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$4s4d\,{}^1D$-$4p^2\,{}^1D$ interaction in the Zn I isoelectronic sequence

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The importance of the interaction between $4s4d\,{}^1D$ and $4p^2\,{}^1D$ is studied in the Zn I isoelectronic sequence from Zn I to W XLV. Multiconfiguration Hartree-Fock calculations have been carried out for the two lowest ${}^1D$ terms in this sequence and used to calculate *gf* values for the ${}^1P$-${}^1D$ transitions. For the heavier elements relativistic effects are important and intermediate-coupling calculations of the *gf* values using multiconfiguration Dirac-Hartree-Fock transition energies have been carried out. Final *gf* values take into account relativistic effects in an approximate way, as well as core-polarization effects. The latter are found to be as important for the ${}^1P$-${}^1D$ transitions as for the ${}^1S$-${}^1P$ resonance transition even for high-ionization stages. The *gf* values for transitions from the lowest ${}^1D$ terms were found to be small due to destructive interference. Little experimental data exist with which the present results can be compared. Furthermore, it is shown that much of the earlier experimental material concerning the ${}^1D$ terms are in error. Comparison with a few very recent experimental investigations shows good agreement, however, and the present results point to the need for further experimental studies of this sequence, even towards the neutral end.

I. INTRODUCTION

The spectra of highly ionized atoms in the Zn I isoelectronic sequence are presently of considerable interest in fusion related research. The available spectroscopic information about these spectra is very limited,[1-3] and for many of the highly ionized species only the resonance transition, $4s^2\,{}^1S - 4s4p\,{}^1P$, has been observed.[4,5] More surprisingly, even the lighter elements have been studied only fragmentarily. Though analogous to the Mg I sequence, the Zn I sequence is somewhat more complicated to analyze due to the large number of low-lying terms, especially for high stages of ionization. Configurations of the type $4l\,4f$ are asymptotically degenerate with the $4s^2\,{}^1S$ ground state in the Zn I sequence, while configurations involving $4f$ electrons in the Mg I sequence are well above the ground state. The greater complexity of the Zn I sequence probably contributes to the fact that this sequence has been studied less extensively experimentally than the Mg I sequence.

On the theoretical side, a number of studies have been made of the energy and oscillator strength of the resonance transition,[6-10] but again very little work has been done on other transitions.

This paper presents the first study of the $4s4p\,{}^1P - {}^1D$ transitions in the Zn I sequence with the effects of correlation taken into account. Two ${}^1D$ terms are considered in this work which will be designated ${}^1_aD$ and ${}^1_bD$: ${}^1_aD$ is the lowest ${}^1D$ term and ${}^1_bD$ the second lowest. The dominant eigenvector component of ${}^1_aD$, say, is not the same for the whole sequence but the relative phase between the two largest components does remain constant for the ${}^1_aD$ state. In this case the relative phase has a greater effect on the *gf* value than the absolute size of the eigenvector components, so a scheme that labels the terms according to their position in the spectrum is more useful *for isoelectronic comparisons* than a scheme based on the dominant eigenvector component. With increasing ionization the actual states lose their *LS* character. However, for convenience the same labels will be used for the whole sequence. Two configurations in particular contribute to the low ${}^1D$ terms, $4p^2$ and $4s\,4d$, both of which combine strongly with $4s4p$. In the Mg I sequence the equivalent configurations, $3p^2$ and $3s3d$, cross over in the beginning of the sequence. The same happens in the Zn I sequence with $4p^2\,{}^1D$ being the dominant component of the (lowest) ${}^1_aD$ term in all spectra except Zn I, where $4p^2\,{}^1D$ apparently is above the ionization limit[11] (as is the case for $3p^2\,{}^1D$ in Mg I). However, the crossing in the Zn I sequence has only recently been noticed[12] and the original classification[1] of the lowest ${}^1D$ term was $4s4d\,{}^1D$.

The primary motivation for this paper is to point out the consequences of the strong interaction between the $4p^2$ and $4s4d\,{}^1D$ terms which lead to destructive interference between the contributions to the transition probability for the transition to $4s4p\,{}^1P$ from ${}^1_aD$. The occurrence of destructive interference on this transition turns out to be in agreement with observations. It was noted already by Rao[13] that the $4s4p\,{}^3P_1 - {}^1_aD_2$ transition appears to be stronger than $4s4p\,{}^1P_1 - {}^1_aD_2$ in the first spectra in this sequence (Ge III to Se V). At the same time, the strength of the spin-forbidden ${}^3P - {}^1_aD$ transition suggests that it might be necessary to introduce spin-orbit interaction in the calculation of the line strengths even for low stages of ionization, and such a calculation has been carried out.

With regard to the ${}^1_bD$ term, it is shown that the reported[1] term in Ge III and As IV is wrongly identified and that the correct ${}^1D$ term lies much higher. New ${}^1_bD$ terms have recently been established[14] in Ga II and Ge III which corroborate this result. Thus the present work points to the need for a revision of the existing analysis of this sequence even for low stages of ionization.

Another purpose of this work is to provide information needed for the experimental reinvestigation of the lifetime of the $4s4p\,{}^1P$ level. It has recently been pointed out[7,9,10] that there exists a considerable discrepancy between observed and calculated lifetimes for this level, a discrepancy which increases with increasing ionization. The discrepancy has been attributed[15] to difficulties in applying cascade corrections to the observed beam-foil decay curves as a result of the existence of a number of cascades originating in levels with a lifetime comparable to that of the ${}^1P$ term. One of these is the ${}^1_bD$ term studied in this paper. To be able to extract the ${}^1P$ lifetime from beam-foil decay curves additional measurements of the lifetimes of levels contributing to the cascades are necessary. Since the ${}^1_bD$ level is unknown, the theoretical transition probabilities presented in this paper are the only information available at present about this cascade contribution.

Finally, the present data for the heavier elements are of importance for determining radiative losses in fusion plasmas. Relativistic effects will be important for these elements. In the study of the resonance transition[9] it was found that it is possible to combine nonrelativistic line-strength calculations, modified by the introduction of the spin-orbit interaction, with observed transition energies in order to obtain *gf* values which take into account both correlation (if included in the nonrelativistic calculation) and relativistic effects. The validity of this approach with respect to the correlation among the outer electrons was demonstrated earlier.[9] That the validity extends to the effects of core polarization has recently been confirmed by calculations using the relativistic random-phase approximation (RRPA), which included core polarization.[10] The results of these calculations were in agreement with the nonrelativistic multiconfiguration Hartree-Fock (MCHF) (length) results[9] modified for spin-orbit effects and scaled by the ratio between the relativistic and nonrelativistic transition energy. The same approach has been used in this work for the ${}^1P-{}^1D$ transitions, although no evidence exists at the moment that the procedure necessarily will be reliable in this case. Since none of the transition energies have been observed for heavier elements, multiconfiguration Dirac-Hartree-Fock (MCDHF) calculations were performed for the transition energies using the Desclaux computer program.[16] The relativistic effects on the ${}^1P-{}^1D$ transition energies are smaller than for the ${}^1S-{}^1P$ transition, as expected.

II. NONRELATIVISTIC CALCULATIONS

The general computational procedure follows that described in our paper on the resonance transition,[9] but some differences to that work will be described here. Briefly, the approach was to calculate MCHF wave functions using the computer program MCHF77.[17] The angular matrix elements involved in the interaction were obtained using a modified version of Hibbert's program[18] and the wave functions used to calculate transition probabilities.[19,20] In order to include the effects of correlation between the outer electrons (outer correlation), the configurations belonging to the complex[21] (i.e., the set of configurations with the same set of principal quantum numbers and the same parity, in this case of the type $4l\,4l'$) were included while correlation with the core (core polarization) was included to first order by including those configurations in the ${}^1D$ state, say, which have $3d\to4p$ or $3d\to4f$ electric dipole transitions to the two main components ($4s4p$ and $4p4d$) of the ${}^1P$ state. Only correlation with the $3d^{10}$ shell is taken into account. Since the number of terms (configuration states) which could be added to the ${}^1D$ state was rather large, only those which combine directly with the two main components

TABLE I. MCHF expansions.

${}^1P$ state

$3d^{10}4s_14p_1+3d^{10}4p_24d_1+3d^{10}4f_14d_2$
$\quad+3d^94f_24s_2^2+3d^94p_34s_1^2+3d^94p_4^3$
$\quad+3d^94f_24p_4^2+3d^94f_3({}^1P)4s_34d_3$

${}^1D$ state (main component $3d^{10}4p_1^2$)

$3d^{10}4p_1^2+3d^{10}4s_14d_1+3d^{10}4d_2^2+3d^{10}4f_14p_2$
$\quad+3d^{10}4f_2^2+3d^94f_3({}^1P)4s_24p_3$
$\quad+3d^94f_4({}^1P)4p_14d_3+3d^94s_34p_4^2$

${}^1D$ state (main component $3d^{10}4s_14d_1$)

$3d^{10}4s_14d_1+3d^{10}4p_1^2+3d^{10}4d_2^2+3d^{10}4f_14p_2$
$\quad+3d^{10}4f_2^2+3d^94f_3({}^1P)4s_24p_4$
$\quad+3d^94f_4({}^1P)4p_34d_1+3d^94s_34p_5^2$

If no coupling scheme is indicated, all possible coupling schemes have been included.

of the ${}^1P$ expansion were added.

Compared to the earlier calculation for ${}^1P$ it was necessary to add the configuration $3d^9\ 4f\ 4s\ 4d$ to the ${}^1P$ expansion in order to include the first-order contribution from $3d \rightarrow 4f$ excitations to both large components of ${}^1D$. The configuration state $3d^9\ 4f({}^1P)\ 4s\ 4d\,{}^1P$ was the only one which combined directly with the components of the ${}^1D$ expansion and only this configuration state has been added to the ${}^1P$ expansion.

Since the ${}^1D$ states have two large components, $4p^2$ and $4s4d$, the description of the configurations added to the ${}^1D$ expansions in terms of correlation orbitals depends on which of the two is chosen as reference state. For this reason as many unconstrained orbitals as possible were determined for each state (the limit set by MCHF77 is 20 orbitals). Only one orbital had to be constrained and was chosen to belong to a configuration which combines with the smaller component ($3d^{10}\ 4p\ 4d$) of the ${}^1P$ state only. The orbital was constrained to be the same as one of the orbitals in the dominant configuration of the ${}^1D$ state and was required not to be a correlation orbital relative to this configuration. The expansions used for the two ${}^1D$ states are given in Table I.

Due to the large number of orbitals it was necessary to neglect some overlap integrals in the calculation of nondiagonal matrix elements, particularly for the ${}^1D$ term. Generally, the neglected overlap integrals were close to unity, except for the lightest atoms. In the case of the interaction between $3d^{10}\ 4f\ 4p$ and $3d^9\ 4f\ 4p\ 4d$, which is a single-particle $3d \rightarrow 4d$ excitation, the cancellation[22] between the single-particle integral $I(3d,\ 4d)$ and the Coulomb-interaction integrals $R^k(nl\ 3d,\ nl\ 4d)$ was determined numerically. Most of the neglected overlap integrals in the ${}^1D$ state are connected with these matrix elements.

A fixed core model was used as in the earlier calculation[9] with the inner $1s,\ 2s, \ldots,\ 3p$ orbitals taken from a Hartree Fock (HF) calculation for $3d^{10}\ 4s^2\ {}^1S$ and the $3d$ orbital taken from an HF calculation for ${}^1P$. All other orbitals were determined variationally, specifically all outer orbitals in the ${}^1P$ state were optimized again upon introduction of the $3d^9\ 4f({}^1P)\ 4s\ 4d$ configuration state.

Some special problems were encountered for specific atoms which necessitated changes in the general expansions shown in Table I. In the calculations for the ${}^1_aD$ state, the interaction with the $3d^9\ 4s_3\ 4p_4^2$ configuration decreased with increasing ionization and became very difficult to determine for ions heavier than approximately Kr VII. For Mo XIII and Sn XXI, the effects of the configuration were taken into account by diagonalizing the energy matrix including the $3d^9\ 4s\ 4p^2$ configuration with the $4s$ and $4p$ orbitals fixed at the $4s_1$ and $4p_2$ orbitals (see Table I) instead of optimizing them. For Sn XXI, the influence of the configuration was small and for the heavier atoms the $3d^9\ 4s\ 4p^2$ configuration was neglected.

The calculations for the ${}^1_bD$ state were somewhat difficult for low stages of ionization. For ions heavier than Ga II, HF calculations predict $4p^2\ {}^1D$ to be lower than $4s\ 4d\ {}^1D$. All $4s\ nd\ {}^1D$ states lie above $4s4d\ {}^1D$ and contribute towards pushing the eigenvalue down. In the calculation for the lower eigenvalue, the $4s\ 4d\ {}^1D$ component is able to take into account the effect of the whole $4s\ nd$ series in which the d orbitals in principle can be bound as well as continuum orbitals. The resulting d orbital is a correlation orbital and will be designated as nd^*, signifying that it represents the interaction with the whole $4s\ md$ series, where $m \geq n$. For heavy elements, however, the $4d^*$ orbital is rather close to a spectroscopic (HF) $4d$ orbital and the main part of the interaction can be understood as being between the two configurations $4p^2$ and $4s4d$ (and can be calculated by diagonalizing the interaction matrix using HF functions for $4p^2$ and $4s4d$). For lighter elements the $4d^*$ orbital deviates more and more from a spectroscopic orbital and in a configuration-interaction (CI) calculation it is necessary to include more and more members of the $4snd$ series (as well as the continuum) to reproduce the MCHF result. In the optimization of an eigenvalue, which is not the lowest one of a given symmetry, part of an interacting series might be below and the rest above the position of the state being sought. In such a case it seems to be easier, although not in principle necessary, to introduce one orbital to represent the interaction from below and another to

TABLE II. Eigenvector compositions of the two lowest ${}^1D$ states in Ga II. Only components larger than 0.025 are shown.

${}^1_aD$ state

$0.7422\,|\,3d^{10}\,4p_1^2\rangle - 0.6668\,|\,3d^{10}\,4s_1 4d_1\rangle$

$+\,0.0284\,|\,3d^{10}\,4d_2^2\rangle + 0.0316\,|\,3d^{10}\,4f_1 4p_2\rangle$

$-\,0.0263\,|\,3d^9\,4f_4({}^1P)4p_1({}^2P)4d_3\rangle$

$-\,0.0259\,|\,3d^9\,4s_3({}^3D)4p_4^2({}^3P)\rangle$

${}^1_bD$ state

$0.6579\,|\,3d^{10}\,4s_1 4d_1\rangle + 0.6728\,|\,3d^{10}\,4p_1^2\rangle$

$-\,0.3077\,|\,3d^{10}\,4s_1 5d\rangle + 0.0656\,|\,3d^{10}\,4d_2^2\rangle$

$+\,0.0998\,|\,3d^{10}\,4f_1 4p_2\rangle$

$+\,0.0343\,|\,3d^9\,4f_3({}^1P)4s_2 4p_4\rangle$

$-\,0.0478\,|\,3d^9\,4f_4({}^1P)4p_3({}^2S)4d_1\rangle$

$-\,0.0421\,|\,3d^9\,4s_1({}^3D)4p_5^2({}^3P)\rangle$

represent the interaction from above. This is the case for Ga II. HF calculations for Ga II place $4s\ 4d\ {}^1D$ below $4p^2\ {}^1D$, which, however, is below $4s\ 5d\ {}^1D$ and the rest of the $4s\ nd$ series. In a 2×2 CI calculation using HF orbitals, $4s\ 4d\ {}^1D$ is likely to be the dominant component in the lowest ${}^1D$ state in Ga II. However, due to the interaction between $4p^2$ and the rest of the (higher-lying) $4snd$ series, $4p^2$ is in effect pushed down more (by $4s\ nd$, $n>4$) than up (by $4s4d$) and in the MCHF calculation $4p^2$ is the dominant component of the lowest ${}^1D$ state (55%). The ${}^1_bD$ state would thus be expected to have a dominant $4s\ 4d\ {}^1D$ component and be the first member of the $4s\ nd$ series. The position of this state corresponds roughly to the HF position of the $4p^2\ {}^1D$ term and the effects of interaction with $4s\ nd$ are relatively minor because $4s4d$ pushes the state up nearly as much as $\sum_{n>4} 4snd$ pushes it down. It is still possible to represent the weak interaction between $\sum_{n\geq 4} 4s\ nd$ and $4p^2$ using one $4s\ 4d^*$ configuration state but it is easier to obtain initial estimates of the correlation orbital by introducing both the Hartree-Fock $4s4d$ and the correlating $4s5d^*$ configurations. The calculations were carried out using frozen $4s$ and $4d$ orbitals taken from a HF calculation for $4s4d\ {}^1D$ and only the $5d^*$ orbital was optimized. The same procedure was applied to the calculation of the ${}^1_bD$ state in Ge III and the results were found to be equivalent to those obtained using one $4s4d^*$ configuration state to represent the $4snd$ series. The cancellation between the single-particle integral $I(4d,\ 5d)$ and the Coulomb interaction integrals $R^k(nl\,4d,\ nl\,5d)$ was carried out numerically and the off-diagonal matrix element between the two configurations was small as expected from Brillouin's theorem.[22] The eigenvector compositions for the two ${}^1D$ states in Ga II are given in Table II. Only contributions larger than 0.025 are shown. It is seen that the largest individual eigenvector component in both states is $4p^2$ but the ${}^1_bD$ state in total has more $4snd\ {}^1D$ than $4p^2$ character, in agreement with expectations.

In Zn I, the ${}^1_bD$ state (dominant eigenvector component $4p^2$) is expected to be in the continuum[11] and no attempt has been made to obtain an MCHF wave function for it.

III. INTERMEDIATE-COUPLING CALCULATIONS

Since a simple intermediate-coupling (IC) calculation was successful in the case of the ${}^1P$ state,[9] a similar but more accurate approach has been adopted here. A diagonalization of the $J=1$ and $J=2$ interaction matrices based on the electrostatic MCHF matrices for ${}^1P$ and ${}^1D$ augmented with the spin-orbit matrices for some of the levels in the complex was carried out. The levels included via the spin-orbit interaction are given in Table III. The reason for including levels of the $4p4f$ configuration in the $J=2$ calculations is that $4p4f\ {}^1D$ has a fairly large coefficient (~0.1) in the ${}^1_bD$ state. However, it turns out that the only significant admixtures due to the spin-orbit interaction is $4s4p\ {}^3P_1$ in the ${}^1P_1$ state, $4p^2\ {}^3P_2$ in the ${}^1_aD_2$ state, and a smaller admixture of $4s4d\ {}^3D_2$ in ${}^1_bD_2$. The angular part of the spin-orbit interaction matrix was calculated using a modified version of Klotz' program.[23] The radial spin-orbit parameters were taken from the MCHF results and the electrostatic energies of the levels added were calculated from the electrostatic energy expressions using the radial integrals from the MCHF calculation. For example, the electrostatic energy of $4p^2\ {}^3P$ was determined as

$$E(4p^2\ {}^3P)=E(4p^2\ {}^1D)-\tfrac{6}{25}F^2(4p,\ 4p)\,,$$

where $E(4p^2\ {}^1D)$ is the diagonal energy of $4p^2\ {}^1D$ in the MCHF calculation. These procedures are somewhat arbitrary and the resulting wave function will only be an approximation to the correct ${}^1P$ or ${}^1D$ wave functions.

TABLE III. Triplet levels included in the intermediate-coupling calculation.

$J=1$ state (dominant components $4s_1 4p_1$ and $4p_2 4d_1$)
$4s_1 4p_1\ {}^3P_1 + 4p_2 4d_1\ {}^3P_1 + 4p_2 4d_1\ {}^3D_1$
$J=2$ states (dominant components $4s_1 4d_1$ and $4p_1^2$)
$4s_1 4d_1\ {}^3D_2 + 4p_1^2\ {}^3P_2 + 4f_1 4p_2\ {}^3D_2 + 4f_1 4p_2\ {}^3F_2$

IV. MULTICONFIGURATION DIRAC-HARTREE-FOCK CALCULATIONS

MCDHF calculations were carried out using the Desclaux computer program[16] to determine the ${}^1P-{}^1D$ transition energies for ions heavier than Br VI. Only the most important configurations within the complex were included (Table IV). The calculations are similar to those carried out by Cheng and Johnson[24] for the Mg sequence except that these authors included also the d^2 configura-

TABLE IV. MCDHF expansions.

$J=1$ state
$4s_{1/2}4p_{1/2}+4s_{1/2}4p_{3/2}+4p_{1/2}4d_{3/2}+4p_{3/2}4d_{3/2}+4p_{3/2}4d_{5/2}$
$J=2$ states
$4s_{1/2}4d_{3/2}+4s_{1/2}4d_{5/2}+4p_{1/2}4p_{3/2}+4p_{3/2}^2$

TABLE V. Calculated ${}^{1}S-{}^{1}D$ energy separations (a.u.) in the Zn I isoelectronic sequence. The observed values for ${}^{1}S-{}^{1}_{a}D$ are also shown.

Ion	${}^{1}S-{}^{1}_{a}D$ MCHF	${}^{1}S-{}^{1}_{a}D$ Observed[a]	${}^{1}S-{}^{1}_{b}D$ MCHF
Zn I	0.2619	0.284 582	
Ga II	0.4727	0.490 804	0.5575
Ge III	0.6320	0.660 541	0.7898
As IV	0.7804	0.818 149	1.0189
Se V	0.9236	0.971 383	1.2404
Br VI	1.0638		1.4581
Kr VII	1.2022		1.6718
Mo XIII	2.0128		2.8949
Sn XXI	3.0740		4.4435
Xe XXV	3.6023		5.2005
Sm XXXIII	4.6573		6.6960
W XLV	6.2382		8.9124

[a] Reference 1.

TABLE VI. Calculated ${}^{1}P-{}^{1}D$ energy separations (a.u.) in the Zn I isoelectronic sequence obtained in MCHF calculations.

Ion	${}^{1}P-{}^{1}_{a}D$	${}^{1}P-{}^{1}_{b}D$
Zn I	0.0610	
Ga II	0.1610	0.2458
Ge III	0.2267	0.3845
As IV	0.2882	0.5267
Se V	0.3481	0.6649
Br VI	0.4071	0.8013
Kr VII	0.4656	0.9352
Mo XIII	0.8120	1.694
Sn XXI	1.269	2.638
Xe XXV	1.497	3.095
Sm XXXIII	1.953	3.992
W XLV	2.638	5.312

tion in the $J=2$ states. Cheng and Johnson found that the $3p^{2}_{3/2}$ $J=2$ level crossed $3s_{1/2}3d_{3/2}$ $J=2$ and $3s_{1/2}3d_{5/2}$ $J=2$ for $Z=50$, approximately, and became the highest of the four $J=2$ levels in $3p^{2}$ and $3s3d$. The same crossing takes place around $Z=70$ in the Zn sequence. The first and fourth eigenvalue of the $J=2$ interaction matrix corresponds to the ${}^{1}D$ terms in the LS limit up to the crossing but after the crossing the ${}^{1}_{b}D$ term corresponds to the third eigenvalue. In the MCDHF calculations these particular eigenvalues were optimized. For $J=1$, the second eigenvalue, corresponding to the ${}^{1}P$ term in the LS limit was optimized. All calculations were made assuming the nucleus to be a point charge.

V. NONRELATIVISTIC RESULTS

The nonrelativistic MCHF wave functions described in Sec. II have been used to calculate the positions of the two lowest ${}^{1}D$ terms and to calculate the *gf* values for the transitions to ${}^{1}P$ from these two ${}^{1}D$ terms. Table V shows the calculated

TABLE VII. Nonrelativistic gf values for the ${}^{1}P-{}^{1}_{a}D$ transitions in the Zn I isoelectronic sequence. Length (l) and velocity (v) values are given.

Ion		$gf^{\mathrm{a}}_{E_{\mathrm{calc}}}$	Cancellation factor	$gf_{E_{\mathrm{calc}}}$ outer correlation	$gf^{a}_{E_{\mathrm{obs}}}$
Zn I	l	1.229	0.473	1.214	1.442
	v	1.646	0.174	1.650	1.403
Ga II	l	0.000 58	0.000 12	0.004 04	0.000 61
	v	0.034 2	0.001 50	0.028 1	0.032 6
Ge III	l	0.252	0.054 6	0.307	0.269
	v	0.358	0.015 6	0.381	0.335
As IV	l	0.484	0.112	0.565	0.517
	v	0.577	0.026 9	0.633	0.540
Se V	l	0.632	0.154	0.725	0.674
	v	0.705	0.035 2	0.781	0.662
Br VI	l	0.727	0.185	0.824	
	v	0.784	0.042	0.871	
Kr VII	l	0.789	0.210	0.888	
	v	0.834	0.047 2	0.927	
Mo XIII	l	0.885	0.294	0.968	
	v	0.920	0.069 7	0.987	
Sn XXI	l	0.821	0.344	0.882	
	v	0.847	0.084 3	0.897	
Xe XXV	l	0.779	0.361	0.831	
	v	0.808	0.090 2	0.846	
Sm XXXIII	l	0.696	0.383	0.736	
	v	0.721	0.097 1	0.751	
W XLV	l	0.594	0.404	0.622	
	v	0.616	0.104	0.637	

[a] Core-polarization effects included.

position of the ${}^1D$ terms relative to the ground state $4s^2\,{}^1S_0$. These values are obtained as the difference between total MCHF energies using the ground-state energy obtained in the earlier calculation.[9] The ${}^1P-{}^1D$ transition energies, calculated as a difference between total MCHF energies, are given in Table VI.

Table VII shows the theoretical *gf* values for the ${}^1P-{}^1_aD$ transitions calculated using the transition energies given in Table VI. The negative phase between the two main eigenvector components (see Table II) together with the convention that the orbitals be positive near the origin leads to destructive interference in the calculation of the transition probability to the ${}^1P$ state and the *gf* values given in Table VII are fairly small. A quantitative measure of the importance of cancellation is given in Column 3, which shows the ratio between the true *gf* value and the value calculated using absolute values of all contributions to the square root of the line strength. These cancellation factors are less than 0.5 in all cases shown and less than 0.1 in many cases, particularly for the velocity value. This means that rather accurate wave functions are necessary in order to obtain reasonably accurate line strengths. At the same time fairly accurate transition energies are necessary in order to obtain accurate *gf* values since the absolute transition energy is relatively small. In order to distinguish between these two sources of error, column 5 (Table VII) gives the *gf* values calculated using the observed energies[1] in the spectra Zn I to Se V. The agreement between length and velocity values is better for all these spectra when the observed energies are used. In particular, very good agreement is obtained in the case of Zn I, suggesting that the fairly large discrepancy obtained using the theoretical transition energy for Zn I is almost entirely due to the error in the determination of the energy. For Ga II and Ge III the difference between length and velocity value remains large when the observed energies are used and the error in the calculated line strengths seems more important than the error in the calculated transition energy. For As IV and Se V the calculated line strengths seem again to be more accurate than the calculated energies.

In the case of Ga II, there is nearly complete cancellation between the contributions from the two large components of the ${}^1D$ state (Table II). This makes the calculated *gf* value very sensitive to small changes in the wave functions—in fact, sensitive to such an extent that the result is dependent even on the degree of self-consistency obtained for ${}^1_aD$. Two MCHF calculations with a lower degree of self-consistency gave *gf* (length) values of 0.016 27 and 0.004 54 compared to the value of 0.000 58 given in Table VII. The corresponding velocity values were 0.1247, 0.0625, and 0.0342. Thus the calculated length *gf* value in Ga II is apparently uncertain to within a factor of

TABLE VIII. Nonrelativistic *gf* values for the ${}^1P-{}^1_bD$ transitions in the Zn I isoelectronic sequence. Length (l) and velocity (v) values are given.

Ion		$gf^{\mathrm{a}}_{E_{\mathrm{calc}}}$	Cancellation factor	$gf_{E_{\mathrm{calc}}}$ outer correlation
Ga II	l	3.64	0.470	3.92
	v	3.67	0.225	3.92
Ge III	l	4.94	0.684	5.34
	v	4.82	0.407	5.26
As IV	l	5.15	0.666	5.56
	v	5.07	0.430	5.51
Se V	l	4.97	0.655	5.38
	v	4.84	0.431	5.28
Br VI	l	4.81	0.651	5.21
	v	4.68	0.437	5.10
Kr VII	l	4.62	0.649	5.01
	v	4.52	0.441	4.91
Mo XIII	l	3.63	0.659	3.92
	v	3.61	0.455	3.88
Sn XXI	l	2.78	0.679	2.97
	v	2.81	0.465	2.97
Xe XXV	l	2.49	0.687	2.65
	v	2.52	0.467	2.66
Sm XXXIII	l	2.06	0.703	2.17
	v	2.10	0.474	2.19
W XLV	l	1.63	0.719	1.70
	v	1.67	0.479	1.73

[a] Core-polarization effects included.

25. The disparity between length and velocity values amounts to a factor of 50 even if the observed transition energy is used. Despite this uncertainty it seems clear that the $^1P-{}^1_aD$ *gf* value in Ga II is very small.

Since the two main contributions to the oscillator strength partially (or nearly completely) cancel each other, fairly small contributions like core-polarization effects can influence the final value more than could be expected for a transition between excited states. Column 4 in Table VII gives the *gf* values calculated from the MCHF wave functions but including outer correlation only. The difference between columns 2 and 4 shows the importance of core polarization for this transition. Except for Zn I, the influence of core polarization is fairly large, especially in the case of the length value. The difference is more than 20% in the case of Ge III (length value) and considerably more for Ga II. However, for Ga II the precise value is rather uncertain for reasons mentioned above. From Mo XIII (9%) to W XLV (5%), the influence of core polarization is similar to that found earlier[9] for the $^1S-{}^1P$ transition. The influence of core polarization on the velocity value is smaller, particularly in the beginning of the sequence.

Table VIII gives the results for the $^1P-{}^1_bD$ transition. For this transition the phase between the eigenvector components in the ^1D state is such that it leads to constructive interference, and the calculated *gf* values are large. However, some cancellation is still present. The cancellation factors in column 3 are between 0.47 and 0.72 for length and between 0.22 and 0.48 for velocity values, where the smallest figures correspond to Ga II. Column 4 shows the *gf* values calculated assuming outer correlation only. The contribution from core polarization is less than 10% in all cases (approximately 8% from Ga II to Mo XIII and decreasing to 5% in W XLV). This is less than found for the $^1S-{}^1P$ (Ref. 9) and $^1P-{}^1_aD$ (Table VII) transitions for the light atoms, but comparable to the core polarization on these transitions for the heavier atoms (Mo XIII and heavier). It is somewhat surprising that core polarization is equally important for transitions between excited states and transitions involving the ground state[9] as found here for the heavier ions. This phenomenon is probably a consequence of the contraction of $4p$ and $4d$ orbitals relative to $4s$ with increasing ionization. The mean radii (a.u.) of the three orbitals (taken from HF calculations for $4s^2\,{}^1S$, $4s4p\,{}^1P$, and $4s4d\,{}^1D$) are 2.898($4s$), 6.110($4p$), and 10.756($4d$) for Zn I, but 0.4202, 0.4161, and 0.4009 for W XLV. Thus for heavier elements the proximity of the outer electrons to the core is approximately the same for all $n=4$ orbitals.

VI. INTERMEDIATE-COUPLING AND MCDHF CALCULATIONS

The necessity for carrying out intermediate-coupling calculations is a result of the destructive interference between the main contributions to the $^1P-{}^1_aD$ oscillator strength, which makes this *gf* value sensitive to even very small additional contributions to the wave functions. Similar observations have been made in the Mg I isoelectronic sequence.[25]

Intermediate-coupling calculations therefore were carried out for the $J=1$ and $J=2$ states, as described in Sec. III. The neglect of relativistic contributions other than the spin-orbit interaction in the IC calculations leads to serious errors in the calculated transition energies for high stages of ionization, especially for the $^1P-{}^1_aD$ transition. The MCDHF calculations using Desclaux's program (Sec. IV) show that the correct transition energies are larger than the MCHF values (Table IX), although the MCDHF/MCHF ratios are considerably smaller than the ratio between observed and MCHF energies for the resonance transition[9]

TABLE IX. Calculated MCDHF transition energies (a.u.) for the ions Kr VII to W XLV. The MCDHF/MCHF ratios are given as well as the observed/MCHF ratios for the $^1S-{}^1P$ resonance transition.

	$^1P-{}^1_aD$		$^1P-{}^1_bD$		$^1S-{}^1P$ [a]
	MCDHF	MCDHF/MCHF	MCDHF	MCDHF/MCHF	observed/MCHF
Kr VII	0.4733	1.017	0.9731	1.040	1.043
Mo XIII	0.8586	1.058	1.792	1.058	1.102
Sn XXI	1.406	1.109	2.863	1.085	1.21
Xe XXV	1.696	1.133	3.414	1.103	1.307
Sm XXXIII	2.309	1.182	4.601	1.153	1.543
W XLV	3.328	1.262	6.204	1.168	2.082

[a] Reference 9; the $^1S-{}^1P$ transition has not been observed for Sn XXI, Sm XXXIII, and W XLV. The values used as "observed" are taken from HFR (Sn XXI) and RRPA (Sm XXXIII and W XLV) calculations (Refs. 6 and 7).

(the latter ratios are reproduced in Table IX). That the relativistic shifts on the ${}^1P-{}^1D$ transitions should be much smaller than on the ${}^1S-{}^1P$ transitions can be understood from the eigenvector compositions of the terms in *jj* coupling. In this coupling scheme the ${}^1P$ term has a very large $4s_{1/2}4p_{3/2}$ component. Thus the large relativistic shift in the ${}^1S-{}^1P$ transition energies is due to a $4s_{1/2}\rightarrow 4p_{3/2}$ excitation, where the shift on a $4s_{1/2}$ electron is much larger than the shift on a $4p_{3/2}$ electron. The ${}^1_aD$ term has $4p_{1/2}4p_{3/2}$ as its main *jj* component and the ${}^1P-{}^1_aD$ transition therefore corresponds to a $4s_{1/2}\rightarrow 4p_{1/2}$ excitation. These two orbitals are degenerate in a hydrogenic approximation for large Z and the relativistic energy shift will consequently be small. $4s_{1/2}4d_{5/2}$ is the dominant eigenvector component of ${}^1_bD$ and the ${}^1P-{}^1_bD$ transition consequently corresponds to a $4p_{3/2}\rightarrow 4d_{5/2}$ excitation. These orbitals have smaller relativistic shifts than $4s_{1/2}$ and $4p_{1/2}$ electrons, although they are not degenerate for large Z.

The relatively small increase in the MCDHF/MCHF ratio for ${}^1P-{}^1_bD$ between Sm XXXIII and W XLV can be attributed to the crossing of $4p_{3/2}^2$ and $4s4d$.

The accuracy of the eigenvectors obtained in the IC calculations can be expected to be better than the accuracy of the energies because the bulk of the neglected relativistic effects, the mass-correction, and the Darwin terms, displaces all levels belonging to a particular configuration as a whole and the IC calculation will therefore give approximately the correct spin-orbit mixing between terms belonging to a given configuration. Nevertheless, because of the crossing described earlier, the approximation can be expected to break down in a region around W XLV. In the MCDHF calculation, ${}^1_bD$ is the third $J=2$ level in W XLV but in the IC calculation ${}^1_bD$ is still the fourth level. However, the IC approximation will also break down with increasing ionization for more general reasons and in the study of the resonance transition[9] it was found that the IC value for W XLV was slightly inaccurate.

The IC calculations for ${}^1P$ and ${}^1D$ were combined to give *gf* values for the ${}^1P_1-{}^1D_2$ transitions. Since both are singlet terms, the ${}^1P_1-{}^1D_2$ *gf* value is equivalent to the ${}^1P-{}^1D$ multiplet value calculated earlier and the difference between the two shows the influence of spin-orbit interaction directly. Since the IC energies are less accurate than the MCHF ones, the latter have been used in the calculation of the oscillator strengths. This, furthermore, means that a comparison with the nonrelativistic results shows directly the influence of relativistic effects on the *line strength*, since both sets of calculations use the MCHF energies. The *gf* values calculated using the IC wave functions (gf^{IC}) as well as the nonrelativistic values (gf^{MCHF}) are shown in Table X. The gf^{MCHF} values are taken from Tables VII and VIII.

Comparison between length and velocity values in Table X shows that the agreement between the two is as good for gf^{IC} as for gf^{MCHF} values. The exception is W XLV, which seems to confirm our earlier conjecture that the IC calculations for W XLV are less accurate than for the other atoms. The good agreement between length and velocity values in the IC calculation is rather surprising.

Table X shows that the influence of relativistic effects on the line strength, as expected, is most pronounced for the ${}^1P-{}^1_aD$ transition and amounts to a reduction of the nonrelativistic value by a factor of more than 2.5 in Sm and W. However, the *gf* values for Zn and Ga are essentially unchanged. This is a consequence of the crossing of $4s4d$ and $4p^2$ in the beginning of the sequence. In Zn I and Ga II, ${}^1_aD$ has a large $4s4d$ eigenvector component and since ζ_{4d} is much smaller than ζ_{4p} the influence of spin-orbit interaction is less significant for $4s4d$ than for $4p^2$. Between Ga II and Ge III the amount of $4p^2$ increases from 55% to 73% and the $4p^2\,{}^3P_2$ admixture increases from 0.1% to 0.5%. From Ge III, the relativistic effects

TABLE X. gf^{IC} values obtained from intermediate-coupling calculations, with core-polarization effects included, computed using the MCHF energies and compared with gf^{MCHF} values. Length (l) and velocity (v) values are given.

Ion		${}^1P-{}^1_aD$		${}^1P-{}^1_bD$	
		gf^{IC}	gf^{MCHF}	gf^{IC}	gf^{MCHF}
Zn I	l	1.23	1.23		
	v	1.65	1.65		
Ga II	l	0.000 58	0.000 58		
	v	0.0341	0.0342		
Ge III	l	0.250	0.252	4.94	4.94
	v	0.355	0.358	4.81	4.82
As IV	l	0.474	0.484	5.15	5.15
	v	0.564	0.577	5.07	5.07
Se V	l	0.606	0.632	4.96	4.97
	v	0.675	0.705	4.83	4.84
Br VI	l	0.677	0.727	4.79	4.81
	v	0.728	0.784	4.67	4.68
Kr VII	l	0.709	0.789	4.60	4.62
	v	0.746	0.834	4.50	4.52
Mo XIII	l	0.609	0.885	3.58	3.63
	v	0.635	0.920	3.56	3.61
Sn XXI	l	0.428	0.821	2.70	2.78
	v	0.438	0.847	2.71	2.81
Xe XXV	l	0.365	0.779	2.40	2.49
	v	0.376	0.808	2.42	2.52
Sm XXXIII	l	0.280	0.696	1.99	2.06
	v	0.297	0.721	2.00	2.10
W XLV	l	0.211	0.594	1.76	1.63
	v	0.243	0.616	1.65	1.67

increase fairly rapidly, particularly after Kr VII. The reason is that the ${}^1P$ term is calculated to be practically pure up to Kr VII. The only effect of a triplet admixture in ${}_a^1D$ is consequently to scale the gf^{MCHF} value in the ratio between singlet and triplet contributions to the ${}_a^1D$ term (assuming that the relative eigenvector composition of the singlet part of the wave function remains constant). Consequently a triplet eigenvector component as large as 0.5 will result in a reduction in the ${}^1P-{}_a^1D$ gf value by "only" 25%. However, when the ${}^1P$ term also acquires a large triplet component, the two combine to give a contribution to the ${}^1P-{}_a^1D$ line strength which can interfere constructively or destructively with the contributions from the singlet parts, thereby influencing the gf value much more drastically.

For the ${}^1P-{}_b^1D$ transition, relativistic effects are much smaller (Table X). Also for this transition, the relativistic effects lead to a reduction in the line strength (except for the length value in W which, as already mentioned, is less reliable). However, the relativistic effects are negligible until after Kr VII and the reduction in line strength is only 3% for the length value in Sm XXXIII.

The relativistic reduction in the line strength is partially canceled by the relativistic increase in the transition energies for the ${}^1P-{}_a^1D$ transition and completely canceled for the ${}^1P-{}_b^1D$ transition. The MCDHF transition energies have been used to scale the gf^{IC} length values to obtain gf values which take into account core polarization as well as relativistic effects, at least in an approximate way, for the ions heavier than Br VI. These final gf values are given in Table XI. For the ${}^1P-{}_a^1D$ transition, the overall relativistic effect on the gf value is a *reduction* by about 10% for Kr VII, increasing to more than a factor of 2 for Sm XXXIII and W XLV. For the ${}^1P-{}_b^1D$ transition, the relativistic effects *increase* the gf value by approximately 3% in Kr VII and 10% in Sm XXXIII.

VII. COMPARISON WITH EXPERIMENT

A limited amount of observational material exists at present for the ${}^1D$ terms in the Zn I isoelectronic sequence. The lowest ${}^1D$ term has been observed in the spectra from Zn I to Se V, while the second lowest ${}^1D$ is reported in Ref. 1 for Ge III and As IV. However, as already noticed by Litzén,[12] the published[1] classifications do not correspond to the dominant eigenvector component except for the lowest ${}^1D$ term in Zn I, which has a dominant $4s4d$ component. The lowest ${}^1D$ term in the rest of the sequence has primarily $4p^2$ character, while the second lowest should be designated $4s4d\,{}^1D$.

TABLE XI. Approximate relativistic gf values for the ${}^1P-{}^1D$ transitions in the Zn I isoelectronic sequence. The intermediate coupling length values (Table X) obtained using the MCHF energies are scaled in the ratio between the MCDHF and MCHF energies (Table IX). Core-polarization effects are included.

Ion	${}^1P-{}_a^1D$	${}^1P-{}_b^1D$
Kr VII	0.721	4.78
Mo XIII	0.644	3.79
Sn XXI	0.475	2.93
Xe XXV	0.414	2.65
Sm XXXIII	0.331	2.29
W XLV	0.266	2.06

Considering the lowest ${}^1D$ term, the observed ${}^1S-{}_a^1D$ energy separations were given in Table V and comparison with the calculated distances shows good agreement. The latter are about 4% smaller than the former from Ga II to Se V. This is approximately twice the deviation observed for the ${}^1S-{}^1P$ separation in Ref. 9.

The lifetime of the lowest ${}^1D$ term has been measured for Zn I[26-28] and Ga II[29-31] and the results are shown in Table XII. The measured lifetimes have been converted to gf values *under the assumption that the lifetime is due exclusively to the* ${}^1P-{}_a^1D$ *transition probability*. Judging from the IC calculations and the observations, this procedure can be expected to lead to reasonable results in Zn I and Ga II but not for the higher stages of ionization because of appreciable probabilities for other decay modes. For Zn I it seems safe to assume that $4s4p\,{}^1P-{}_a^1D$ is the dominant decay mode for ${}_a^1D$. There is very good agreement between the "observed" gf value calculated in this manner from the latest and most ac-

TABLE XII. Observed and calculated transition probabilities for the ${}^1P-{}_a^1D$ transition in Zn I and Ga II. The "observed" gf values are obtained under the assumption that no branching is present in the ${}_a^1D$ state.

Ion	Observed lifetime (nsec)	Observed gf value		Calculated gf value
Zn I	285 ± 14[a]	0.106 ± 0.06	l	1.44
	23.2 ± 2[b]	1.31 ± 0.12	v	1.40
	21.1 ± 0.4[c]	1.44 ± 0.03		
Ga II	15.8 ± 1.0[d]	0.346 ± 0.022	l	0.006
	54 ± 5[e]	0.10 ± 0.01	v	0.0326
	55[f]	0.099		

[a] May, double resonance, Ref. 26.

[b] Osherovich *et al.*, delayed coincidence, Ref. 27.

[c] Shaw *et al.*, electron-photon coincidence, Ref. 28.

[d] Andersen and Sørensen, beam-foil, Ref. 29.

[e] Denne *et al.*, beam-foil, Ref. 30.

[f] Andersen, beam-foil, preliminary value, Ref. 31.

TABLE XIII. Observed and calculated ${}^{1}_{a}D - {}^{1}_{b}D$ separations (cm^{-1}) in the Mg I and Zn I isoelectronic sequences. The calculated values are obtained from MCHF calculations.

Ion	Calculated	Observed	
Mg sequence			
Al II	25 420^{a}	24 608^{c}	
Si III	45 190^{a}	43 550^{d}	
P IV	63 450^{a}	61 012^{e}	
Zn sequence			
Ga II	18 610^{b}		18 466^{f}
Ge III	34 630^{b}	3 804^{g}	29 142^{f}
As IV	52 350^{b}	25 095^{g}	

[a] Froese Fischer, Ref. 25.
[b] Present work.
[c] Kaufman and Hagan, Ref. 33.
[d] Toresson, Ref. 34.
[e] Zetterberg and Magnusson, Ref. 35.
[f] Denne and Litzén, Ref. 14.
[g] AEL, Ref. 1.

curate experimental lifetime[28] and the theoretical *gf* value (also shown in Table XII) obtained using the observed transition energy (Table VII).

For Ga II, it is more doubtful whether it is possible to convert the ${}^{1}_{a}D$ lifetime to *gf* value without considering other decay modes. $4s4p\,{}^{3}P - {}^{1}_{a}D$ transitions have been observed in Ga II[32] but their intensity relative to ${}^{1}P - {}^{1}_{a}D$ are difficult to judge since the published intensity values are visual estimates of photographic blackening and the lines occur in quite different wavelength regions. In addition, the difference between the calculated length and velocity values shows that the theoretical value is of limited accuracy. Nevertheless, it is clear that the theoretical prediction is a very long lifetime which is in agreement with the latest measurements.[30,31]

For the second ${}^{1}D$ term the experimental information is even more scarce. Table XIII shows the calculated ${}^{1}_{a}D - {}^{1}_{b}D$ distances in Ga II, Ge III, and As IV as well as the observed.[1,14] For comparison MCHF determinations[25] of the same distance in three spectra of the Mg I sequence are given. These are calculated without the introduction of core polarization which, however, does not affect the term separations very much. The MCHF results for Al II, Si III, and P IV show good agreement with the observed values,[33-35] while no agreement exists with the values in Ge III and As IV given in Ref. 1. Denne and Litzén[14] have recently established the second ${}^{1}D$ term in Ga II and also a tentative ${}^{1}D$ term in Ge III. Both terms are in good agreement with the MCHF predictions.

The lifetime of the second ${}^{1}D$ term has recently been measured in Ga II.[30] The result is 0.73 ± 0.07 ns, which corresponds to a *gf* value of 3.3 ± 0.3 under the assumption that ${}^{1}P - {}^{1}_{a}D$ is the only decay mode. The theoretical length value given in Table VIII is 3.64. If the observed transition energy is used a value of 3.74 is obtained. Both values are in good agreement with the observed. They are slightly larger than the observed, which could indicate that some cascade effects still are present on the experimental lifetime, especially when it is remembered that taking branching into account will make the "observed" *gf* value smaller.

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