. In the present paper we describe this machine computation for these wave functions and illustrate it with a rather complete investigation of aluminum and the oxygen configurations arising from the electron distribution $(2p)^3(3p)$. In the investigation of aluminum, we propose to consider all levels of ionization of this atom and, in so doing, point up the behavior and accuracy of the calculation for the various orbital electrons.

II. GENERAL EXPRESSION FOR THE ENERGY

Our first problem is the choice of form for the radial portion of the orbitals, and this we have written in the previous paper as

$$R_{1s}=2Z_1^{3/2}r\exp[-Z_1r], \tag{1a}$$

$$R_{2s}=(1/2\sqrt{2})Z_2^{3/2}Z_5^{3/2}[Z_4-Z_2Z_5r]r\exp[-Z_2r/2], \tag{1b}$$

$$R_{2p}=(1/2\sqrt{6})Z_3^{5/2}r^2\exp[-Z_3r/2], \tag{1c}$$

$$R_{3s}=Z_7^{3/2}r(Z_8-Z_7Z_9r-Z_7^2Z_{10}r^2)\exp[-Z_7r/3], \tag{1d}$$

$$R_{3p}=Z_{11}^{5/2}r^2(Z_{12}-Z_{11}Z_{13}r)\exp[-Z_{11}r/3], \tag{1e}$$

where of course,

$$\psi_{nlm}(r,\theta,\varphi)=[R_{nl}(r)/r]\Theta_{lm}(\theta)\Phi_m(\varphi),$$

with the angular portion of the wave function supplied by the well-known spherical harmonics.

Normality is obviously present in Eqs. (1a) and (1c). We must, however, assure normality in the other orbitals and orthonormality between orbitals possessed of the same orbital angular momentum. Z_4, Z_5, Z_8, Z_9, Z_{10}, Z_{12}, and Z_{13} allow us to meet these orthonormality requirements. The relations which assure our meeting these requirements may be written down in terms of the independent parameters Z_1, Z_2, Z_3, Z_7, Z_{11} as

$$Z_4=Z_5/a,\quad a=(2Z_1+Z_2)/6Z_2, \tag{2a}$$

$$Z_5=[4a^2/(1-6a+12a^2)]^{1/5}, \tag{2b}$$

$$Z_8=(3Z_7Z_{10}AD-12Z_7^2Z_{10})/A^2, \tag{2c}$$

$$Z_9=Z_{10}D, \tag{2d}$$

$$\begin{aligned}Z_{10}=[C^7A^4]^{1/2}/[&18Z_7^5C^4A^2D^2-144Z_7^6C^4DA\\&+288Z_7^7C^4-36Z_7^5D^2A^2C^3+144Z_7^6DC^3A^2\\&+144Z_7^6A^3C^2D-576Z_7^7A^2C^2-240Z_7^6A^4CD\\&+720Z_7^7A^4+24Z_7^5A^4C^2D^2]^{1/2},\end{aligned} \tag{2e}$$

$$Z_{12}=HZ_{13}, \tag{2f}$$

$$Z_{13}=[8/3^6(2H^2-30H+135)]^{1/2}, \tag{2g}$$

where certain of the constants included are given by

$$A=Z_1+\tfrac{1}{3}Z_7, \tag{3a}$$

$$B=\tfrac{1}{2}Z_2+\tfrac{1}{3}Z_7, \tag{3b}$$

$$C=\tfrac{2}{3}Z_7, \tag{3c}$$

$$\begin{aligned}D=(&4Z_4Z_7^2B^3-4Z_4Z_7^2A^2B-12Z_2Z_5Z_7^2B^2\\&+20Z_2Z_5Z_7^2A^2)(Z_4Z_7AB^3-Z_4Z_7A^2B^2\\&-3Z_2Z_5Z_7AB^2+4Z_2Z_5Z_7A^2B)^{-1},\end{aligned} \tag{3d}$$

$$H=30Z_{11}/(3Z_3+2Z_{11}). \tag{3e}$$

In the previous paper we wrote down the general expressions for the total energy, the Hamiltonian, and the integrals (I_{nl}, F^k, and G^k) contributing to the energy. We shall simply refer to these equations here.

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* Based on work performed under the auspices of the U. S. Air Force Ballistic Missiles Division.

[1] R. G. Breene, Jr., Phys. Rev. **111**, 1111 (1958).

The problem is precisely the same one; we must write the general expression for the total energy in terms of the integrals. In the present case, however, due to the complexity of the integrals concerned, we are unable to write down closed form expressions for the F^k and G^k. Our procedure is rather to program on the machine the F^k and G^k in terms of generalized integrals which we represent as A^k. As an example, $F^0(2s,3s)$ was written and programed as

$$\begin{aligned}
F^0(2s,3s)=&\tfrac{1}{8}[Z_2^3Z_5^3Z_7^3]\{Z_4^2Z_8^2A^0(2,Z_2;\,2,\tfrac{2}{3}Z_7)\\
&-2Z_4^2Z_7Z_8Z_9A^0(2,Z_2;\,3,\tfrac{2}{3}Z_7)\\
&+2Z_4^2Z_7Z_8Z_{10}A^0(2,Z_2;\,4,\tfrac{2}{3}Z_7)\\
&-2Z_4^2Z_7^3Z_9Z_{10}A^0(2,Z_2;\,5,\tfrac{2}{3}Z_7)\\
&+Z_4^2Z_7^2Z_9^2A^0(2,Z_2;\,4,\tfrac{2}{3}Z_7)+Z_4^2Z_7^4Z_{10}^2A^0(2,Z_2;\,6,\tfrac{2}{3}Z_7)\\
&-2Z_2Z_4Z_5Z_8^2A^0(2,\tfrac{2}{3}Z_7;\,3,Z_2)\\
&+4Z_2Z_4Z_5Z_7Z_8Z_9A^0(3,Z_2;\,3,\tfrac{2}{3}Z_7)\\
&-4Z_2Z_4Z_5Z_7^2Z_8Z_{10}A^0(3,Z_2;\,4,\tfrac{2}{3}Z_7)\\
&+4Z_2Z_4Z_5Z_7^3Z_9Z_{10}A^0(3,Z_2;\,5,\tfrac{2}{3}Z_7)\\
&-2Z_2Z_4Z_5Z_7^2Z_9^2A^0(3,Z_2;\,4,\tfrac{2}{3}Z_7)\\
&-2Z_2Z_4Z_5Z_7^4Z_{10}^2A^0(3,Z_2;\,6,\tfrac{2}{3}Z_7)\\
&+Z_2^2Z_5^2Z_8^2A^0(2,\tfrac{2}{3}Z_7;\,4,Z_2)\\
&-2Z_2^2Z_5^2Z_7Z_8Z_9A^0(3,\tfrac{2}{3}Z_7;\,4,Z_2)\\
&+2Z_2^2Z_5^2Z_7Z_8Z_{10}A^0(4,Z_2;\,4,\tfrac{2}{3}Z_7)\\
&-2Z_2^2Z_5^2Z_7^3Z_9Z_{10}A^0(4,Z_2;\,5,\tfrac{2}{3}Z_7)\\
&+Z_2^2Z_5^2Z_7^2Z_9^2A^0(4,Z_2;\,4,\tfrac{2}{3}Z_7)\\
&+Z_2^2Z_5^2Z_7^2Z_{10}^2A^0(4,Z_2;\,6,\tfrac{2}{3}Z_7)\}.
\end{aligned}\tag{4}$$

In Eq. (4) the $A^0(i,j;\,k,l)$ are the expressions for specific integrals of products of orbitals. As an example:

$$\begin{aligned}
A^0(2,a;\,6,b)=&\int_0^\infty\int_0^\infty\frac{1}{r_>}r^2e^{-ar}r'^6e^{-br'}drdr'\\
=&-\frac{6!}{b^2(a+b)^7}-\frac{10\times5!}{b^3(a+b)^6}-\frac{60\times4!}{b^4(a+b)^5}\\
&-\frac{240\times3!}{b^5(a+b)^4}-\frac{600\times2!}{b^6(a+b)^3}-\frac{720}{b^7(a+b)^2}+\frac{720}{a^2b^7}.
\end{aligned}\tag{5}$$

Utilizing the expressions of which Eqs. (4) and (5) are examples, the total energy of an atom in a general form has been programed on the IBM-704 electronic data processing machine. The procedure for the minimization of this energy expression by the machine is as follows. We first determine the coefficients of the I_{nl}, F^k, G^k and provide these together with the atomic number as input data to the machine. In addition, the range and increment for our independently varying parameters, Z_1, Z_2, Z_3, Z_7, and Z_{11} are furnished as input data. We also furnish as input data the q_{nl}, a_k, b_k which are appropriate to the atom under consideration. For each set of values of these independently varying parameters, the machine evaluates the expression for the total energy of the atom, always assuring us, of course, of orthonormality through Eqs. (2). In evaluating a given, say, F^k during this computational procedure, the machine first evaluates the requisite A^k which are stored. It subsequently evaluates the desired F^k. Finally, of course, the machine completes the energy evaluation by using the F^k and the other expressions as needed. Thus, one might say that a chain of evaluations is carried out in this variation program as compared to the immediate single-step evaluations which are possible to the simpler program.

A modification of this approach has resulted in large savings of machine time. We first treat the atom stripped of its $3s$ and $3p$ electrons by the small variation program and, subsequently, use the values thus obtained for Z_1, Z_2, and Z_3 as starting values in a treatment of the complete atom by our large variation program.

III. WAVE FUNCTIONS FOR Al I THROUGH Al XII

We have utilized these programs to treat all degrees of ionization of the aluminum atom. This program has been applied not only to check our results but also to investigate the program itself—to determine the value of the approximations which we have adopted. The results have been compared with the familiar work of Moore[2] and are presented in Table I.

The table contains the computed total atomic energy, the computed ionization potential, and the experimental ionization potential for each of the levels of ionization considered. In addition, we indicate the percentage error between the experimental and our theoretical results as well as the absolute discrepancy between these two figures. The general trend from high percentage errors for the outermost electrons to negligible errors for the innermost electrons would certainly be expected since this is merely a reflection of the fact that our probabilities are greater for accurately computing large numbers than for so computing small numbers. This should be considered insofar as the 27.2% error figure in our first ionization potential is

TABLE I. The energies and ionization potentials for aluminum.

Ion	Configuration	Energy ev	Ionization potential (ev) Calc	Ionization potential (ev) Exptl	Percent error	Absolute error
I	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)$	6537.36	4.35	5.984	27.2	1.63
II	$(1s)^2(2s)^2(2p)^6(3s)^2$	6533.01	16.11	18.823	14.4	2.72
III	$(1s)^2(2s)^2(2p)^6(3s)$	6516.90	26.85	28.44	5.6	1.59
IV	$(1s)^2(2s)^2(2p)^6$	6490.05	109.47	119.96	8.7	10.49
V	$(1s)^2(2s)^2(2p)^5$	6380.66	144.99	153.77	5.7	8.78
VI	$(1s)^2(2s)^2(2p)^4$	6235.67	175.06	190.42	8.06	15.36
VII	$(1s)^2(2s)^2(2p)^3$	6060.61	245.51	241.93	1.48	−3.58
VIII	$(1s)^2(2s)^2(2p)^2$	5815.10	281.45	285.13	1.29	3.68
IX	$(1s)^2(2s)^2(2p)$	5533.65	327.38	330.1	0.83	2.72
X	$(1s)^2(2s)^2$	5206.27	389.38	398.5	2.29	9.12
XI	$(1s)^2(2s)$	4816.89	438.43	441.9	0.79	3.47
XII	$(1s)^2$	4378.46	2070.06	2085.46 ±0.37	0.74	15.4
XIII	$(1s)$	2308.40				

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[2] *Atomic Energy Levels*, National Bureau of Standards Circular No. 467, edited by Charlotte E. Moore (U. S. Government Printing Office, Washington, D. C., 1949).

concerned. Actually, in the over-all calculation, the first ionization potential seems reasonably good. Nor need we flatter ourselves with the ionization potential for Al XII since one is almost completely assured of excellent results in this region with quite poor approximations.

The notable item is the peaking in percentage error of the ionization potentials at each closed shell or semiclosed shell position. There is an exception in that the ionization potential for Al XII is percentagewise less than that for Al XI; however, we can hardly be surprised at this since the ionization potential increases by some 1500 volts or fivefold. The reason for this behavior is evidently to be found in our choice of angular portion of the atomic wave function. Of course this choice can be corrected for by introducing configuration interactions. If we consider the ionization potential for, say, Al III, we are effectively dealing with an alkali-like situation in which our angular portion is quite well accounted for by the associated Legendre function. As we move away from this alkali-like configuration, we find a discrepancy in ionization potential increasing as is to be expected. Thus, although we might improve our radial functions to a large degree by the addition of products of polynomials and exponentials to all of them, we still would anticipate this worsening trend in ionization potentials as more electrons are added to a closed shell configuration.

There is a rather notable exception to the trend remarked in the last paragraph, however—the ionization potential for Al VI. If the error is meaningful and not simply accidental, it would appear to point up a specific weakness in these radial orbitals. The indication would be that improved orbitals are most needed for the p electrons; although this can hardly be concluded from this single value.

IV. CONFIGURATIONS IN OXYGEN ARISING FROM $(1s)^2(2s)^2(2p)^3(3p)$

As a second check of our variation calculation for atomic wave functions, we have determined the wave functions for the fourteen pure configurations arising from oxygen with the electron arrangement $(1s)^2(2s)^2(2p)^3(3p)$.

We know that we may obtain all these wave functions as a linear combination of whatever wave functions lie at the origin of the Slater diagram.[3] In the case of

TABLE II. The diagonal elements in the Hamiltonian block for oxygen $(2p)^3(3p)$ corresponding to $M_L = M_S = 0$.

Electron distribution	Energy (au)	Z_1	Z_2	Z_3	Z_{11}
$\psi_{\text{I}}[(-1^-0^+1^+)(0^-)]$	73.886	7.653	5.944	4.798	1.796
$\psi_{\text{II}}[(-1^+0^-1^+)(0^-)]$	73.937	7.653	5.936	4.818	1.797
$\psi_{\text{VII}}[(-1^+1^-1^+)(-1^-)]$	73.835	7.654	5.948	4.780	1.770
$\psi_{\text{VIII}}[(0^-0^+1^+)(-1^-)]$	73.837	7.654	5.947	4.779	1.819

TABLE III. The Hamiltonian block corresponding to the origin position of the Slater diagram for oxygen $(1s)^2(2s)^2(2p)^3(3p)$.

	ψ_{I}	ψ_{II}	ψ_{III}	ψ_{IV}	ψ_{V}	ψ_{VI}	ψ_{VII}	ψ_{VIII}	ψ_{IX}	ψ_{X}	ψ_{XI}	ψ_{XII}	ψ_{XIII}	ψ_{XIV}
ψ_{I}	−73.88630	0.05071	0.10123	0.00059	0.00007	0	0	0.00069	0	0	0	0	0.00047	0
ψ_{II}	0.05071	−73.93704	0.05071	0.00007	0	0.00007	0	0	0	0	0	0	0	0.00116
ψ_{III}	0.10123	0.05071	−73.88630	0	0.00007	0.00059	0	0	0	0.00047	0	0	0	0.00069
ψ_{IV}	0.00059	0.00007	0	−73.88630	0.05071	0.10123	0	0.00047	0	0	0	0	0.00069	0
ψ_{V}	0.00007	0	0.00007	0.05071	−73.93704	0.05071	0	0	0	0.00116	0	0	0.00159	0
ψ_{VI}	0	0.00007	0.00059	0.10123	0.05071	−73.88630	0	0	0	0.00069	0	0	0	0.00047
ψ_{VII}	0	0	0	0	0	0	−73.83473	0	0.00049	0	0.00177	0.00049	0	0
ψ_{VIII}	0.00069	0	0	0.00047	0	0	0	−73.83696	0	0.00015	0	0	0.00057	0.00237
ψ_{IX}	0	0	0	0	0	0	0.00049	0	−73.83473	0	0.00049	0.00177	0	0
ψ_{X}	0	0	0.00047	0	0.00116	0.00069	0	0.00015	0	−73.83696	0	0	0.00237	0.00057
ψ_{XI}	0	0	0	0	0	0	0.00177	0	0.00049	0	−73.83473	0.00049	0	0
ψ_{XII}	0	0	0	0	0	0	0.00049	0	0.00177	0	0.00049	−73.83473	0	0
ψ_{XIII}	0.00047	0	0	0.00069	0.00159	0	0	0.00057	0	0.00237	0	0	−73.83696	0.00015
ψ_{XIV}	0	0.00116	0.00069	0	0	0.00047	0	0.00237	0	0.00057	0	0	0.00015	−73.83696

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[3] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

TABLE IV. The coefficients in the expansion for the pure configuration wave functions. The symbol $\psi({}^2P:{}^1S)$, for example, refers to the ${}^1S$ configuration of O I arising from the ${}^2P$ configuration of O II.

	$\psi({}^2P:{}^1S)$	$\psi({}^2P:{}^1D)$	$\psi({}^2P:{}^1P)$	$\psi({}^2P:{}^3S)$	$\psi({}^2P:{}^3P)$	$\psi({}^2P:{}^3D)$	$\psi({}^2D:{}^1D)$	$\psi({}^2D:{}^1F)$	$\psi({}^2D:{}^3F)$	$\psi({}^2D:{}^3D)$	$\psi({}^2D:{}^3P)$	$\psi({}^2D:{}^1P)$	$\psi({}^4S:{}^3P)$	$\psi({}^4S:{}^5P)$
ψ_{I}	0.46299	−0.46619	0	0	0.00869	0.00400	0	0	0.00676	−0.00352	−0.20129	−0.16617	−0.50002	0.50001
ψ_{II}	0.25977	−0.26253	0	0	0.00295	−0.00173	0	0	−0.00300	0.00302	0.71777	0.59023	0.00015	−0.00003
ψ_{III}	0.46300	−0.46620	0	0	0.00869	0.00400	0	0	−0.00110	−0.00208	−0.20148	−0.16631	0.49995	−0.49999
ψ_{IV}	0.46631	0.46281	0	0	0.01160	−0.00682	0	0	0.00391	0.00076	−0.16552	0.20194	−0.49999	−0.50000
ψ_{V}	0.26170	0.26066	0	0	0.00018	0.00457	0	0	−0.00001	0.00001	0.59060	−0.71745	0.00001	0
ψ_{VI}	0.46632	0.46280	0	0	0.01161	−0.00683	0	0	−0.00393	−0.00074	−0.16564	0.20185	0.49998	0.50000
ψ_{VII}	0	0	0.50000	0.50000	0	0	0.70711	0.70711	0	0	0	0	0	0
ψ_{VIII}	0.00707	−0.00140	0	0	−0.49972	−0.50025	0	0	0.50162	−0.49833	0.00180	0.00022	0.00392	−0.00073
ψ_{IX}	0	0	0.50000	−0.50000	0	0	0	0	0	0	0	0	0	0
ψ_{X}	0.01082	0.00514	0	0	−0.50035	0.49940	0	0	−0.49864	−0.50140	0.00361	−0.00591	−0.00392	−0.00073
ψ_{XI}	0	0	0.50000	0.50000	0	0	−0.70711	−0.70711	0	0	0	0	0	0
ψ_{XII}	0	0	0.50000	−0.50000	0	0	0	0	0	0	0	0	0	0
ψ_{XIII}	0.01080	0.00516	0	0	−0.50040	0.49947	0	0	0.49803	0.50189	−0.00363	0.00589	0.00392	0.00073
ψ_{XIV}	0.01068	−0.00510	0	0	−0.49910	−0.50073	0	0	−0.50161	0.49835	−0.00479	−0.00520	−0.00393	0.00074

oxygen with a $3p$ electron, there are fourteen wave functions which give $M_L=0$, $M_S=0$. This means that there will be a nondiagonal 14×14 block of the Hamiltonian corresponding to this position on the Slater diagram. Further, it will mean that in order to obtain the wave functions corresponding, it will be necessary for us to diagonalize this 14×14 matrix. Before diagonalization, however, we must determine the matrix elements of the Hamiltonian and this, of course, is where our large variation program enters. By means of this large variation program, we are able to determine the diagonal elements for this block. Subsequently, by making use of the effective nuclear charges which we obtain from our variation calculation, we can quite readily evaluate the off-diagonal elements of this block. First, however, let us list the fourteen single-determinant functions as follows:

$\psi_{\mathrm{I}}[(-1^{-}0^{+}1^{+})(0^{-})]$, $\psi_{\mathrm{VIII}}[(0^{-}0^{+}1^{+})(-1^{-})]$,
$\psi_{\mathrm{II}}[(-1^{+}0^{-}1^{+})(0^{-})]$, $\psi_{\mathrm{IX}}[(-1^{-}1^{-}1^{+})(-1^{+})]$,
$\psi_{\mathrm{III}}[(-1^{+}0^{+}1^{-})(0^{-})]$, $\psi_{\mathrm{X}}[(0^{-}0^{+}1^{-})(-1^{+})]$,
$\psi_{\mathrm{IV}}[(-1^{-}0^{-}1^{+})(0^{+})]$, $\psi_{\mathrm{XI}}[(-1^{-}-1^{+}1^{+})(+1^{-})]$,
$\psi_{\mathrm{V}}[(-1^{-}0^{+}1^{-})(0^{+})]$, $\psi_{\mathrm{XII}}[(-1^{-}-1^{+}1^{-})(+1^{+})]$,
$\psi_{\mathrm{VI}}[(-1^{+}0^{-}1^{-})(0^{+})]$, $\psi_{\mathrm{XIII}}[(-1^{-}0^{-}0^{+})(+1^{+})]$,
$\psi_{\mathrm{VII}}[(-1^{+}1^{-}1^{+})(-1^{-})]$, $\psi_{\mathrm{XIV}}[(-1^{+}0^{-}0^{+})(+1^{-})]$.

As an example the symbol $\psi_{\mathrm{I}}[(-1^{-}0^{+}1^{+})(0^{-})]$ may be defined as follows. Within the bracket the first set of parentheses refers to the $2p$ electrons while the second set of parentheses refers to the $3p$ electron. The number is the magnetic quantum number with sign as indicated, and the sign appearing as a superscript on each number refers to the spin.

Although there are fourteen diagonal positions in this block of the Hamiltonian, it turns out that there are only four different energies. This means then that we have but four variation calculations to carry out utilizing our large variation program. As an example, the general energy expression corresponding to one of these energies may be written as

$$\begin{aligned} E[(-1^{-}0^{+}1^{+})(0^{-})] &= 2I_{1s}+2I_{2s}+3I_{2p}+I_{3p} \\ &+F^0(1s,1s)+F^0(2s,2s)+3F^0(2p,2p)+4F^0(1s,2s) \\ &+6F^0(2s,2p)-(3/25)F^2(2p,2p)-2G^0(1s,2s) \\ &-G^1(1s,2p)-G^1(2s,2p)-(3/25)G^2(2p,2p) \\ &+2F^0(1s,3p)+2F^0(2s,3p)+3F^0(2p,3p) \\ &-G^0(2p,3p)+6F^0(1s,2p)-\tfrac{1}{3}G^1(2s,3p) \\ &-\tfrac{1}{3}G^1(1s,3p)-(3/25)G^2(2p,3p). \end{aligned} \tag{6}$$

Table II presents the results of our variation calculation. These results consist of the energies as indicated together with the effective nuclear charge for the various electron configurations which now must be utilized in the diagonalization of our Hamiltonian block. The off-diagonal elements are then evaluated by means of the results for the diagonal elements.

Let us recall that no diagonal elements of our Hamiltonian exist between two wave functions for which more than two electrons change their quantum state. For the case when two electrons, i and j, change their states to, say, i' and j', the nondiagonal matrix element of the Hamiltonian between two such determinants is

$$(a|H|b)=\left(ij\left|\frac{1}{r_{ij}}\right|i'j'\right)-\left(ij\left|\frac{1}{r_{ij}}\right|j'i'\right). \tag{7}$$

These diagonal elements may be evaluated in terms of the G^k and F^k insofar as their radial portions are concerned and they may be evaluated in terms of the Slater a_k and b_k insofar as their angular portions are concerned. As an example, one may obtain for a typical off-diagonal element:

$$\begin{aligned}\left[(-1^-0^+1^+)(0^-)|H|(-1^+0^-1^+)(0^-)\right]\\ =(3/25)F^2(2p,2p)=0.05071466.\end{aligned} \tag{8}$$

Thus, having carried out the variation part of the calculation, we were then in a position to set up the block of the Hamiltonian corresponding to the origin of the Slater diagram. This we have displayed in Table III.

As available subroutine for the IBM-704 electronic data processing machine was utilized for the eigenvector-eigenvalue problem posed by this matrix. In Table IV we have displayed the coefficients in the expansions for the wave functions corresponding to the pure configurations. Each of the terms in a given expansion is a single determinant whose effective nuclear charges are given in Table II.

Finally, the eigenvalues corresponding to the various configurations are given in Table V. For comparison with experiment the energy separations of certain of the configurations above the ^5P state are indicated. Also indicated are the corresponding experimental separations as given by Moore. The energy of the lowest level (^5P) has been observed by Moore as 2033.3 ev. Our result, on the other hand, is 2012.48 ev, a variance which is somewhat less than that obtained for the ground state of O. The ground state energy for oxygen we calculated as 2018.28 ev as compared to an experimental value of 2043.3 ev.

TABLE V. Configuration energies and comparison of separations with experiment. The symbol (^2P) ^1S refers to a ^1S configuration arising from the ^2P configuration of O II.

Energy (au)	Configuration	Energy (cm^{-1})	Energy above (^4S) ^5P (calc)	Energy above (^4S) ^5P (exp)
−73.7560	(^2P) ^1S	−16 183 712	50 940	44 318
−73.7571	(^2P) ^1D	−16 183 969	50 683	41 970
−73.8320	(^2P) ^1P	−16 200 393	34 259	41 042
−73.8339	(^2P) ^3P	−16 200 811		
−73.8340	(^2P) ^3S	−16 200 824		
−73.8353	(^2P) ^3D	−16 201 119	33 533	40 656
−73.8365	(^2D) ^1D	−16 201 383	33 269	30 005
−73.8365	(^2D) ^1F	−16 201 383	33 269	27 370
−73.8389	(^2D) ^3F	−16 201 909	32 743	27 089
−73.8397	(^2D) ^3D	−16 202 094	32 558	26 669
−73.9655	(^2D) ^3P	−16 229 694		
−73.9656	(^2D) ^1P	−16 229 701		
−73.9870	(^4S) ^3P	−16 234 395	257	5
−73.9881	(^4S) ^5P	−16 234 652		

V. CONFIGURATION INTERACTION FOR THE EXCITED ^3P CONFIGURATIONS

As is apparent from Table V, there are three ^3P configurations for O with a $3p$ electron arising from the ^4S, ^2D, and ^2P states of O II. We now propose to combine these three through a configuration interaction analysis.

Let us designate the three wave functions as ψ_{II}, ψ_{IV}, ψ_{X}. Then the matrix of the Hamiltonian corresponding to these three configurations is

$$\begin{array}{c} \text{II} \\ \text{IV} \\ \text{X} \end{array}\begin{bmatrix} -73.986955 & 0.0010182 & -0.0000436 \\ 0.0010182 & -73.965529 & 0.266387 \\ -0.0000436 & 0.266387 & -73.833899 \end{bmatrix}.$$

We now diagonalize this and obtain as energies corresponding to our coupled configurations

$$\psi_A(^3P) \sim 2016.88 \text{ ev},$$
$$\psi_B(^3P) \sim 2013.37 \text{ ev},$$
$$\psi_C(^3P) \sim 2002.34 \text{ ev}.$$

The unmixed ^3P corresponding energy-wise to ψ_A —ψ_{II}—had an energy of 2012.45 ev, so that we have improved the energy by about five volts. ψ_{IV} had an energy of 2011.86 ev while ψ_{V} had an energy of 2008.28 ev.

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