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Analytical Self-Consistent Field Calculations for Mn^{3+} and Its Excited Configurations*

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Analytical self-consistent field functions were calculated for the Mn^{3+} ground state, and for several Mn^{3+} excited configurations with two and three open shells of different symmetries. The cusp condition is precisely satisfied. The deviations from the nodal condition for the radial functions $P_{i\lambda}(r)$ never exceeded 0.00010. The energy levels of the three-open-shell states, calculated in this work, have been neither measured nor calculated before.

INTRODUCTION

FOR some time, the transition elements have been an important subject for analytical self-consistent field (SCF) calculations. This endeavor was started with the work of Watson[1,2] who calculated the ground states, and some excited states with one open shell, for the first group of transition atoms. Later, Clementi[3,4] made extensive calculations, including the negative ions of the iron series.

A remarkable contribution to the SCF theory was made by Löwdin,[5,6] in the relation to the cusp condition, the scaling problem, and the virial theorem.

Calculations of the excited states with two and three open shells of different symmetries were facilitated by the expansion method of Roothaan.[7] The calculated tables of vector coupling coefficients cover all the states of $s^l p^m d^n$ and f^l configurations.[8]

Our group has applied the SCF expansion method to a number of cases.[9–14] Special attention was paid to the excited configurations[10,13] of Cr and Cr^{3+}. (All these calculations have been nonrelativistic. It would be premature to speak here about an application of an analytical relativistic theory.[15])

In this work the analytical SCF calculations were carried out for the ground state and for several excited states of Mn^{3+}, including the excited configurations $3d^24s4p$, $3d^34s$, and $3d^34p$.

The computation was done with a program[7] for an IBM-7094 computer.

RESULTS AND DISCUSSION

The notation, the atomic units and the terminology used are the usual ones and are closely related to those employed in recent works.[9–13] Some of the important results are presented in Tables I–V.[16]

It is assumed that the results represent the Hartree-Fock radial functions $P_{i\lambda}(r)$ to about three decimal places. Registered deviations from the nodal condition for the functions $P_{i\lambda}(r)$ did not exceed 0.00010. The cusp condition was exactly satisfied so that the wave functions are particularly accurate in the immediate vicinity of the nucleus.

A comparison with experiment,[17] done in a usual way,[9,10] is presented in Table I. However, no experimental values were available for comparison with the results on the three-open-shell excited states.

The calculated total energy for the ground state

TABLE I. Total energies E for states of Mn^{3+}.

Configuration	State	Calculated total energy	Estimate of correlation energy difference
$3d^24s4p$	^1H	−1146.1274	...
	^3H	−1146.2972	...
	^5P	−1146.3355	...
	^5F	−1146.4483	...
	^5G	−1146.4507	...
$3d^34s$	^5F	−1147.3907	0.0049
$3d^34p$	^5G	−1147.1464	−0.0099
$3d^4$	^5D	−1147.9047	0

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[15] M. Synek, Phys. Rev. **136**, A1552 (1964).

[16] The analytical expansions of the wave functions, the orbital energies and the values for the virial theorem are given in Tables II–V. These tables are deposited as Document No. 8442 with the American Documentation Institute, Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. A copy may be secured by citing the Document number and by remitting \$1.25 for photoprints, or \$1.25 for 35 mm microfilm. Advance payment is required. Make checks or money order payable to: Chief, Photoduplication Service, Library of Congress.

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happens to agree with the calculated value of Clementi[4] to almost eight significant figures. However, no theoretical values were available for comparison with the results on the two-open-shell and three-open-shell excited states.

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Exact Calculation of *K*-Shell and *L*-Shell Photoeffect*†

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An exact calculation of the atomic photoelectric effect is made. The expressions for the differential and total cross sections are developed explicitly for the K and L shells, for a pure Coulomb potential. The final electron is described by a partial-wave decomposition, and the interaction with the radiation field is treated in lowest order perturbation theory. The cross sections are evaluated numerically, and the contribution of the L shell is found to be non-negligible when compared with the K shell. The results for the K shell are compared with previous work, and agreement is obtained. The new results for the L subshells are presented and compared with the available experimental work.

I. INTRODUCTION

INVESTIGATIONS of the atomic photoelectric effect have been concerned primarily with the K shell. This is because about 80% of the total atomic effect is due to the K shell; and because the simplest picture possible, that of just a pure Coulomb potential due to a nucleus of charge Ze, is most nearly approximated by the K shell, away from threshold.[1] The assumption of any more general type of potential necessitates a numerical solution of the Dirac equation for the initial and final electron states, and such a solution was essentially impossible before the development of modern fast computers. Thus the L and higher shells have usually been neglected on the basis that the effects of screening are appreciable, so that calculations based on a pure Coulomb potential would have questionable significance.

In the original period of investigation the theoretical work was primarily nonrelativistic, except for the papers of Sauter,[2] Hall,[3] and Hulme *et al.*[4] Since the revival of interest, several years ago, all of the work has been relativistic. K-shell differential and total cross sections have been obtained in the form of analytical expressions, approximate in αZ, where α is the fine-structure constant and approximately 1/137. Some of these are valid for a general energy,[5–8] and some have been obtained for the high- or low-energy limit.[9–11] Additionally, there have been numerical evaluations in the various energy limits.[12–14] The most recent and most extensive numerical work is that of Pratt *et al.*,[15] giving differential and total K-shell cross sections for a number of Z's and for photon energies from 0.2 to 2 MeV.

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† Based in part on a doctoral dissertation submitted by one of us (W.R.A.) to the Department of Physics, the University of Notre Dame.

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[5] In succeeding footnotes, the symbols (HE) and (GE) indicate high energy and general energy, respectively.

[6] D. Moroi and C. J. Mullin (to be published) (GE). It has been shown here that for any initial s state, characterized by principal quantum number n, the corresponding differential and total cross sections can be written as $1/n^3$ times that for the K shell, to the neglect of relative order α^2Z^2. This result was previously obtained by R. H. Pratt, Ref. 16. This affords an easy way of determining approximate differential and total cross sections for s states of higher shells.

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