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Oscillator Strengths for Highly
Ionized Atomic Systems

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I ABSTRACT

A general program for multi-configuration Hartree-Fock calculations (MCHF77) and a technical report describing the use of the program have been prepared. The program will be available for distribution.

Several f-value trends have been studied using the MCHF approach.

i) $4s^2 1S - 4s 4p^1 P$ Transitions in the Zn Sequence

The effect of core polarization from the $3d^{10}$ shell was included in the calculation and relativistic effects estimated. The former decreases with increasing nuclear charge and does not account for the discrepancy of almost a factor two in theoretical and observed f-values for Kr VII. The present f-values are the most accurate theoretical ones determined to date.

ii) $3s^2 4s^2 S - 3s^2 4p^2 P$ Transition in the Al Sequence

The incomplete $n = 3$ subshell in the core introduces both correlation in and with the core reducing the f-value even at high Z . At the same time cross-overs of configurations occur, but only some cause irregularities in the f-value trends.

iii) $\{3p^2, 3s 3d\}^1 D - \{3p 3d, 3s 4f\}^1 F$ and $3s 3d^3 D - \{3p 3d, 3s 4f\}^3 F$ Transitions in the Mg Sequence

Accurate f-values have been determined. Few experimental values are available, but generally good agreement is observed.

Correlation and spin-orbit interaction were combined in an energy level calculation for $Ar^{+2} 2p^5 3p^5$. When radial functions for an average configuration are used, interaction with configurations differing by a single electron reduced the spread in the levels. Cowan achieves a similar result by multiplying all Slater integrals by a factor between 0.80 - 0.90.

II RESEARCH PROGRESS

Research progress proceeded in three different but related areas.

i) Software for Atomic Structure Calculations

Theoretical f-values for isoelectronic sequences were computed using the multi-configuration Hartree-Fock (MCHF) method for which a general computer program, MCHF72, had been developed [1] and distributed to numerous users. A recent analysis [2] had shown how the stability of the methods implemented in the program could be improved, yielding a more rapid rate of convergence in some cases. It was also found that by introducing rotations into the solution process, the systems of equations could be solved on a one-at-a-time basis leading to considerable simplification.

All these changes were incorporated into MCHF77 as well as some requested from present users of the code. The result is a more efficient, more robust code capable of handling a wider range of problems. In some instances accuracy has also been tightened.

A technical report describing the way in which the program can be used has been prepared [3]. The program MCHF77 has been accepted for publication [4] by Computer Physics Communications and several prepublication copies has been distributed.

The program developed by Klotz [5] for the calculation of spin-orbit interaction, and modified by Saxena [6] to accept data in a more natural spectroscopic notation has been adapted to allow for a more convenient combination of both electrostatic and spin-orbit interaction. We expect this program to be important in future research.

ii) F-Value Trends

Radiative transition rates for resonance transitions of certain elements of the Cu and Zn sequence are important in fusion plasma

research, yet large discrepancies exist between theoretical f-values and those deduced from beam-foil experiments for moderately ionized systems. For example, for Kr VIII $4s^2 S - 4p^2 P$

$$f_{\text{obs}} = 0.55 [7]$$

$$f_{\text{HF}} = 0.865$$

$$f_{\text{MCHF}} = 0.739 .$$

The latter, an accurate theoretical value [8] verified also by a many-body perturbation calculation [9], is a considerable improvement over the cruder HF value but still is not anywhere near the error claimed for the experimental value. This situation is typical of the Zn sequence also.

Accurate MCHF f-values have been computed for the $4s^2 S - 4p^2 P$ transition of the Cu sequence as well as the $4s^2 1S - 4s 4p^1 P$ transition of the Zn sequence. Both were mentioned in the original proposal but the Cu calculations had been completed before the grant was awarded and will not be included in this report. Calculations for the Zn sequence have just been completed.

Unlike the relativistic random phase approximation (RRPA)[10], and Cowan's [11] relativistic results for the Zn sequence which have been published recently, our calculation includes not only the correlation between the outer two electrons, but also correlation with the $3d^{10}$ group in the core, an effect referred to as core polarization. On the other hand, relativistic effects are estimated by using observed energy differences and by including spin-orbit interactions. Table 1 presents non-relativistic f-values for several approximations as more correlation is added. It shows

TABLE 1

Non-relativistic f Values for the Zn-sequence

	HF		+ Outer Correlation		+ Core Polarization	
	length	velocity	length	velocity	length	velocity
Zn I	1.98	.95	1.73	1.65	1.53	1.45
Ga II	2.53	1.45	1.97	1.87	1.71	1.63
Ge III	2.51	1.51	1.96	1.85	1.71	1.63
As IV	2.40	1.50	1.90	1.80	1.67	1.61
Se V	2.29	1.47	1.84	1.75	1.63	1.57
Br VI	2.19	1.44	1.78	1.70	1.58	1.54
Kr VII	2.10	1.40	1.72	1.65	1.54	1.50
Mo XIII	1.69	1.20	1.43	1.39	1.30	1.29
Sn XXI	1.35	1.00	1.15	1.14	1.07	1.08
Xe XXV	1.23	0.92	1.05	1.05	0.99	0.99
Sm XXXIII	1.04	0.79	0.90	0.90	0.85	0.86
W XLV	0.84	0.65	0.73	0.74	0.70	0.72

clearly that core polarization reduces the f -value by about 13% at the neutral end, that the effect decreases slowly with increasing nuclear charge but even for Mo VII still accounts for a reduction of only 9.0%.

In Table 2 the present f -values corrected for relativistic effects are compared with several direct relativistic methods and experiment. The RRPA and Cowan results both include only outer correlation and excellent agreement is observed up to at least Xe XXV between these values and our approximate relativistic values including only outer correlation. We conclude that our relativistic correction is reliable in this region, and that our approximate relativistic results including both outer correlation and core polarization are the most accurate theoretical values in this region. Even so, except for the neutral atom, the theoretical values are 25-100% larger than the observed. Since relativistic effects increase the f -values, the source of the discrepancy in the theoretical value cannot be explained.

The calculations for the Cu sequence suggested that correlation within the core, a factor usually neglected in theoretical f -value computations, might be a contributing factor. In order to understand better the role of the core, a calculation for the $4s^2S - 4p^2P$ transition of the Al sequence was undertaken. It soon became apparent that the fact that the $n = 3$ shell was incomplete was of great importance, that cross-overs with the "plunging" configuration mentioned by Weiss [16] may cause irregularities in the trend. However, unlike other cases considered by Weiss not all cross-overs produce irregularities. The results have been submitted for publication.

TABLE 2

A Comparison of the Present Approximate Relativistic
f-values with other Theoretical Values and Experiment

	HF	+ Outer Correlation	+ Core Polarization	RRPA [10]	Cowan [11]	Obs.
Zn I	2.02	1.77	1.56	1.59		1.35 ^a
Ga II	2.58	2.01	1.75	1.97		1.39 ^a
Ge III	2.56	2.00	1.74	1.98		1.38 ^a
As IV	2.46	1.94	1.71			1.12 ^a
Se V	2.36	1.89	1.68			0.96 ^a
Br VI	2.27	1.84	1.64	1.84	1.91	0.82 ± .12 ^b , 0.82 ^c
Kr VII	2.19	1.79	1.61		1.85	0.94 ± .04 ^d , 0.87 ^c
Mo XIII	1.86	1.54	1.40	1.54	1.57	
Sn XXI	1.63	1.31	1.22		1.32	
Xe XXV	1.60	1.25	1.18	1.24	1.24	
Sm XXXIII	1.60	1.19	1.12	1.15		
W XLV	1.75	1.19	1.15	1.15	1.16	

a) Sorensen [12]

b) Pinnington et al [13]

c) Knystanatas and Drouin [14]

d) Irwin et al [15]

Finally, the MCHF method is particularly well suited for cases which are essentially two-electron problems such as states of the Mg sequence, where correlation with the core is small. Several calculations have been reported recently [19, 18] but none have attempted f-value trends for $1D - 1F$ or $3D - 3F$ transitions. Particularly for the $3s\ 3d - 3s\ 4f$ transition, where relativistic effects will remain small for reasonably high Z , the MCHF approach should be able to yield accurate f-values. Some of the f-values in this sequence are of interest in astrophysics [19]. They conceivably could also be useful for cascading analysis for beam-foil data being part of the more dominant "yrast" cascade [20].

Calculations for these cases are nearing completion. Some preliminary results are presented in Table 2 and several observations may be noted. Generally there is good agreement between the length and velocity form of the f-value indicating that the MCHF approximation has indeed accounted for correlation between the outer electrons. For Fe ($Z = 26$) there is excellent agreement between the theoretical and observed transition energy supporting our assumption that relativistic effects will remain small even at high Z . Finally, there is unusually good agreement between the present results and those from beam-foil experiments.

TABLE 3

f-values for D-F Transitions of the Mg Sequence

Z	$\lambda(\text{\AA})$		present f-values		other f-values	
	th	obs	len	vel	theory	exp.
i) 3s 3d 1D - 3s 4f 1F						
12	11607	12084	.4723	.4715	.52 ^a	
13	7685	7471	.6236	.6243	1.1 ^b	
14	2665	2559	.2321	.2299	1.1 ^b , .43 ^c	
15	1067		1.4361	1.4326		
16	690.6		1.1414	1.1348		
17	471.1		.9393	.9315		
18	341.2		.8421	.8339		
20	203.6		.7561	.7487		
26	73.67	73.47 ^d	.6942	.7041	.702 ^d	
30	46.42		.6852	.6746		
50	11.47		.6774	.6728		
ii) 3s 3d 3D - 3s 4f 3F						
13	3630.	3588	0.6165	0.6462	.678 ^e	0.562 ^f , 0.422 ^g
14	1520	1501	1.0073	0.9463	.987 ^c	0.93 ^h , 0.42 ⁱ
15	883.9	877	0.9164	0.9052		0.77 ^j , 0.40 ^k
16	574.0		0.8670	0.8715		
18	299.8		0.8499	0.8655		
20	185.3		0.8552	0.8724		
26	70.19	70.0 ^d	0.8978	0.8875	.906 ^d	
50	11.30		0.9609	0.9543		

TABLE 3 - CON'T.

Z	$\lambda(\text{\AA})$		f-value		other	
	th	obs	len	vel	theory	exp.
iii) 3s 3d 3D - 3p 3d 3F						
14	1838	1782	0.0015	0.0008	0.0 ^c	
15	1414	1370	0.1515	0.1150		0.127 ^j
16	1162		0.1952	0.1676		
18	855.5	825	0.2040	0.1914		0.20 ^l
20	675.5	650	0.1921	0.1864		
26	413.3	384	0.1510	0.1507		
50	162.0		0.0761	0.0772		

a) Trefftz [21]

b) Weiss et al [22]

c) Trefftz and Zare [23]

d) Cowan and Widing [24]

e) Weiss [25]

f) Andersen et al [26]

g) Andersen et al [27]

h) Livingston et al [28]

i) Berry et al [29]

j) Livingston et al [30]

k) Curtis et al [31]

l) Livingston [7]

iii) Analysis of Spectra

Term energies of multiply ionized atoms are of fundamental interest in Auger-electron and X-ray spectroscopy. Recently Nordgren et al [32] analyzed the L X-ray emission spectrum of argon from which the relative energy levels in $2p^5 3p^5$ of Ar^{+2} can be deduced. Ridder and the principal investigator have collaborated on a theoretical analysis of these energy levels.

Though not part of the original proposal, the research problem required similar techniques to those being developed for oscillator strengths. Because of the 2p-hole, both correlation and spin-orbit interreaction are important. In fact, the problem exhibits many of the properties of more highly ionized systems.

A manuscript which has been submitted for publication is attached.

iv) REFERENCES

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II PRINCIPAL INVESTIGATOR'S CONTRIBUTION

During the period, May 1 - August 31, the principal investigator devoted at least three months full time to this research project, the amount specified in the proposed budget. During the remainder of the year, September 1 - April 30, 10 - 20% of the principal investigator's time is devoted to the research project and collaboration with the research associate, Dr. Jorgen E. Hansen, who is working on the grant full time.

III RESEARCH PUBLICATIONS

1. "A General Program for Multi-Configuration Hartree-Fock Calculations," Computer Phys. Commun. (accepted for publication).
2. "A General Multi-Configuration Hartree-Fock Program - MCHF 77", Technical Report No. 225, Computer Science Department, Penn State Univ., 1977.
3. "The $4s^2 2S - 4p^2 2P$ Transition of the Al Sequence," submitted to Canadian J. Phys. (copy attached).
4. "Levels of $2p^5 3p^5$ in Ar^{2+} ," with D. Ridder, to be submitted to J. Phys. B (copy attached).
5. "The $4s^2 1S - 4s 4p^1 1P$ Transition of the Zn Sequence," with J. E. Hansen (in preparation, to be submitted to Phys. Rev.).
6. "Oscillator Strengths for some D-F Transitions of the Magnesium Sequence," (in progress).