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

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Analytic wave functions are utilized to obtain a general expression for the atomic energy for atoms having one or more electrons in the 1*s*, 2*s*, and 2*p* orbitals. A minimization of this energy expression, containing three independently variable parameters, has been programed on the IBM 704 electronic data processing machine. As an example, this program has been utilized for obtaining the best analytic wave functions for the single ground configuration of O^- and the three ground configurations of O.

I. INTRODUCTION

THE best single determinant atomic wave functions are, of course, obtained by a numerical solution of the Hartree-Fock equations. Although the Slater-type determinants composed of analytic orbitals obtained from a variation treatment of the atomic energy cannot be expected to yield equally good functions, linear combinations of these determinants hold out the hope of even better and more descriptive functions. With this in mind we have chosen certain forms for the orbitals in question and programed a variation treatment of the energy expression resulting from these orbitals. The program has been written for and carried out on the IBM 704 electronic data processing machine. Because of the complexity involved in the inclusion of the higher orbitals in the calculations, two different methods of calculation and, hence, two separate programs have been undertaken. The first and simplest of these applies to atoms composed of 1*s*, 2*s*, and 2*p* electrons, and it is on this program that we report here. The second of these programs concerns itself with atoms having 1*s*, 2*s*, 2*p*, 3*s*, and 3*p* electrons in ground and excited configurations, and we shall report on this program in a later paper. Although this latter program is functioning satisfactorily, the calculational technique appears to be sufficiently different to warrant separate treatment. The programs have been set up so as to be readily adaptable to any atoms having the requisite type electrons, and we concern ourselves here with O and O^- only as examples. Thus, our first program yields the determinantal functions associated with the three configurations (^1S, ^1D, ^3P) described by $(1s)^2(2s)^2(2p)^4$ and the single configuration of $O^-(^2P)$ described by $(1s)^2(2s)^2(2p)^5$.

II. GENERAL EXPRESSION FOR THE ENERGY

In obtaining the general expression for the energies we must first choose a desirable form for the analytic orbitals.[1] The expressions which we have developed are largely adapted from hydrogenlike orbitals and may be written down as

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

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

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

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

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

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.

We shall here consider only Eqs. (1a)–(1c). Normalization is obviously inherent in Eqs. (1a) and (1c). Normalization for the 2*s* function and orthogonality of the 1*s* and 2*s* functions are furnished by the parameters Z_4 and Z_5. In addition these parameters furnish a degree of control over the node of the 2*s* function. In order to guarantee the requisite orthonormality we shall maintain the following relationships between the dependent parameters Z_4 and Z_5 and the independent parameters Z_1, Z_2, and Z_3:

$$Z_5=[4a^2/(1-6a+12a^2)]^{1/5},\quad a=(2Z_1+Z_2)/6Z_2, \tag{1f}$$

$$Z_4=Z_5/a. \tag{1g}$$

Let us now recall the familiar expression for the atomic energy:

$$E=\sum_{nl}q(nl)I_{nl}+\tfrac{1}{2}\sum_{a,b,k}a^k(l^am^a,l^bm^b)F^k(n^al^a,n^bl^b)$$
$$-\sum_k \underset{b,a}{S}\, b^k(l^am^a,l^bm^b)G^k(n^al^a,n^bl^b), \tag{2}$$

where these energies are, of course, the diagonal elements of the Hamiltonian:

$$H=\sum_{i=1}^{Z}\left(-\tfrac{1}{2}\nabla_i^2+\frac{Z}{r_i}\right)+\sum_{i>j}\frac{1}{r_{ij}}$$

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

[1] For the various previous choices see: J. C. Slater, Phys. Rev. **36**, 51 (1930); C. Zener, Phys. Rev. **36**, 51 (1930); Morse, Young, and Hurwitz, Phys. Rev. **48**, 948 (1935); L. Goldberg and A. M. Glogston, Phys. Rev. **56**, 696 (1939); W. E. Duncanson and C. A. Coulson, Proc. Roy. Soc. (London) **A62**, 37 (1944); Boys and Sahni, Proc. Roy. Soc. (London) **A246**, 463 (1954); Per-Olov Löwdin, Phys. Rev. **103**, 1746 (1956), and others.

in atomic units, with

$$I_{nl}=-\tfrac{1}{2}\int_0^\infty R_{nl}(r)\left[\frac{d^2}{dr^2}+\frac{2Z}{r}-\frac{l(l+1)}{r^2}\right]\times R_{nl}dr, \tag{3a}$$

$$F^k(n^al^a,n^bl^b)=\int_0^\infty\int_0^\infty R_{nl}^2(r)R_{n'l'}^2(r')\times(r_<^k/r_>^{k+1})drdr', \tag{3b}$$

$$G^k(n^al^a,n^bl^b)=\int_0^\infty\int_0^\infty R_{nl}(r)R_{n'l'}(r)R_{nl}(r')R_{n'l'}(r')\times(r_<^k/r_>^{k+1})drdr'. \tag{3c}$$

We remark that Eqs. (3a), (3b), and (3c) are the energies of the bare nuclear field, the Coulomb interaction, and the exchange interaction, respectively. The a^k and b^k are the results of integrating the angular portion of the wave function multiplied by the angular portion of the expansion of $1/r_{ij}$ over the angular coordinates. These, of course, have been evaluated once for all by Slater.[2] Our task then is simply the evaluation of Eqs. (3) utilizing Eqs. (1). Our results are as follows:

$$I_{1s}=-Z_1^2/2-Z_1[Z-Z_1], \tag{4a}$$

$$I_{2s}=-\tfrac{1}{2}\{[-Z_4^2/4+Z_5^2/2+Z_4/2-3Z_5/2]\times Z_2^2Z_5^3/4+[Z_4^2/4-Z_4Z_5+3Z_5^2/2]ZZ_2Z_5^3\}, \tag{4b}$$

$$I_{2p}=Z_3^2/12-(Z_3^2/12)[\tfrac{5}{2}+3(Z-Z_3)/Z_3], \tag{4c}$$

$$F^0(1s,1s)=5Z_1/8, \tag{5a}$$

$$F^0(2s,2s)=(Z_2Z_5^6/512)[10Z_4^4-100Z_4^3Z_5+432Z_4^2Z_5^2-924Z_4Z_5^3+837Z_5^4], \tag{5b}$$

$$F^0(2p,2p)=93Z_3/512, \tag{5c}$$

$$F^0(1s,2s)=(Z_2^3Z_5^3Z_4^2/8)[-(4Z_1+Z_2)/(2Z_1+Z_2)^3+1/Z_2^2]-(Z_2^4Z_4Z_5^4/2)\times[-(5Z_1+Z_2)/(2Z_1+Z_2)^4+1/Z_2^3]+(3Z_2^2Z_5^5/4)[-(6Z_1+Z_2)/(2Z_1+Z_2)^5+1/Z_2^4], \tag{5d}$$

$$F^0(1s,2p)=Z_3/4-Z_3^5(6Z_1+Z_3)/4(2Z_1+Z_3)^5, \tag{5e}$$

$$F^0(2s,2p)=(Z_3Z_5^3/16)[Z_4^2-12Z_5^2-6Z_4Z_5]+[Z_3^5Z_5^3/16(Z_2+Z_3)^4]\times\left[6Z_4Z_5-\frac{Z_4^2(3Z_2+Z_3)}{(Z_2+Z_3)}-\frac{12Z_5^2(4Z_2+Z_3)}{(Z_2+Z_3)}+\frac{4Z_2Z_4Z_5(9Z_2+4Z_3)}{(Z_2+Z_3)^2}-\frac{60Z_2^2Z_5^2(2Z_2+Z_3)}{(Z_2+Z_3)^3}\right], \tag{5f}$$

$$F^2(2p,2p)=45Z_3/512, \tag{5g}$$

$$G^0(1s,2s)=[Z_1^3Z_5^3/(2Z_1+Z_2)^5]\times[20Z_2^3Z_4^2-200Z_2^4Z_4Z_5/(2Z_1+Z_2)+528Z_2^5Z_5^2/(2Z_1+Z_2)^2], \tag{6a}$$

$$G^0(2p,2p)=F^0(2p,2p), \tag{6b}$$

$$G^1(1s,2p)=112Z_1^3Z_3^5/(2Z_1+Z_3)^7, \tag{6c}$$

$$G^1(2s,2p)=[Z_3^5Z_5^3/(Z_2+Z_3)^7]\times[7Z_2^3Z_4^2/2-49Z_2^4Z_4Z_5/(Z_2+Z_3)+185Z_2^5Z_5^2/(Z_2+Z_3)^2], \tag{6d}$$

$$G^2(2p,2p)=F^2(2p,2p). \tag{6e}$$

Now Eqs. (2)–(6) may be combined with the help of the Slater coefficients in an obvious fashion to obtain a particular energy expression.

Equation (2) with the indicated substitutions has been programmed on the IBM 704 electronic data processing machine. In so doing the Z_1, Z_2, and Z_3 have been programmed as independently variable parameters, the upper and lower limits of their individual values being input data. Finally, the $q(nl)$, a^k, and b^k have been left as input data so that various atoms and configurations may be treated by an adjustment of these parameters. This then is the general problem readily adaptable to various atoms, and we have now but to consider our results for the atoms of our particular interest here.

III. RESULTS FOR O AND O$^-$

We have mentioned our intention of treating the three configurations of oxygen (^1S, ^1D, ^3P) arising from the electronic distribution $(1s)^2(2s)^2(2p)^4$. A prefatory remark is in order here. First, let us specify an electron configuration possible to this distribution by specifying the distribution of the $2p$ electrons, e.g., $\psi_A(-1^-001^+)$ where the m_l values are indicated by the digits and the spins by the superior signs. Now a Slater diagram[3] tells us directly that a single determinant yields the proper wave functions for both the ^3P and the ^1D configurations. On the other hand, the ^1S state must be a linear combination of three determinants as we may observe from a consideration of the same diagram. This means that we must diagonalize the corresponding 3×3 block of the Hamiltonian in order to obtain such a linear combination. This we have done, with the following result:

$$\psi(^1S)=0.000619\psi_{\text{I}}(-1^-001^+)+0.999998\psi_{\text{II}}(-1-111)+0.000619\psi_{\text{III}}(-1^+001^-).$$

On the basis of this result we have chosen the single determinant ψ_{II} to represent $\psi(^1S)$.

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

[3] The applicable one here appears as Fig. 1(c), p. 1298, of J. C. Slater, Phys. Rev. 34, 1293 (1929).

TABLE I. The parameters and energies corresponding to the ^2P configuration of O$^-$ and the ^1S, ^1D, and ^3P configurations of O. All energies are, of course, negative.

Configuration	Z_1	Z_2	Z_3	Energy au	Energy (ev)	Energy (cm^{-1})	Energy observed (ev)
O$^-$ ^2P	7.669	5.560	3.942	73.927846	2010.84	16 222 452	2044.75
O ^1S	7.661	5.734	4.346	74.063166	2014.52	16 252 125	2039.1
O ^1D	7.661	5.728	4.361	74.109080	2015.77	16 262 199	2041.3
O ^3P	7.661	5.718	4.389	74.201366	2018.28	16 282 451	2043.3

Our results are given as Table I. In this table we have displayed the values of the independent parameters giving minimum energy in each case. There appears to be no reason for listing the values for the dependent parameters as they may be obtained immediately from Eqs. (1d) and (1e). These parameters through Eqs. (1) provide the best analytic functions obtainable under the present stipulated conditions. Let us consider the energies appearing in the table.

We have listed the energies in atomic, electron volt, and reciprocal centimeter units, since we shall have reason to utilize each of these units. First off, the energy expression was written for the machine in atomic units, since these are far and away the most convenient. We may remark that we have obtained the energy minimum accurate certainly to seven digits and probably to eight. There is uncertainty in the last digit due to roundings off which must occur in the machine during the calculation. This, by the way, is the limit of the machine. Such accuracy allows four-digit accuracy in the variable parameters but this constitutes the limit. Thus, we have restricted ourselves to parameters containing four figures. In comparing our results with experiment, let us first consider the energy in electron volts.

Although earlier data supported a binding energy of 2.2 ev for the outermost $2p$ electron in the negative oxygen ion, it would appear from the results of Branscomb and Smith that this value should be 1.45 ev.[4] We obtain the binding energy of this electron by determining the difference between the atomic energies of O and O$^-$. A study of Table I shows that our outermost $2p$ electron is unbound. The minimum energy of this electron or lack of binding is obviously 3.68 ev (^1S configuration for O). We might now consider the level separation in oxygen.

According to Dieke,[5] the separation of the ^1D and ^3P levels is 16 400 cm^{-1}, while it is apparent that we have obtained 20 252. This would indicate that our $2p$ electron energies are rather good. Dieke gives a separation of 33 600 cm^{-1} for the separation of the ^1S and ^3P levels while we obtain 30 327 cm^{-1}, and the same comment could be made about the $2p$ energies. In order to compare the energies of the innermost $1s$ electrons, let us consider O VIII and O VII. We may minimize Eq. (4a) directly to obtain $Z_1=8$ and an ionization potential of 870.4 electron volts while Moore[6] gives an experimental value of 871.12. By utilizing Eqs. (4a) and (5a), we may obtain for O VII an energy

$$E=Z_1^2-2ZZ_1+\tfrac{5}{8}Z_1,$$

minimization of which yields an energy of 1607.46 volts for $Z_1=7.688$. This means that our ionization potential for O VII is 737.06 volts as compared to Moore's 739.11 volts. The fact that these energies agree quite well is certainly not startling, but we did wish to point up the fact that the innermost and outermost electrons seem to be provided quite good energies by this calculation. Therefore, differences which occur between theory and experiment can be expected to arise chiefly from the inner $2p$ electrons, and differences do arise as is apparent from Moore's experimental value of 2043.3 volts as opposed to our value of 2018.28 volts. We shall consider the origin of these discrepancies in a great deal more detail in a subsequent paper.

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[4] L. M. Branscomb and S. J. Smith, Phys. Rev. **98**, 1127 (1955).

[5] G. H. Dieke, in *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1957), p. 7–30.

[6] *Atomic Energy Levels*, edited by C. E. Moore, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1948), Vol. 1.