

Accurate Analytical Self-Consistent Field Functions for Atoms. III. The $1s^2 2s^m 2p^n$ States of Nitrogen and Oxygen and Their Ions

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(Received 23 January 1963; revised manuscript received 11 March 1963)

Self-consistent field functions have been determined in analytical form for all the neutral and positively ionized states and for some negatively ionized states of nitrogen and oxygen associated with the configurations $1s^2 2s^m 2p^n$, where $m, n \geq 0$. The functions determined differ from numerical Hartree-Fock functions by no more than a few units in the third decimal place, and usually by much less.

I. INTRODUCTION

IN the first paper¹ in this series, self-consistent field (SCF) functions were presented in analytical form for the $1s^2 2s$ and $1s^2 2s^2$ states of the atoms and ions of the first row of the periodic table. In the second paper,² such functions were given for all the neutral species of the first row, for the ground state, and for those excited states which have the same configuration as the ground state. The present paper gives such functions for a large number of states of nitrogen and oxygen and their negative and positive ions, namely, all the states arising from the configurations $1s^2 2s^m 2p^n$, where m and n may be any integers provided we have at most 8 electrons in N or 9 in O.

These calculations arose from a need for theoretical evaluation of the opacity of air at high temperatures.³ Such an evaluation must employ wave functions for a very large number of discrete and continuous states of N and O and their positive ions, and the transition probabilities between such states. Clearly, the present results constitute only a modest beginning in this large undertaking. However, the speed and capacity of current and future digital computers should make the task feasible.

II. CHOICE OF BASIS SETS

We explored the possibility of selecting basis sets which identically satisfy the cusp conditions. If an occupied orbital of angular momentum λ is represented by

$$\phi = r^\lambda f_\lambda(r) Y_{\lambda\alpha}(\theta, \varphi), \quad (1)$$

the cusp condition is

$$(f_\lambda'/f_\lambda)_{r=0} = -Z/(\lambda+1), \quad (2)$$

where f_λ' means df_λ/dr .

¹ C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, *Rev. Mod. Phys.* **32**, 186 (1960).

² E. Clementi and C. C. J. Roothaan, *Phys. Rev.* **127**, 1618 (1962).

³ B. H. Armstrong, J. Sokoloff, R. W. Nicholls, D. H. Holland, and R. E. Meyerott, *J. Quant. Spectr. Radiative Transfer* **1**, 143 (1961).

If we let f_λ be expanded according to

$$f_\lambda = c e^{-Zr/(\lambda+1)} + r^2 \sum_i c_i r^{p_i} e^{-\zeta_i r}, \quad (3)$$

where the p_i are non-negative integers, and the ζ_i are completely arbitrary, then the condition (2) is satisfied provided $c \neq 0$. This can also be stated as follows: To satisfy condition (2) the basis set for angular momentum λ must have one member with principal quantum number $n = \lambda + 1$ and orbital exponent $\zeta = Z/(\lambda + 1)$, while all the other principal quantum numbers are at least $\lambda + 3$, and the exponents are arbitrary.

Identical satisfaction of the cusp condition is obviously an attractive criterion for the selection of basis sets. However, it is also important to minimize the number of basis functions needed to represent the Hartree-Fock functions with a particular degree of accuracy. Possible basis set choices were examined for the ground states of neutral N and O. A fixed cusp representation was found for the s orbitals which was as efficient as any known to us. However, the $2p$ orbital could be represented with fewer functions if we did *not* impose the cusp condition. Since a very large number of calculations were involved, we let efficiency be the overriding factor, and therefore obtained correct cusps for the s orbitals but not for the $2p$ orbitals.

A more detailed discussion of the fixed cusp basis sets, together with results obtained for a number of representative atoms, will be presented in a future publication.

III. VALIDITY OF THE SCF PROCEDURE FOR EXCITED STATES

One may raise the question whether the application of the variational principle is valid to obtain wave functions for excited states. In answer, first, the variational principle is unconditionally valid for an excited state that is the lowest state of a symmetry species. More precisely, the calculated energy for any wave function of that symmetry will be higher than or equal to the true energy of the lowest state of the symmetry species. We note that the symmetry includes parity and

TABLE I. Optimized exponents of the basis functions. ζ_1 , ζ_2 , and ζ_3 have fixed values as discussed in the text.

| | | s orbitals | | p orbitals | | | | | s orbitals | | p orbitals | | |
|----------|-------|------------|-----------|------------|-----------|-----------|------|-----------|------------|-----------|------------|-----------|-----------|
| | | ζ_4 | ζ_5 | ζ_6 | ζ_7 | ζ_8 | | | ζ_4 | ζ_5 | ζ_6 | ζ_7 | ζ_8 |
| s^2p^5 | 2P | | | | | | | O^- | 3.689 | 1.986 | 1.066 | 2.448 | 4.99 |
| sp^6 | 2S | | | | | | | | 3.714 | 2.039 | 1.060 | 2.447 | 4.99 |
| s^2p^4 | 3P | N^- | 3.184 | 1.700 | 0.913 | 2.107 | 4.44 | O_I | 3.873 | 2.214 | 1.468 | 2.866 | 5.79 |
| | 1D | | 3.185 | 1.706 | 0.880 | 2.078 | 4.36 | | 3.876 | 2.217 | 1.436 | 2.841 | 5.70 |
| | 1S | | 3.187 | 1.714 | 0.830 | 2.031 | 4.25 | | 3.876 | 2.221 | 1.385 | 2.782 | 5.50 |
| sp^5 | 3P | | 3.212 | 1.767 | 0.906 | 2.105 | 4.44 | | 3.895 | 2.279 | 1.432 | 2.818 | 5.67 |
| | 1P | | 3.220 | 1.745 | 0.844 | 2.069 | 4.47 | | 3.858 | 2.187 | 1.387 | 2.779 | 5.45 |
| p^6 | 1S | | ... | ... | 0.904 | 2.114 | 4.43 | | ... | ... | 1.390 | 2.741 | 5.40 |
| s^2p^3 | 4S | N_I | 3.366 | 1.923 | 1.353 | 2.561 | 5.60 | O_{II} | 4.062 | 2.458 | 1.893 | 3.347 | 7.26 |
| | 2D | | 3.370 | 1.929 | 1.288 | 2.512 | 5.34 | | 4.068 | 2.464 | 1.835 | 3.329 | 7.07 |
| | 2P | | 3.372 | 1.933 | 1.245 | 2.480 | 5.20 | | 4.075 | 2.468 | 1.796 | 3.314 | 6.93 |
| sp^4 | 4P | | 3.413 | 2.021 | 1.321 | 2.590 | 5.91 | | 4.082 | 2.547 | 1.833 | 3.281 | 6.96 |
| | 2D | | 3.387 | 1.975 | 1.264 | 2.557 | 5.63 | | 4.070 | 2.497 | 1.782 | 3.279 | 6.79 |
| | 2S | | 3.392 | 1.981 | 1.217 | 2.516 | 5.43 | | 4.086 | 2.506 | 1.740 | 3.260 | 6.65 |
| | 2P | | 3.328 | 1.867 | 1.240 | 2.555 | 5.46 | | 3.982 | 2.356 | 1.762 | 3.278 | 6.60 |
| p^5 | 2P | | ... | ... | 1.256 | 2.528 | 5.46 | | ... | ... | 1.763 | 3.248 | 6.64 |
| s^2p^2 | 3P | N_{II} | 3.565 | 2.176 | 1.692 | 2.977 | 6.96 | O_{III} | 4.260 | 2.716 | 2.209 | 3.701 | 8.35 |
| | 1D | | 3.568 | 2.180 | 1.630 | 2.942 | 6.66 | | 4.275 | 2.723 | 2.163 | 3.784 | 8.84 |
| | 1S | | 3.571 | 2.184 | 1.542 | 2.909 | 6.39 | | 4.271 | 2.724 | 2.073 | 3.732 | 8.30 |
| sp^3 | 5S | | 3.623 | 2.307 | 1.726 | 2.913 | 6.92 | | 4.372 | 2.863 | 2.230 | 3.580 | 7.97 |
| | 3D | | 3.587 | 2.243 | 1.646 | 2.964 | 6.93 | | 4.300 | 2.785 | 2.152 | 3.662 | 7.98 |
| | 3P | | 3.604 | 2.249 | 1.610 | 2.961 | 6.88 | | 4.268 | 2.776 | 2.117 | 3.670 | 7.94 |
| | 1D | | 3.519 | 2.115 | 1.592 | 3.036 | 7.28 | | 4.235 | 2.649 | 2.104 | 3.767 | 8.50 |
| | 3S | | 3.450 | 2.014 | 1.616 | 3.008 | 6.95 | | 4.121 | 2.537 | 2.127 | 3.717 | 8.20 |
| | 1P | | 3.529 | 2.126 | 1.549 | 2.993 | 6.87 | | 4.213 | 2.648 | 2.059 | 3.705 | 7.88 |
| p^4 | 3P | | ... | ... | 1.616 | 2.972 | 6.88 | | ... | ... | 2.114 | 3.665 | 7.85 |
| | 1D | | ... | ... | 1.591 | 2.972 | 6.87 | | ... | ... | 2.090 | 3.680 | 7.89 |
| | 1S | | ... | ... | 1.553 | 2.966 | 6.85 | | ... | ... | 2.052 | 3.685 | 7.86 |
| s^2p | 2P | N_{III} | 3.765 | 2.434 | 2.000 | 3.300 | 7.87 | O_{IV} | 4.513 | 2.990 | 2.503 | 3.938 | 8.83 |
| sp^2 | 4P | | 3.850 | 2.546 | 2.026 | 3.196 | 7.44 | | 4.651 | 3.108 | 2.526 | 3.848 | 8.56 |
| | 2D | | 3.759 | 2.461 | 1.935 | 3.343 | 7.92 | | 4.481 | 3.006 | 2.448 | 4.142 | 9.59 |
| | 2S | | 3.804 | 2.475 | 1.848 | 3.300 | 7.52 | | 4.420 | 2.991 | 2.352 | 4.019 | 8.50 |
| | 2P | | 3.665 | 2.305 | 1.906 | 3.371 | 8.32 | | 4.380 | 2.849 | 2.417 | 4.096 | 9.75 |
| p^3 | 4S | | ... | ... | 1.980 | 3.345 | 7.87 | | ... | ... | 2.479 | 4.040 | 8.88 |
| | 2D | | ... | ... | 1.926 | 3.351 | 7.86 | | ... | ... | 2.427 | 4.071 | 8.88 |
| | 2P | | ... | ... | 1.891 | 3.351 | 7.89 | | ... | ... | 2.394 | 4.098 | 9.00 |
| s^2 | 1S | N_{IV} | 4.034 | 2.709 | ... | ... | ... | O_V | 4.800 | 3.265 | ... | ... | ... |
| sp | 3P | | 3.938 | 2.740 | 2.325 | 3.549 | 7.84 | | 4.784 | 3.314 | 2.842 | 4.579 | 9.50 |
| | 1P | | 3.850 | 2.595 | 2.153 | 3.676 | 9.92 | | 4.600 | 3.148 | 2.666 | 4.408 | 12.00 |
| p^2 | 3P | | ... | ... | 2.268 | 3.718 | 8.31 | | ... | ... | 2.767 | 4.387 | 9.36 |
| | 1D | | ... | ... | 2.211 | 3.727 | 8.48 | | ... | ... | 2.713 | 4.445 | 9.48 |
| | 1S | | ... | ... | 2.131 | 3.729 | 8.55 | | ... | ... | 2.634 | 4.502 | 9.66 |
| s | 2S | N_V | 4.137 | 2.964 | ... | ... | ... | O_{VI} | 5.114 | 3.554 | ... | ... | ... |
| p | 2P | | ... | ... | 2.557 | 4.812 | 9.00 | | ... | ... | 3.057 | 5.275 | 10.00 |

multiplicity as well as angular momentum. However, the individual orbital momenta are not good quantum numbers for the true solutions of the Schrödinger equation, and orbital structure should not be used to

distinguish symmetry species. Most of the states calculated by us are the lowest of a symmetry species; those which are not are marked with an asterisk in Table III.

For this second category of excited states the varia-

TABLE II. Expansion coefficients.

| | 1s Orbitals | | | | | 2s Orbitals | | | | | 2p Orbitals | | | | |
|-----------|-------------|---------|---------|---------|---------|-------------|----------|---------|---------|----------|-------------|----------|----------|--|--|
| | c_1 | c_2 | c_3 | c_4 | c_5 | c_6 | c_7 | c_8 | c_9 | c_{10} | c_{11} | c_{12} | c_{13} | | |
| $s^2 p^4$ | 3P | 0.94815 | 0.05564 | 0.01908 | 0.00216 | -0.00000 | -0.20165 | 0.09975 | 0.60601 | 0.43805 | 0.52249 | 0.52941 | 0.07847 | | |
| | 1D | 0.94819 | 0.05569 | 0.01896 | 0.00212 | 0.00000 | -0.20258 | 0.10043 | 0.60936 | 0.43341 | 0.52059 | 0.53228 | 0.08412 | | |
| | 1S | 0.94825 | 0.05577 | 0.01878 | 0.00207 | 0.00001 | -0.20397 | 0.10094 | 0.61501 | 0.42616 | 0.51716 | 0.53731 | 0.09301 | | |
| $s p^5$ | 3P | 0.94779 | 0.05458 | 0.02103 | 0.00221 | 0.00002 | -0.20803 | 0.09419 | 0.60235 | 0.41817 | 0.51524 | 0.53640 | 0.08064 | | |
| | 1P | 0.94716 | 0.05454 | 0.02119 | 0.00419 | 0.00149 | -0.20977 | 0.09466 | 0.61027 | 0.43202 | 0.51124 | 0.55058 | 0.08403 | | |
| | 1S | 0.94760 | 0.05026 | 0.02778 | ... | ... | ... | ... | ... | ... | 0.51420 | 0.53613 | 0.08428 | | |
| $s^2 p^3$ | 4S | 0.94809 | 0.05593 | 0.01865 | 0.00234 | -0.00013 | -0.20847 | 0.07963 | 0.54986 | 0.49041 | 0.60685 | 0.43324 | 0.03434 | | |
| | 2D | 0.94817 | 0.05603 | 0.01842 | 0.00228 | -0.00011 | -0.20952 | 0.07955 | 0.55363 | 0.48622 | 0.59480 | 0.44695 | 0.04046 | | |
| | 2P | 0.94822 | 0.05608 | 0.01828 | 0.00224 | -0.00010 | -0.21022 | 0.07904 | 0.55628 | 0.48317 | 0.58767 | 0.45545 | 0.04456 | | |
| $s p^4$ | 4P | 0.94794 | 0.05483 | 0.02065 | 0.00175 | -0.00067 | -0.21451 | 0.07030 | 0.55585 | 0.48114 | 0.61642 | 0.43340 | 0.02930 | | |
| | 2D | 0.94756 | 0.05479 | 0.02074 | 0.00281 | 0.00037 | -0.21493 | 0.07447 | 0.56216 | 0.47574 | 0.60742 | 0.44517 | 0.03449 | | |
| | 2S | 0.94762 | 0.05486 | 0.02057 | 0.00275 | 0.00040 | -0.21593 | 0.07396 | 0.56575 | 0.47204 | 0.59680 | 0.45727 | 0.03919 | | |
| p^5 | 2P | 0.94672 | 0.05455 | 0.02130 | 0.00505 | 0.00232 | -0.21289 | 0.08244 | 0.56388 | 0.47829 | 0.60586 | 0.44760 | 0.03828 | | |
| | 2P | 0.94747 | 0.05025 | 0.02800 | ... | ... | ... | ... | ... | ... | 0.59672 | 0.45195 | 0.03947 | | |
| | 2P | 0.94848 | 0.05671 | 0.01694 | 0.00230 | -0.00029 | -0.22096 | 0.06291 | 0.50758 | 0.52831 | 0.70909 | 0.32448 | 0.01589 | | |
| $s^2 p^2$ | 1D | 0.94854 | 0.05678 | 0.01676 | 0.00226 | -0.00027 | -0.22150 | 0.06294 | 0.50902 | 0.52673 | 0.69463 | 0.34246 | 0.01796 | | |
| | 1S | 0.94863 | 0.05687 | 0.01652 | 0.00219 | -0.00025 | -0.22233 | 0.06263 | 0.51283 | 0.52298 | 0.68061 | 0.36327 | 0.01997 | | |
| | 3S | 0.94846 | 0.05531 | 0.01965 | 0.00109 | -0.00183 | -0.22580 | 0.05075 | 0.49977 | 0.53451 | 0.71205 | 0.31463 | 0.01780 | | |
| $s p^3$ | 3D | 0.94798 | 0.05527 | 0.01970 | 0.00218 | -0.00035 | -0.22559 | 0.05620 | 0.50902 | 0.52552 | 0.70712 | 0.32979 | 0.01649 | | |
| | 3P | 0.94802 | 0.05534 | 0.01954 | 0.00216 | -0.00031 | -0.22604 | 0.05354 | 0.50758 | 0.52881 | 0.70167 | 0.33888 | 0.01651 | | |
| | 1D | 0.94693 | 0.05504 | 0.02023 | 0.00457 | 0.00226 | -0.22330 | 0.06481 | 0.51622 | 0.52096 | 0.70625 | 0.34172 | 0.01317 | | |
| p^4 | 3S | 0.94634 | 0.05475 | 0.02092 | 0.00587 | 0.00350 | -0.21895 | 0.07290 | 0.52130 | 0.69488 | 0.69488 | 0.34863 | 0.01559 | | |
| | 1P | 0.94699 | 0.05511 | 0.02005 | 0.00451 | 0.00225 | -0.22427 | 0.06360 | 0.51749 | 0.51991 | 0.69425 | 0.35540 | 0.01565 | | |
| | 3P | 0.94750 | 0.05065 | 0.02744 | ... | ... | ... | ... | ... | ... | 0.70479 | 0.33526 | 0.01698 | | |
| $s^2 p$ | 1D | 0.94755 | 0.05073 | 0.02726 | ... | ... | ... | ... | ... | ... | 0.70133 | 0.34157 | 0.01683 | | |
| | 1S | 0.94761 | 0.05086 | 0.02700 | ... | ... | ... | ... | ... | ... | 0.69517 | 0.35193 | 0.01676 | | |
| | 2P | 0.94933 | 0.05788 | 0.01399 | 0.00220 | -0.00050 | -0.23522 | 0.04866 | 0.46891 | 0.56572 | 0.78978 | 0.23186 | 0.01063 | | |
| $s p^2$ | 4P | 0.94894 | 0.05614 | 0.01755 | 0.00142 | -0.00154 | -0.23938 | 0.03048 | 0.44867 | 0.59160 | 0.80056 | 0.21362 | 0.01440 | | |
| | 2D | 0.94831 | 0.05603 | 0.01776 | 0.00253 | 0.00027 | -0.23860 | 0.04353 | 0.46956 | 0.56477 | 0.78927 | 0.23793 | 0.01005 | | |
| | 2S | 0.94840 | 0.05615 | 0.01743 | 0.00249 | 0.00033 | -0.23931 | 0.03662 | 0.46394 | 0.57539 | 0.76528 | 0.26785 | 0.01098 | | |
| p^3 | 2P | 0.94693 | 0.05564 | 0.01867 | 0.00513 | 0.00352 | -0.23408 | 0.05656 | 0.47323 | 0.55986 | 0.76405 | 0.26982 | 0.00778 | | |
| | 4S | 0.94781 | 0.05159 | 0.02571 | ... | ... | ... | ... | ... | ... | 0.80618 | 0.21622 | 0.01116 | | |
| | 2D | 0.94790 | 0.05172 | 0.02540 | ... | ... | ... | ... | ... | ... | 0.79304 | 0.23434 | 0.01052 | | |
| s^2 | 2P | 0.94795 | 0.05181 | 0.02520 | ... | ... | ... | ... | ... | ... | 0.78486 | 0.24588 | 0.01006 | | |
| | 1S | 0.95074 | 0.05962 | 0.00918 | 0.00283 | -0.00081 | -0.25055 | 0.01009 | 0.42031 | 0.62476 | ... | ... | ... | | |
| | 3P | 0.94981 | 0.05727 | 0.01433 | 0.00162 | -0.00092 | -0.25381 | 0.00887 | 0.43968 | 0.59728 | 0.90253 | 0.10137 | 0.01259 | | |
| p^2 | 1P | 0.94816 | 0.05693 | 0.01508 | 0.00423 | 0.00316 | -0.25052 | 0.04402 | 0.43865 | 0.59125 | 0.80447 | 0.22291 | 0.00388 | | |
| | 3P | 0.94870 | 0.05332 | 0.02197 | ... | ... | ... | ... | ... | ... | 0.88804 | 0.12329 | 0.00947 | | |
| | 1D | 0.94876 | 0.05340 | 0.02175 | ... | ... | ... | ... | ... | ... | 0.86958 | 0.14678 | 0.00814 | | |
| s | 1S | 0.94886 | 0.05353 | 0.02142 | ... | ... | ... | ... | ... | ... | 0.84741 | 0.17576 | 0.00688 | | |
| | 2S | 0.95116 | 0.05902 | 0.00902 | 0.00230 | -0.00004 | -0.26893 | 0.00810 | 0.40452 | 0.64316 | ... | ... | ... | | |
| | 2P | 0.95018 | 0.05552 | 0.01659 | ... | ... | ... | ... | ... | ... | 0.97326 | 0.03030 | 0.00697 | | |

TABLE II (continued).

| | 1s Orbitals | | | | | | 2s Orbitals | | | | | | 2p Orbitals | | | | | |
|----------|-------------|---------|---------|---------|----------|----------|-------------|----------|---------|----------|----------|----------|-------------|----------|----------|----------|--|--|
| | c_1 | c_2 | c_3 | c_4 | c_5 | c_6 | c_7 | c_8 | c_9 | c_{10} | c_{11} | c_{12} | c_{13} | c_{14} | c_{15} | c_{16} | | |
| s^2p^5 | 0.95329 | 0.04888 | 0.01885 | 0.00216 | 0.00009 | -0.20954 | -0.02870 | 0.10719 | 0.60887 | 0.42769 | 0.50003 | 0.53713 | 0.09529 | | | | | |
| s^2p^6 | 0.95276 | 0.04790 | 0.02081 | 0.00264 | 0.00045 | -0.21495 | -0.02638 | 0.10245 | 0.61837 | 0.41501 | 0.49708 | 0.53950 | 0.09756 | | | | | |
| s^2p^4 | 0.95328 | 0.04914 | 0.01844 | 0.00226 | -0.00000 | -0.21582 | -0.02263 | 0.08914 | 0.56180 | 0.47212 | 0.56192 | 0.47078 | 0.05386 | | | | | |
| $1D$ | 0.95331 | 0.04918 | 0.01833 | 0.00223 | 0.00001 | -0.21634 | -0.02250 | 0.08884 | 0.56380 | 0.47008 | 0.55748 | 0.47528 | 0.05737 | | | | | |
| $1S$ | 0.95337 | 0.04924 | 0.01818 | 0.00218 | 0.00002 | -0.21710 | -0.02270 | 0.08943 | 0.56712 | 0.46601 | 0.54649 | 0.48270 | 0.06647 | | | | | |
| s^2p^5 | 0.95289 | 0.04809 | 0.02050 | 0.00216 | 0.00000 | -0.22076 | -0.02028 | 0.08403 | 0.57117 | 0.45984 | 0.55082 | 0.47938 | 0.05989 | | | | | |
| $1P$ | 0.95210 | 0.04795 | 0.02089 | 0.00423 | 0.00176 | -0.21955 | -0.02153 | 0.08804 | 0.56753 | 0.46819 | 0.54403 | 0.48162 | 0.07058 | | | | | |
| $1S$ | 0.95262 | 0.04391 | 0.02734 | ... | ... | ... | ... | ... | ... | ... | 0.53152 | 0.48838 | 0.07463 | | | | | |
| s^2p^5 | 0.95348 | 0.04959 | 0.01744 | 0.00225 | -0.00014 | -0.22522 | -0.01829 | 0.07454 | 0.52164 | 0.50882 | 0.66438 | 0.36826 | 0.02255 | | | | | |
| $2D$ | 0.95355 | 0.04966 | 0.01724 | 0.00221 | -0.00012 | -0.22584 | -0.01828 | 0.07436 | 0.52272 | 0.50771 | 0.65748 | 0.37834 | 0.02436 | | | | | |
| $2P$ | 0.95359 | 0.04971 | 0.01711 | 0.00218 | -0.00010 | -0.22626 | -0.01801 | 0.07347 | 0.52353 | 0.50741 | 0.65272 | 0.38510 | 0.02585 | | | | | |
| s^2p^4 | 0.95329 | 0.04843 | 0.01974 | 0.00150 | -0.00073 | -0.23004 | -0.01585 | 0.06892 | 0.53033 | 0.49701 | 0.65300 | 0.37936 | 0.02695 | | | | | |
| $2D$ | 0.95284 | 0.04839 | 0.01984 | 0.00259 | 0.00042 | -0.22967 | -0.01625 | 0.07042 | 0.52894 | 0.50065 | 0.64727 | 0.38842 | 0.02888 | | | | | |
| $2S$ | 0.95289 | 0.04846 | 0.01967 | 0.00254 | 0.00045 | -0.23030 | -0.01570 | 0.06853 | 0.52823 | 0.50250 | 0.64142 | 0.39619 | 0.03090 | | | | | |
| $2P$ | 0.95185 | 0.04814 | 0.02051 | 0.00486 | 0.00257 | -0.22638 | -0.01919 | 0.08036 | 0.53157 | 0.49963 | 0.63996 | 0.39581 | 0.03159 | | | | | |
| $2P$ | 0.95265 | 0.04427 | 0.02681 | ... | ... | ... | ... | ... | ... | ... | 0.64119 | 0.39278 | 0.03219 | | | | | |
| s^2p^5 | 0.95412 | 0.05040 | 0.01531 | 0.00212 | -0.00029 | -0.23732 | -0.01511 | 0.06151 | 0.48776 | 0.54092 | 0.74136 | 0.28411 | 0.01340 | | | | | |
| $1D$ | 0.95417 | 0.05046 | 0.01514 | 0.00210 | -0.00027 | -0.23767 | -0.01475 | 0.05995 | 0.48597 | 0.54381 | 0.74807 | 0.28429 | 0.01044 | | | | | |
| $1S$ | 0.95428 | 0.05053 | 0.01494 | 0.00206 | -0.00025 | -0.23819 | -0.01497 | 0.06067 | 0.48963 | 0.53962 | 0.72860 | 0.30824 | 0.01228 | | | | | |
| s^2p^3 | 0.95408 | 0.04901 | 0.01823 | 0.00078 | -0.00186 | -0.24163 | -0.00889 | 0.04177 | 0.47156 | 0.56362 | 0.74091 | 0.27706 | 0.01757 | | | | | |
| $3D$ | 0.95353 | 0.04896 | 0.01833 | 0.00182 | -0.00032 | -0.24104 | -0.01136 | 0.05149 | 0.48394 | 0.54726 | 0.73572 | 0.29059 | 0.01588 | | | | | |
| $1D$ | 0.95357 | 0.04899 | 0.01826 | 0.00178 | -0.00030 | -0.24128 | -0.01260 | 0.05193 | 0.49217 | 0.53586 | 0.73165 | 0.29751 | 0.01570 | | | | | |
| $1P$ | 0.95236 | 0.04876 | 0.01886 | 0.00413 | 0.00246 | -0.23830 | -0.01327 | 0.05939 | 0.48411 | 0.54805 | 0.73300 | 0.30313 | 0.01155 | | | | | |
| $3S$ | 0.95172 | 0.04849 | 0.01957 | 0.00541 | 0.00368 | -0.23464 | -0.01696 | 0.07287 | 0.49265 | 0.53476 | 0.71920 | 0.31342 | 0.01335 | | | | | |
| $1P$ | 0.95242 | 0.04879 | 0.01876 | 0.00411 | 0.00241 | -0.23888 | -0.01426 | 0.06276 | 0.49045 | 0.53909 | 0.71843 | 0.31749 | 0.01477 | | | | | |
| $3P$ | 0.95290 | 0.04500 | 0.02544 | ... | ... | ... | ... | ... | ... | ... | 0.73201 | 0.29647 | 0.01676 | | | | | |
| $1D$ | 0.95294 | 0.04506 | 0.02529 | ... | ... | ... | ... | ... | ... | ... | 0.73061 | 0.30053 | 0.01610 | | | | | |
| $1S$ | 0.95300 | 0.04515 | 0.02507 | ... | ... | ... | ... | ... | ... | ... | 0.72575 | 0.30874 | 0.01583 | | | | | |
| s^2p | 0.95516 | 0.05156 | 0.01195 | 0.00211 | -0.00050 | -0.25034 | -0.01115 | 0.04210 | 0.44575 | 0.58918 | 0.80024 | 0.21503 | 0.01114 | | | | | |
| $4P$ | 0.95473 | 0.04985 | 0.01577 | 0.00110 | -0.00148 | -0.25396 | -0.00413 | 0.01734 | 0.42377 | 0.62434 | 0.81698 | 0.19261 | 0.01414 | | | | | |
| $2D$ | 0.95406 | 0.04974 | 0.01603 | 0.00210 | 0.00033 | -0.25305 | -0.00905 | 0.03979 | 0.44985 | 0.58364 | 0.82055 | 0.20204 | 0.00775 | | | | | |
| $2S$ | 0.95414 | 0.04978 | 0.01590 | 0.00205 | 0.00032 | -0.25345 | -0.01088 | 0.04725 | 0.46560 | 0.56232 | 0.78734 | 0.23763 | 0.01082 | | | | | |
| $2P$ | 0.95261 | 0.04942 | 0.01687 | 0.00452 | 0.00363 | -0.24901 | -0.01217 | 0.05391 | 0.44855 | 0.58019 | 0.78493 | 0.24198 | 0.00664 | | | | | |
| $4S$ | 0.95345 | 0.04612 | 0.02304 | ... | ... | ... | ... | ... | ... | ... | 0.82378 | 0.19279 | 0.01120 | | | | | |
| $2D$ | 0.95352 | 0.04621 | 0.02280 | ... | ... | ... | ... | ... | ... | ... | 0.81458 | 0.20609 | 0.01042 | | | | | |
| $2P$ | 0.95357 | 0.04627 | 0.02264 | ... | ... | ... | ... | ... | ... | ... | 0.81008 | 0.21374 | 0.00949 | | | | | |
| $1S$ | 0.95668 | 0.05315 | 0.00698 | 0.00253 | -0.00082 | -0.26391 | -0.00731 | 0.01732 | 0.40549 | 0.64345 | ... | ... | ... | | | | | |
| $3P$ | 0.95571 | 0.05096 | 0.01221 | 0.00143 | -0.00083 | -0.26678 | -0.00372 | 0.01006 | 0.40501 | 0.64496 | 0.93309 | 0.07134 | 0.00953 | | | | | |
| $1P$ | 0.95406 | 0.05065 | 0.01300 | 0.00371 | 0.00318 | -0.26379 | -0.00907 | 0.03802 | 0.41573 | 0.61633 | 0.82222 | 0.20038 | 0.00297 | | | | | |
| s^2p^3 | 0.95452 | 0.04775 | 0.01909 | ... | ... | ... | ... | ... | ... | ... | 0.89477 | 0.11329 | 0.00963 | | | | | |
| $1D$ | 0.95457 | 0.04780 | 0.01892 | ... | ... | ... | ... | ... | ... | ... | 0.88222 | 0.13003 | 0.00836 | | | | | |
| $1S$ | 0.95465 | 0.04788 | 0.01868 | ... | ... | ... | ... | ... | ... | ... | 0.86544 | 0.15310 | 0.00656 | | | | | |
| s | 0.95709 | 0.05259 | 0.00658 | 0.00248 | 0.00006 | -0.28005 | 0.00041 | -0.02343 | 0.36550 | 0.71007 | ... | ... | ... | | | | | |
| p | 0.95609 | 0.04959 | 0.01395 | ... | ... | ... | ... | ... | ... | ... | 0.97106 | 0.03035 | 0.00785 | | | | | |

TABLE III. Calculated energies and comparison to experiment. Energies are in atomic units. Blanks indicate an absence of experimental data.

| | | Calculated energies | | Calculated energies minus experimental energies | | Calculated energies | | Calculated energies minus experimental energies | | | |
|----------|---------|---------------------|-----------------------------|---|-----------------------------|---------------------|-----------------------------|---|-----------------------------|----------|------------|
| | | Total | Relative to ground state | Total | Relative to ground state | Total | Relative to ground state | Total | Relative to ground state | | |
| s^2p^5 | 2P | | | | | O^- | -74.788567 | 0 | 0.360977 | 0 | |
| sp^6 | 2S | | | | | | -74.112572 | 0.675995 | | | |
| s^2p^4 | 3P | N^- | -54.321106 | 0 | | O_I | -74.809149 | 0 | 0.286200 | 0 | |
| | 1D | | -54.265951 | 0.055155 | | | -74.729000 | 0.080149 | 0.294419 | 0.008219 | |
| | 1S | | -54.185656 | 0.135450 | | | -74.610734 | 0.198415 | 0.331029 | 0.044829 | |
| | 3P | | -53.864775 | 0.456331 | | | -74.183667 | 0.625482 | | | |
| | 1P | | -53.628647 | 0.692459 | | | -73.871757 | 0.937392 | | | |
| p^6 | $^1S^*$ | | -53.204446 | 1.116660 | | | -73.305804 | 1.503345 | | | |
| s^2p^3 | 4S | N_I | -54.400789 | 0 | 0.200986 | 0 | O_{II} | -74.372527 | 0 | 0.222818 | 0 |
| | 2D | | -54.296006 | 0.104783 | 0.218182 | 0.017196 | | -74.233258 | 0.139269 | 0.239923 | 0.017105 |
| | 2P | | -54.227925 | 0.172864 | 0.242468 | 0.041482 | | -74.142007 | 0.230520 | 0.268988 | 0.046170 |
| | 4P | | -53.988133 | 0.412656 | 0.212142 | 0.011156 | | -73.819524 | 0.553003 | 0.229466 | 0.006648 |
| | 2D | | -53.783457 | 0.617332 | | | | -73.557421 | 0.815106 | 0.281752 | 0.058934 |
| | 2S | | -53.683204 | 0.717585 | | | | -73.423186 | 0.949341 | 0.280602 | 0.057784 |
| | 2P | | -53.583728 | 0.817061 | | | | -73.311229 | 1.061298 | 0.315392 | 0.092574 |
| p^6 | $^2P^*$ | | -53.221754 | 1.179035 | | | | -72.828058 | 1.544469 | | |
| s^2p^2 | 3P | N_{II} | -53.887956 | 0 | 0.178845 | 0 | O_{III} | -73.100158 | 0 | 0.202523 | 0 |
| | 1D | | -53.807355 | 0.080601 | 0.190082 | 0.011237 | | -72.997241 | 0.102917 | 0.214044 | 0.011521 |
| | 1S | | -53.690103 | 0.197853 | 0.228199 | 0.049354 | | -72.846294 | 0.253864 | 0.260614 | 0.580910 |
| | 5S | | -53.747299 | 0.140657 | 0.105036 | -0.073809 | | -72.905175 | 0.194983 | 0.123703 | -0.078820 |
| | 3D | | -53.473978 | 0.413978 | 0.173005 | -0.005840 | | -72.566142 | 0.534016 | 0.190641 | -0.011882 |
| | 3P | | -53.394804 | 0.493152 | 0.174856 | -0.003989 | | -72.465021 | 0.635137 | 0.189980 | -0.012543 |
| | 1D | | -53.178486 | 0.709470 | 0.231867 | 0.053022 | | -72.204839 | 0.895319 | 0.246689 | 0.044166 |
| | 3S | | -53.151774 | 0.736182 | 0.208738 | 0.029893 | | -72.179442 | 0.920716 | 0.226361 | 0.023838 |
| | 1P | | -53.101140 | 0.786816 | 0.206365 | 0.027520 | | -72.105046 | 0.995112 | 0.239842 | 0.037319 |
| | $^3P^*$ | | -52.864760 | 1.023196 | | | | -71.796825 | 1.303333 | 0.213653 | 0.011130 |
| | $^1D^*$ | | -52.786453 | 1.101503 | | | | -71.696837 | 1.403321 | 0.247938 | 0.045415 |
| | $^1S^*$ | | -52.670534 | 1.217422 | | | | -71.548372 | 1.551786 | 0.191345 | -0.011178† |
| s^2p | 2P | N_{III} | -52.815767 | 0 | 0.114388 | 0 | O_{IV} | -71.094684 | 0 | 0.188808 | 0 |
| | 4P | | -52.629796 | 0.185971 | 0.088390 | -0.025998 | | -70.853443 | 0.241241 | 0.106058 | -0.082750 |
| | 2D | | -52.377489 | 0.438278 | 0.141420 | 0.027032 | | -70.547715 | 0.546969 | 0.158667 | -0.030141 |
| | 2S | | -52.245740 | 0.570027 | 0.136609 | 0.022221 | | -70.383256 | 0.711428 | 0.152637 | -0.036171 |
| | 2P | | -52.151122 | 0.664645 | 0.163140 | 0.048752 | | -70.280234 | 0.814450 | 0.181511 | -0.007297 |
| | 4S | | -52.026184 | 0.789583 | 0.101974 | -0.012414 | | -70.111809 | 0.982875 | 0.119284 | -0.069524 |
| | 2D | | -51.892058 | 0.923709 | 0.161951 | 0.047563 | | -69.945389 | 1.149295 | 0.176859 | -0.011949 |
| | $^2P^*$ | | -51.803982 | 1.011785 | 0.125532 | 0.011143 | | -69.835773 | 1.258911 | 0.132258 | -0.056550 |
| s^2 | 1S | N_{IV} | -51.082298 | 0 | 0.153784 | 0 | O_V | -68.257692 | 0 | 0.182537 | 0 |
| sp | 3P | | -50.854765 | 0.227533 | 0.074854 | -0.078930 | | -67.975765 | 0.281927 | 0.089033 | -0.093504 |
| | 1P | | -50.517055 | 0.565243 | 0.123643 | -0.030141 | | -67.576576 | 0.681116 | 0.140250 | -0.042287 |
| | 3P | | -50.356131 | 0.726167 | 0.080011 | -0.073773 | | -67.372244 | 0.885448 | 0.093431 | -0.089106 |
| | 1D | | -50.257409 | 0.824889 | 0.118204 | -0.035580 | | -67.252081 | 1.005611 | 0.132541 | -0.049996 |
| | $^1S^*$ | | -50.112301 | 0.969997 | 0.051548 | -0.102236 | | -67.074798 | 1.182894 | 0.053864 | -0.128673 |
| s | 2S | N_V | -48.326838 | 0 | 0.062726 | 0 | O_{VI} | -64.178032 | 0 | 0.077059 | 0 |
| p | 2P | | -47.957768 | 0.369070 | 0.064451 | 0.001725 | | -63.736678 | 0.441354 | 0.077760 | 0.000701 |
| ... | 1S | N_{VI} | -44.736154 | 0 | 0.056680 | 0 | O_{VII} | -59.111133 | 0 | 0.069141 | 0 |

* States which are not the lowest of a symmetry species.

† Experimental value in doubt.

tional principle still holds if the trial functions are constrained by orthogonality with respect to the exact wave function(s) of the lower state(s). Since such exact wave functions are not known, one is usually satisfied if *approximate* orthogonality with respect to the *approximate* lower state wave function(s) is assured. In practice this is achieved by solving the Hartree-Fock problem for the different states without any explicit constraints at all.

As an example, let us take the $1s^22p$ and the $1s^23p$ states of the Li atom, and let us assume that the self-consistent field orbitals are determined for each state as a separate problem. It is easily seen that the SCF equations are slightly different for the two cases. This leads to a small difference in the $1s$ orbitals, but, of course, to a large difference between the $2p$ and $3p$ orbitals, since for these we must take solutions *without* and *with* one radial node, respectively. The $2p$ and $3p$ orbitals, however, are eigenfunctions of nearly identical effective Hamiltonians and are, therefore, nearly orthogonal. The near-identity of the $1s$ orbitals and the near-orthogonality of the $2p$ and $3p$ orbitals assures the near-orthogonality of the 3-electron state functions.

In the present application, *exact* orthogonality is assured between our state functions representing the higher and the lower states of the same symmetry, since in all cases they involve a double $2s$ - $2p$ promotion. We, therefore, feel confident that our SCF solutions for the excited states are reasonable approximations to the exact wave function.

IV. RESULTS

The calculations were carried out on the IBM 7090 using a program, described elsewhere,⁴ which permits automatic exponent optimization.

The $1s$ orbital is represented rather well by three basis functions, specifically, a $1s$ function with $\zeta=Z$ (for the cusp) and two $3s$ functions [$p_i=0$ in Eq. (3)] with $\zeta=Z\pm\Delta$, where $\Delta=0.96$ for N and $\Delta=1.12$ for O . Furthermore, it was found that this representation is quite insensitive to the presence or absence of outer electrons, as long as the $1s$ orbital is doubly occupied. Such a result was, of course, to be expected; nevertheless, we verified it in a number of cases. These three basis functions also span the inner loop of the $2s$ orbital.

The outer loop of the $2s$ orbital is represented by two additional $3s$ functions; the optimum exponents for these two functions depend strongly on the occupation of the $2s$ and $2p$ shells, and to a lesser extent on the different states within the same configuration. These exponents were carefully optimized for each state.

The $2p$ orbital is represented by three $2p$ functions; the optimum exponents strongly depend on occupation and state, and were also carefully optimized for each state.

The best exponents are summarized in Table I and the expansion coefficients in Table II. Table III shows a comparison of computed and experimental energy levels. Very good agreement for this comparison cannot be expected, since the Hartree-Fock energy is in error by the so-called correlation energy,⁵ which is strongly dependent on shell structure.

The experimental energies have been obtained from Moore's Tables,⁶ with the exception of O^- , for which the electron affinity was obtained from the work of Branscomb *et al.*⁷ The experimental multiplets are averaged and the correction for infinite nuclear mass included. The total experimental energies are subject to a systematic uncertainty of about 0.003 a.u. which is not present in the relative energies.

For each configuration, it can be seen that the state of highest spin has the smallest energy difference from experiment. This result reflects the "precorrelation" introduced by the Hartree-Fock exchange potential for electrons having parallel spins. Negative numbers in the final column of Table III indicate smaller correlation energy for the excited state than for the ground state. These negative numbers occur in excited configurations where the ground state spin of the species is smaller than that of some state of the excited configuration.

In several cases we compared the present orbitals with more accurate calculations, carried out with larger basis sets. These comparisons convinced us that the present orbitals never differ from the actual Hartree-Fock function by more than 10^{-3} , and usually by much less.

Because of the loose binding of the $2p$ orbitals, the negative ions may constitute an exception to the foregoing statement. A more detailed study of negative ion states, with the use of larger basis sets, might prove rewarding.

The calculated energies for N^- and O^- are higher than for the corresponding neutral atoms. However, both ions are expected to have more correlation energy than their parent atoms, since they have additional electron interactions. Reasonable estimates of this correlation energy predict that O^- is stable while N^- is only barely stable, if at all.

A considerable effort failed to reveal energy minima in O^{--} or N^{--} . Instead, a smooth reduction of energy occurred as the $2p$ orbital moved outward.

Further details concerning these results, such as numerical tabulations, are available upon request. Program decks are also available. The exponents of Table I may be used with our program to reproduce our results quickly, or as a starting point to determine more accurate orbitals by enlarging the basis sets.

⁵ See, for instance, E. Clementi, *J. Chem. Phys.* **38**, 2248 (1963).

⁶ Charlotte E. Moore, NBS Circular 467 (U. S. Government Printing Office, Washington, D. C., 1949), Vol. 1.

⁷ L. M. Branscomb, D. S. Burch, S. J. Smith, and S. Geltman, *Phys. Rev.* **111**, 504 (1958).

⁴ C. C. J. Roothaan and P. S. Bagus, *Methods in Computational Physics* (Pergamon Press, Inc., New York, 1962), Vol. II.