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*Present address: Faculté des Sciences, Université de Lyon, 69 Villeurbanne, France.

‡On leave of absence from the University of Toledo, Toledo, Ohio 43606.

¹K. T. Compton and J. C. Boyce, *J. Franklin Inst.* **205**, 497 (1928).

²P. G. Kruger, *Phys. Rev.* **36**, 855 (1930).

³R. Whiddington and H. Priestley, *Proc. Roy. Soc. (London)* **A145**, 462 (1934).

⁴T. Y. Wu, *Phys. Rev.* **66**, 291 (1944).

⁵U. Fano, in *Atomic Physics*, edited by V. W. Hughes, B. Bederson, V. W. Cohen, and F. M. J. Pichanick (Plenum, New York, 1969), p. 209.

⁶R. P. Madden and K. Codling, *Phys. Rev. Letters* **10**, 516 (1963).

⁷R. P. Madden and K. Codling, *Astrophys. J.* **141**, 364 (1965).

⁸J. W. Cooper, U. Fano, and F. Prats, *Phys. Rev. Letters* **10**, 518 (1963).

⁹C. E. Kuyatt, J. A. Simpson, and S. R. Mielczarek, *Phys. Rev.* **138**, A385 (1965).

¹⁰P. D. Burrow and G. J. Schulz, *Phys. Rev. Letters* **22**, 1271 (1969).

¹¹J. T. Grissom, R. N. Compton, and W. R. Garrett, *Phys. Letters* **30A**, 117 (1969).

¹²N. Oda, F. Nishimura, and S. Tahira, *Phys. Rev. Letters* **24**, 42 (1970).

¹³S. M. Silverman and E. N. Lassetre, *J. Chem.*

Phys. **40**, 1265 (1964).

¹⁴M. E. Rudd, *Phys. Rev. Letters* **15**, 580 (1965).

¹⁵U. Fano, *Phys. Rev.* **124**, 1866 (1961).

¹⁶P. G. Burke, D. D. McVicar, and K. Smith, *Phys. Rev. Letters* **11**, 559 (1963).

¹⁷H. O. Knox and M. R. H. Rudge, *J. Phys. B* **2**, 521 (1969).

¹⁸H. O. Dickinson and M. R. H. Rudge, *J. Phys. B* **3**, 1284 (1970).

¹⁹E. Holøien, *J. Chem. Phys.* **29**, 676 (1958); and *Phys. Norvegica* **1**, 53 (1961).

²⁰J. Middtdal, *Phys. Rev.* **138**, A1010 (1965).

²¹G. W. F. Drake and A. Dalgarno, *Phys. Rev. A* **1**, 1325 (1970).

²²E. Holøien, *Nucl. Instr. Methods* **90**, 229 (1970); and (private communication).

²³L. Lundin, H. Oona, W. S. Bickel, and I. Martinson, *Physica Scripta* **2**, 213 (1970).

²⁴W. L. Wiese, M. W. Smith, and B. M. Glennon, *Atomic Transition Probabilities*, U. S. Natl. Bur. Std. National Reference Data Series-4 (U. S. GPO, Washington, D. C. 1966), Vol. I.

²⁵P. M. Becker and J. S. Dahler, *Phys. Rev.* **136**, A73 (1964).

²⁶J. Bromander and H. G. Berry (unpublished).

²⁷S. Goldsmith, *J. Phys. B* **2**, 1075 (1969).

²⁸B. Edlén and F. Tyrén, *Nature* **143**, 940 (1939); and (unpublished).

²⁹M. Siegbahn and L. Lundin (unpublished).

Analytic Self-Consistent-Field Wave Functions for the $(3d)(4s)$ Configuration of the Transition-Metal Ions

James M. Minor and Raymond W. Mires

Department of Physics, Texas Technological University, Lubbock, Texas 79409

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The Roothaan method has been used to calculate analytic self-consistent-field functions for the excited $(3d)(4s)$ configuration for the first-row transition-metal ions which normally have a $(3d)^2$ ground configuration. Wave functions are calculated for both 1D and 3D multiplets arising from the excited configuration. The separations of these two multiplet levels from the ground $(3d)^2\ ^3F$ level deviate from experiment by 3–8%.

INTRODUCTION

In two recent publications^{1,2} the effect of electron correlation on the multiplet structure of open-shell atoms and ions was investigated. The electron configurations of interest were $(2p)^2$ and $(3d)^2$, and the starting point for all of the calculations was the self-consistent-field (SCF) functions. The results were very satisfying and prompted an extension of the method to the case of two nonequivalent electrons outside of closed shells. For this purpose, the $(3d)(4s)$ excited configuration of those transition-metal ions which normally have a $(3d)^2$ ground configuration was chosen. However, the SCF func-

tions for the 1D and 3D levels arising from this excited configuration were not available. This and the need for such functions in optical studies and configuration interaction calculations made it apparent that the SCF functions for this configuration should be generated and made available in the literature.

In this paper, the results of an SCF calculation based on the expansion method³ are reported for the two multiplet levels of the $(3d)(4s)$ configuration of the transition-metal ions Ti III through Ni IX. For the first three ions in this series, the results are compared with experimental data. All the computation was done in double precision on an IBM 360/50

computer.

RESULTS AND DISCUSSION

The results of this calculation are shown in Table I of Ref. 4. The choice of basis set was a compromise to ensure a reasonable computation time and yet produce sufficiently accurate wave solutions for energy calculations. The diagonalization threshold for all of the solutions was 10^{-6} , and the SCF threshold was of the order of 10^{-5} . The notation, units, and terminology are the usual ones.

Table I is organized according to atomic number and the particular multiplet as given on the first line of each block. Under "basis" are shown the Slater-type orbitals (STO) used to expand the SCF solutions. The basis sets are grouped according to the azimuthal symmetry of the SCF orbital. In each group, the n and l values for each STO are given in the first column and the orbital exponents ζ are given in the second column. Under "eigenvectors and orbital energies" are presented the expansion coefficients that multiply each STO in the expansion, grouped according to the SCF orbital being expanded. Below these are the orbital ener-

gies, the total energy, and how well the virial theorem was satisfied.

Table II of Ref. 4 compares the results with experiment for those ions where experimental data were available.⁵ In this table, the theoretical energies were calculated as the difference between the total energy of each multiplet from Table I and the calculated total energy of the $(3d)^2\ ^3F$ level from Table I of Ref. 2. Also for the $(3d)(4s)\ ^3D$ level, the experimental energy is the average over the three spin-orbit split J levels. From this table, it is clear that the calculated energies for the excited configuration are in good agreement with experiment. However, the calculated $(3d)(4s)\ ^1D\text{-}^3D$ spacing is considerably different from that obtained by taking differences in the experimental energies; but this is to be expected since, in each case, it is the difference between two large numbers both of which may have considerable error.

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¹J. M. Minor and R. W. Mires, Phys. Rev. **185**, 16 (1969).

²J. M. Minor and R. W. Mires, Phys. Rev. A **1**, 14 (1970).

³C. C. J. Roothaan and P. S. Bagus, in *Methods in Computational Physics*, edited by B. Alder, S. Fernbach, and M. Rotenberg (Academic, New York, 1963), Vol. 2.

⁴ASIS-National Auxiliary Publication Service Document

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⁵C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Std. Circular No. 467 (U. S. GPO, Washington, D. C., 1949).