MASTER

C00-4264-13

Oscillator Strengths for Highly
Ionized Atomic Systems

Final Report
for period May 1, 1977-December 30, 1979
Contract No. EG-77-S-02-4264

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December 1979

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Abstract

Oscillator strengths (or f -values) for resonance transitions in highly ionized atoms have assumed importance in fusion plasma research. Beam-foil spectroscopy has been able to deduce some of these values but present experimental limitations restrict its applicability. A theoretical study of trends along an isoelectronic sequence has provided an alternative approach.

The Multi-configuration Hartree-Fock method (MCHF) is a general theoretical method for determining wavefunctions for atomic states from which oscillator strengths can be computed. A first-order theory has been shown to yield reliable f -values provided the ionization energy is predicted with reasonable accuracy and the transition matrix element is not sensitive to cancellation effects. General computer programs have been developed for this method and extended to include the dominant relativistic effects.

I. Introduction

Highly ionized heavy atoms (Mo, W, Au) appear as impurities in Tokamak devices for fusion research and induce strong radiative energy loss. Atomic oscillator strengths (or f-values) are a prerequisite for the analysis and the control of the impurity problem¹⁾.

One approach to the determination of such f-values is through the study of trends in an isoelectronic sequence where only the nuclear charge, Z, varies. For low degrees of ionization, experimental energy levels are available and the energy relative to the ionization limit may be used as a check on the accuracy of the wavefunction. Some experimental f-values also may be available. For neutral atoms these provide a check on the accuracy of a theoretical f-value and often good agreement with experiment is observed. For the more highly ionized systems, where experimental results are obtained from beam-foil data, systematic discrepancies have been found even though relativistic effects are still small.

The purpose of this research was to perform accurate theoretical f-value calculations using the multiconfiguration Hartree-Fock (MCHF) method²⁾ in order to predict f-values for highly ionized systems. Several trends for sequences with two or three electrons outside closed shell were studied.

II. Theoretical Determination of f-values.

The f-value for a transition from an initial state to a final state is defined in terms of a transition matrix element

$$I = \langle \psi' | O_p | \psi \rangle \quad (1)$$

where O_p is either a dipole length or velocity operator and ψ, ψ' are the total wave functions for the initial and final states respectively.

In the independent particle model, ψ may be approximated by a Hartree-Fock configuration state function, Φ^{HF} . The latter neglects correlation in the motion of the electrons. Such correlation effects can be included in a multi-configuration Hartree-Fock (MCHF) approximation of ψ .

As in perturbation theory, an expansion of the exact total wave function in terms of configuration state functions, can be partitioned so that

$$\psi = \psi_0 + \psi_1 + \dots$$

where $\psi_0 = \Phi^{\text{HF}}$ plus configurations state functions which have a large component in ψ , and ψ_1 includes all configuration states which interact with ψ_0 . The configuration states defining the latter still, unfortunately, form an infinite set. Experience has shown that for transition probability studies an approximate wave function should include enough configuration states so that the energy relative to the ionization limit for the electron undergoing the transition is predicted fairly accurately. This restricts the configuration states to selected pair-correlation functions. For two-electron systems outside a closed shell, only the correlation between the two electrons enters into this phase of the calculation.

Once a set of configuration states has been determined to yield sufficiently accurate ionization energies, additional correlation effects must be included which may not contribute appreciably to the energy but affect the transition matrix element to first order.

An expansion for ψ' , similar to the one in Eq. (2) for ψ , naturally leads to an expansion for I , namely

$$I = I_0 + I_1 + \dots$$

where

$$I_0 = \langle \psi'_0 | O_p | \psi_0 \rangle$$

$$I_1 = \langle \psi'_0 | O_p | \psi_1 \rangle + \langle \psi'_0 | O_p | \psi_0 \rangle.$$

Since the operator of Eq. (1) is a one-electron operator, selection rules apply and many configuration states in ψ_1 (or ψ'_1) make no contribution to I_1 . Thus the problem of determining I_1 is considerably simpler than a full correlation study. For two electron systems the additional configurations involve correlation between the electron undergoing the transition and the core, an effect on the transition matrix element referred to as "core polarization".

A final check on the accuracy of the non-relativistic f-value is the lack of agreement in the length and velocity form along the sequence. Though agreement using theoretical values of the transition energy does not assure accuracy, the lack of agreement, particularly when observed energies are used, does indicate a lack of accuracy. No precise error bounds can be obtained at present for systems with more than a few electrons.

For the more highly ionized atoms, relativistic effects become important. However, Younger and Weiss³⁾ have shown that relativistic effects on transition matrix elements I for $\Delta n = 0$ transitions are less than 10% for up to 40 stages of ionization, provided no level crossings occur. The effects on the transition energy is much greater.

In this research we have used the Desclaux' multiconfiguration Dirac Fock program⁴⁾, at times, to determine a relativistic transition energy when observed values were not available. Only a few configurations were included in such calculations. The effect of spin-orbit interaction on the wave-function was taken into account by an intermediate coupling calculation. This approach was used in the study of the resonance transition for the Zn sequence.

An alternative approach has been to include certain relativistic corrections in the energy diagonalization phase of the MCHF calculation. Only those corrections which shift the energy of one configuration relative to another, namely the mass-velocity correction, the Darwin term, and the spin-spin contact term were included. The MCHF radial functions may then be used in an intermediate coupling calculation which includes spin-orbit interactions, electrostatic interactions, and the "relativistic shift" effects mentioned above. This procedure has been checked in the helium sequence on the $1s2p\ ^3P^o_1$ and $^1P^o_1$ state. Unlike Laughlin⁵⁾ who performed a first order perturbation study of intercombination lines and concluded that the breakdown of LS coupling was not accurately predicted beyond twelve stages of ionization, we found our results were reasonably accurate up to FeXXV. In fact, we found that the spin-orbit parameter computed by MCHF was not accurate for low Z, and only after several degrees of ionization were $^3P^o_1$ and $^1P^o_1$ mixed through spin-orbit interaction so as to produce an f-value for an intercombination line in reasonable agreement with the relativistic random phase results of Lin et al⁶⁾. The main difference between our approach and Laughlin's is that in our intermediate coupling calculations the relativistic shift corrections modify the effect of the spin-orbit interaction.

At the same time our spin-orbit parameter is an approximation to the spin-orbit operator. A report on this study performed by M. Godefroid is in preparation.

III. F-value Trends.

The theoretical methods outlined in the previous section have been applied to the study of several trends.

a) The Zn Sequence.

Radiative transition rates for resonance transitions of certain elements of the Cu and Zn sequence were important in fusion plasma research, yet large discrepancies existed between theoretical f-values and those deduced from earlier beam-foil experiments for moderately ionized systems.

Some examples are given below:

Kr VIII $4s^2 S - 4p^2 P$ (Ref. 7) Kr VII $4s^2 1S - 4s4p^1 P$ (Ref. 8)

$$f_{\text{obs}} = 0.550$$

$$f_{\text{obs}} = 0.94$$

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

$$f_{\text{HF}} = 2.19$$

$$\begin{matrix} (\text{Rel}) \\ f_{\text{MCHF}} \end{matrix} = 0.772$$

$$\begin{matrix} (\text{Rel}) \\ f_{\text{MCHF}} \end{matrix} = 1.61$$

The MCHF theoretical values represent considerable improvements over the cruder HF values but still are not anywhere near the experimental values. The simulation study performed by Younger and Wiese⁹⁾ suggested that the source of the discrepancy lay in the analysis of the beam-foil decay curve; that cascade effects produced a "growing-in" of the measured decay curve. Livingston et al¹⁰⁾ have repeated a study of

Kr VIII obtaining a value of $f = 0.78 \pm 0.03$, in excellent agreement with theory.

The primary cascade is from the $4s4d\ ^1D$ state but for many of the more highly ionized species only the resonance transition has been observed. As in the analagous Mg I sequence, there is strong interaction with $4p^2\ ^1D$ and the crossing of the $\ ^1D$ sequences has only recently been observed¹¹⁾. A study of the $4s4d\ ^1D - 4p^2\ ^1D$ interaction was undertaken and gf values predicted for transistons from $4s4p\ ^1P$ to these two states¹²⁾. Some of the earlier experimental data was found to be in error.

b) The Mg Sequence.

Accurate relativistic and non-relativistic f-values have been published for S-P and P-D transitions but not for D-F transitions of the Mg sequence. A fairly large number of beam-foil results were available for the $\ ^3D - ^3F$ transitions of this sequence. A theoretical study of this transiion was performed¹³⁾.

In the $\ ^1,3F$ sequence there is strong interaction, at least at the lower stages of ionization, between $3s4f$ and $3p3d$. It was found that the theoretical f-values are in excellent agreement with the beam-foil results for transitions to the lower $\ ^3F$ state which is predominantly $3s4f$ for Mg I and Al II, and predominantly $3p3d$ for higher degrees of ionization. Large discrepancies exist with beam-foil data to the upper $\ ^3F$ state as seen in Figure 1.

Figure 1. Theoretical and experimental f -values for transitions from the $3D$ state to $3F_u$ (upper) and $3F_l$ (lower). Open circles represent experimental values for the lower state, and closed circles for the upper state.

c). The Al Sequence.

The $3p^2 P \rightarrow 3d^2 D$ and $3p^2 P \rightarrow 3p^2 2D$ transitions of the Al sequence have been a long standing test case for theory and experiment alike. Again there is reasonable agreement between theory and experiment for transitions to the lower $2D$ state, but systematic discrepancies seem to be present for transitions to the upper $2D$. 14)

The experimental f-values were deduced from beam-fail data. Since the latter measures the lifetime of a state, calculations were undertaken to determine lifetimes of some of the more important cascades. The results are presented in Table 1.

Table 1. Life times of some 2P , 2D , and 2F states in the Al I sequence (in units of 10^{-9} sec.).

	Al I	Si II	P III	IV	Cl V	Ar VI
$3p^2\ ^2D$		850.00	17.60	6.400	3.500	2.300
$3d\ ^2D$	12.5	0.35	0.14	0.091	0.069	0.056
$(^3P)3d\ ^2F^o$		0.55	0.24	0.160	0.130	0.110
$(^1P)3d\ ^2F^o$					0.069	0.048
$4p\ ^2P^o$	210000.0		2.71			
$4d\ ^2D$	37.0	1.12	1.16			
$4f\ ^2F^o$	54.9	3.10	0.67	0.200*	0.055*	0.032*

* Upperbounds to lifetimes.

Clearly, the lifetimes of the lower $3p^2\ ^2D$ states are much longer than those of the cascades, whereas those of the upper $3d\ ^2D$ states are either shorter or of similar duration. Transitions from both $3s3p(^1,^3P)3d\ ^2F^o$ and $3s^2\ 4f\ ^2F^o$ may contribute to the cascade problem for the

higher stages of ionization. For lower degrees of ionization where the discrepancy is not as large, the theoretical results may be in error due to the neglect of core polarization. At first sight it would appear that core polarization should affect the f -values for both $2D$ states in a similar way, but because of a difference in phases there could be cancellation in one case and enhancement in the other. Indeed, the correction for the $3p^2 2D$ state exhibits cancellation but because the transition matrix element itself is smaller a larger percentage reduction is observed than for $3d 2D$. For the latter in Si II, a reduction of 1.7% was obtained, leaving a discrepancy of 11.8% with experiment to be accounted for.

d) Excited State Transitions.

Most f -value trends investigated to date have been either for $\Delta n = 0$ transitions or for resonance transitions. Little attention has been given to transitions between excited states since these are not as important in fusion research or in astrophysics. However, such studies are needed to complete our understanding of f -value trends.

A study of the $4s^2 S - 4p^2 P$ transition¹⁴⁾ in the Al I sequence was undertaken to determine the effect of the incomplete $1s^2 2s^2 2p^6 3s^2$ core. Since the electron undergoing the transition is well outside the core, both in the initial and the final state, one could naively expect a smooth f -value trend. Instead marked irregularities are present as seen in Figure 2.

Figure 2. f-value trends for the $4s^2S - 4p^2P$ transition in the Al I sequence.

These irregularities are produced by energy level crossings with "plunging" configurations, configurations with all electrons in the $n = 3$ shell and lying in the continuum at lower stages of ionization. Such configurations have a fairly small interaction matrix element with an excited state and perturb the wavefunction appreciably only in the vicinity of the cross-over. In fact, more irregularities may be present

since the curve in Fig. 2 is a "smooth" curve passing through the f -values for integral values of Z only.

In a theoretical calculation the nuclear charge Z may be treated as a continuous variable and it is enlightening to consider the behavior of f -value trends in the presence of cross-overs.

Consider the 2S states of the boron sequence. In B I the lowest state is $2s^2 3s^2 S$ and the next $2s 2p^2 ^2S$, but in C II the two states already have reversed order. Thus the energy levels of these two interacting configurations cross between $Z = 5$ and $Z = 6$. Model configuration interaction calculations were performed for non-integral Z values using fixed core Hartree-Fock radial functions. As is well known, when the energies of two interacting configurations cross the eigen energy of the upper/lower eigen state varies continuously and the two eigen energy curves do not actually cross. The dominant component of the eigenfunction changes, though the relative phases remain the same along the curve.

In Figure 3, f -values are plotted for transitions from the ground state to these two excited states. In this case there is an allowed transition matrix element between the ground state 2P configuration and each of the two interacting 2S configurations. Since these matrix elements are relatively constant over the present range of Z values, we have an enhancement of the f -value to one eigenstate (the upper). For each eigenstate the f -value is a smooth, continuous curve. Notice, however, that a discontinuity is present when f -values trends are plotted for a given dominant component,

Figure 3. The $2s^2 2p \ ^2P - \ ^2S$ f-values as a function of Z from model CI calculations for Boron sequence.

producing a curve similar to the Fano profile¹⁵⁾ for a line in the continuum. (Since the $2p \rightarrow 3s$ and $2s \rightarrow 2p$ dipole matrix elements are almost equal in magnitude in this case, the peak of the enhancement and zero of the f-value occur at the cross-over point). Here the cross-over occurs near the middle of the interval and f-values for integral Z -values can be joined by a relatively smooth curve. Thus irregularities in f-value trends may be "missed" when only integral values of Z are considered.

In Figure 4 f-values are plotted for transitions from the $2s^2 3p \ ^2P$ state which have allowed transitions only to the $2s^2 3s$ component of the $\ ^2S$ states. Again, the f-values for the two eigenstates (upper or lower) are continuous but now the f-values for the states with a given dominant component

Figure 4. The $2s^2 3p^2 P - 2s^2 3s$ f-values as a function of Z from model CI calculations for Boron sequence.

are also continuous, though a "resonance window" is observed in the $3s^2 S - 3p^2 P$ f-value trend whereas a "resonance peak" is present in the $2s2p^2^2 S - 3p^2 P$ trend. At the cross-over point the amount of $2s^2 3s$ present in the eigenstate is exactly 50%. Thus, the effect of the interaction is to reduce the f-value by a half, assuming the transition energy is relatively unchanged. In retrospect the dips in the $4s^2 S - 4p^2 P$ f-value trends (Fig. 2) should have been more pronounced and cross-overs occurring between non-integral Z -values should have produced further irregularities.

IV. Conclusion

This research has shown that reliable f-values for many transitions can be obtained using the MCHF method for at least moderately ionized systems. Further studies are needed to determine the adequacy of the simpler relativistic corrections incorporated into an intermediate coupling calculations. Work is underway to include the more accurate nuclear spin-orbit, spin-other orbit, and spin-spin interactions in the calculation rather than a simple spin-orbit parameter.

Considerable discrepancies still exist between theory and experiment for f-value trends in the $4s^2 1S - 4s 4p^1 P$ resonance transition in the Zn I isoelectronic sequence, and the $3p^2 P \rightarrow 3d^2 D - 3s4f^3 F$ transition in the Mg I isoelectronic sequence. Further experimental investigations would be valuable, though for both the Zn I and the Al I sequence, the energy level data needed for including the cascading corrections is often not available.

This research also has shown that there are similarities between f-value trends between excited states, where the parameter is the nuclear charge, and the problem of photo-ionization cross-sections in the continuum, where the parameter is the energy of the free-electron. Since observed energy level data can be used to check the adequacy of a theoretical wave-function further studies for excited states could help elucidate some of the many problems encountered in continuum problems where energy cannot be used as a check on theory and experimental data is scarce.

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VI. Research Publications

A. Journal Publications

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2. "A General Multi-Configuration Hartree-Fock Program," Comput. Phys. Commun. 14 (1978) 145-153.
3. "Theoretical Oscillator Strengths for the Resonance Transitions in the Zn I Isoelectronic Sequence," (with J. E. Hansen) Phys. Rev. A 17 (1978) 1956-1965.
4. " $4s 4d \ ^1D - 4p^2 \ ^1D$ Interaction in the Zn I Isoelectronic Sequence" (with J. E. Hansen) Phys. Rev. A 19 (1979) 1819.
5. "The $4s \ ^2S - 4p \ ^2P$ Transitions in the Al Sequence," Can. J. Phys. 56 (1978) 983.
6. "Oscillator Strengths for Some D - F Transitions in the Mg Sequence," J.O.S.A. 69 (1979) 118.
7. "Theoretical Energy Levels of $3F^0$ Rydberg Series for Mg I, Al II, and Si III," Physica Scripta (to appear).
8. "Effect of Correlation in the $3d^n$ Core on the Resonance Transition in Cu II" (with R. Glass) Physica Scripta (to appear).

B. Conference Proceedings or Abstracts

1. "The Multiconfiguration Hartree-Fock Method for Atomic Energy Levels and Transition Probabilities," Invited talk presented at the Sixth International Conference on Atomic Physics, Riga, 1978 Conference paper No. C00-4264-3.
2. "Theoretical Energy Levels of $3F^0$ Rydberg Series for Mg I, Al II, and Si III," Paper presented at the Nobel Symposium on Many-Body Effects, Aspenasgarden, Sweden, June, 1979 (to appear in Physica Scripta) Conference paper No. C00-4264-9.
3. "Effect of Correlation in the $3d^n$ Core on the Resonance Transition in Cu II," (with R. Glass), Paper presented at the Nobel Symposium on Many-Body Effects, Aspenasgarden, Sweden, June, 1979 (to appear in Physica Scripta) Conference paper No. C00-4264-10.
4. "Calculations of Transition Probabilities in the Zn Sequence," (with J. E. Hansen), Paper presented at the EGAS Conference, Paris (July 1979) Conference paper No. C00-4264-11.
5. "Some MCHF results for Rydberg States," (with J. E. Hansen) Paper presented at the Symposium on Atomic Spectroscopy, Tucson, (September 1979) Conference paper No. C00-4264-12.

C. Technical Reports

1. "A General Multi-Configuration Hartree-Fock Program-MCHF77," (1977) Technical Report No. C00-4264-1.
2. "Energy levels and gf values for Fe XIV," (1978) Technical Report No. C00-4264-4.
3. "Oscillator Strengths and Transition Probabilities for the Intercombination Transitions in Fe XXII," (R. Glass) (1979) Technical Report No. C00-4264-6 (accepted for publication).
4. "The $2s\ 2p\ ^3P_1^0 \rightarrow 2s^2\ ^1S_0$ Intercombination Line in Beryllium-like Krypton, Molybdenum and Tungsten," (R. Glass) (1979) Technical Report No. C00-4264-7 (accepted for publication).
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