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Theoretical oscillator strengths for the resonance transitions in the Zn I isoelectronic sequence

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Nonrelativistic *gf* values for the $4s^2\,{}^1S$-$4s\,4p\,{}^1P$ transition based on multiconfiguration Hartree-Fock wave functions are reported for a number of ions from Zn I to W XLV. In addition to the correlation among the outer electrons, the effects of core polarization associated with the $3d^{10}$ subshell are taken into account to first order. Relativistic effects are estimated by using observed energies and allowing for spin-orbit interactions. When only the correlation among the outer electrons is taken into account, these approximate relativistic *gf* values agree well with relativistic calculations published recently, which also include only outer-shell correlation. The final values are compared with experimental observations. It is found that the discrepancy between theory and experiment is reduced by taking core polarization into account, and that there is good agreement for Zn I. However, for the heavier ions a discrepancy remains which increases with increasing ionization to a factor of 2 in Kr VII. Possible reasons for this discrepancy are discussed.

I. INTRODUCTION

The realization that highly ionized atoms stripped to configurations with a few electrons outside closed shells contribute significantly to the total energy losses from Tokamak plasmas[1] has resulted in a number of calculations of oscillator strengths for resonance transitions in one- and two-electron ions. For high stages of ionization relativistic effects become appreciable and both approximately[2,3] and fully relativistic[4,5] approaches have been developed. At the same time it is necessary to consider correlation effects.[6,7] In relativistic calculations for atoms with two electrons outside complete shells the correlation between the two outer electrons (called "outer correlation" in this paper) has been taken into account in different ways[4,8-10] while the correlation with the core (called core polarization) has been neglected. (The combined effects of outer correlation and core polarization will be called "full correlation.") Whereas correlation between shells with different principal quantum numbers is expected to decrease with increasing ionization, the decrease can be very slow and the question of whether core polarization is important or not is therefore, to a large degree, a question of whether it is appreciable at the neutral end of the particular isoelectronic sequence.

In the Cu I and Zn I isoelectronic sequences large discrepancies exist between observed and calculated oscillator strengths towards the neutral end of the sequences where oscillator strengths have been measured experimentally. (Exceptions are the neutral atoms where agreement is fairly good.) The measured oscillator strengths for the ions are smaller than the calculated ones which correspond to longer lifetimes for the excited levels involved than calculated theoretically. The discrepancy has been attributed to neglect of core polarization in the theoretical calculations, as well as to difficulties in the evaluation of cascade corrections to the experimentally measured decay curves produced by the beam-foil method. The latter has been used nearly exclusively for the experimental determination of lifetimes for ions in the isoelectronic sequences under consideration.

It has been shown in the Cu I sequence that core-polarization effects are too small to account for the discrepancy[7] although they do increase the lifetime of the excited state. The Zn I sequence could be expected to be similar but core polarization could conceivably be somewhat more important than in the Cu I sequence. To study this problem we have performed fairly accurate nonrelativistic multiconfiguration Hartree-Fock (MCHF) calculations of the oscillator strengths for the resonance transition, $4s^2\,{}^1S_0$-$4s4p\,{}^1P_1$. The calculations show that core polarization indeed does lead to an increase in the lifetime of the ${}^1P_1$ level but that the increase is unable to account for the discrepancy between theory and experiment.

It has been observed[4] that in the dipole length approximation the main relativistic effect on the oscillator strength for the resonance transitions with $\Delta n = 0$ in one- and two-electron atoms is to change the value of the transition energy while the difference between the relativistic and nonrelativistic values of the line strength S is small. This observation was made for the Li I and Be I isoelectronic sequences[4] and has been confirmed for the Na I (Ref. 11) and Mg I (Refs. 10 and 12) sequences also. For the $4s$-$4p$ transition in the copperlike W XLVI spectrum the difference between the relativistic and nonrelativistic line strength is only 4%.[7] This observation makes it possible to combine nonrelativistic line strengths, calculated taking correlation into account, with observed energy values to obtain oscillator strengths for which both relativistic and correlation effects have been taken into account although in an approximate way. (Instead of observed energy values, for large Z it is possible to use relativistic energy values calculated without or with a limited amount of correlation.) That this is possible in the Zn I isoelectronic sequence has been checked by comparing the gf values obtained in this way, with available results of relativistic calculations which include only outer correlation.[8,9] Therefore, it is necessary when making the comparison to neglect core polarization in the nonrelativistic calculation. Also the mixing between the $4s4p\ ^1P$ and ^3P terms caused by the spin-orbit interaction must be considered. However, this can be done in a simple way and the comparison shows good agreement between the two sets of values. Hence it seems possible to report fairly accurate approximately relativistic gf values which take into account the effects of not only outer correlation but also core polarization.

II. COMPUTATIONAL PROCEDURE

The calculations reported here are obtained using the computer program MCHF77.[13] Input data for the interaction matrices were generated using a modified version of Hibbert's program[14] and the wave functions obtained were used to calculate gf values.[15,16]

The aim of the calculations was to include the first-order corrections to the HF oscillator strengths by including in the MCHF expansions for one state those configurations which have an allowed dipole transition to the principal component of the other state. In practice, it turned out to be necessary to include those configurations which have an allowed transition to any of the two largest components in order to achieve reasonable accuracy. To include the interactions in the complex,[17] the expansions $\{4s^2, 4p^2, 4d^2, 4f^2\}$ and $\{4s4p_1, 4p_24d_1, 4d_24f\}$ were used for the ^1S and ^1P states, respectively, where the notation $4p_1$, $4p_2$, etc. is used in the latter to denote the fact that the two orbitals were not constrained to be the same. These configurations give rise, as expected, to the main correlation effect on the oscillator strength, an effect which persists for high degree of ionization. The contribution from $4p^2$ to the ^1S state and from $4p_24d_1$ to the ^1P state is about 0.2 (amplitude) over the range of Z considered (Zn I to W XLV). The magnitude of this component is the reason that configurations which have an allowed dipole transition to it must be included in the expansions.

Core polarization was taken into account by including in the MCHF expansion for one state those configuration states which can be reached by a $3d \rightarrow 4f$ or $3d \rightarrow 4p$ excitation from the two leading components of the other state. In terms of pair-correlation functions, the $(3d, 4s)$ replacements $(4p, 4p)$ and $(4f, 4p)$ were included while for the $(3d, 4p)$ pair the $(4s, 4p)$ and $(4s, 4f)$ functions were taken into account. In the ^1S state, the $3d^94f(^1P)4p4d$ configuration state which has a dipole transition to the $3d^{10}4p4d$ component of the ^1P state is included although it does not interact directly with the $3d^{10}4s^2$ component. The other ^1S states belonging to $3d^94f4p4d$ do not contribute directly to the oscillator strength and also give smaller contributions to the energy. Therefore they have been neglected. The expansions used are given in Table I.

Correlation with the $3p^6$ shell, which for large Z has a larger mean radius than the $3d^{10}$ shell, has been neglected here for the following reason. In the study of the Cu I sequence[7] it was found that the main contribution to the oscillator strength from correlation with the $3p$ shell for large Z came from $3p \rightarrow s$ excitations. In the present case, a $3p(^1S) \rightarrow 4s(^1P)$ excitation is impossible and the $3p(^1S) \rightarrow 5s(^1P)$ excitation is expected to be less important. A $3p(^1P) \rightarrow 4s(^1S)$ excitation is possible but its contribution is proportional to the amount of $3p^54s^24p$ in the ^1S state which is small due to Brillouin's theorem.[18] The effect of introducing the $3p^54s4p5s$ configuration in the ^1S state and $3p^54s^25s$ in the ^1P state was considered in the case of Ga II and was found to be small. The same was found for the $3p \rightarrow 4d$ excitations in Ga II.

To ascertain the quality of the wave functions a number of additional calculations were made for Ga II which are described in the Appendix. As a result of these tests, in the ^1S expansion given in Table I, the $3d^94s4p^2$ configuration determined variationally was replaced by the same configura-

TABLE I. MCHF expansions.

^1S state

$$3d^{10}4s_1^2 + 3d^{10}4p_1^2 + 3d^{10}4d_1^2 + 3d^{10}4f_1^2$$
$$+ 3d^94f_24s_24p_2 + 3d^94s_24p_3^2$$
$$+ 3d^94s_24p_35p_1 + 3d^94f_2(^1P)4p_14d_2$$

$4s_2$ and $4p_3$ orbitals frozen, taken from a HF calculation for $3d^{10}4s4p\ ^1P$

^1P state

$$3d^{10}4s_14p_1 + 3d^{10}4p_24d_1 + 3d^{10}4f_14d_2$$
$$+ 3d^94f_24s_2^2 + 3d^94p_34s_1^2$$
$$+ 3d^94p_4^3 + 3d^94f_24p_4^2$$

If the coupling is unspecified, all possible coupling schemes have been included tion with frozen $4s$ and $4p$ orbitals plus the $3d^9 4s4p5p$ configuration. This was found to give a slightly better approximation to the correlation effects on the oscillator strength as described in the Appendix. The $3d^9 4s4p^2 \leftrightarrow 3d^9 4s4p5p$ interaction has a single-particle part since the $4p \rightarrow 5p$ replacement does not change the angular quantum number l. There is extensive cancellation between the single-particle integral

$$I(4p,5p) = -\frac{1}{2}\langle 4p|\frac{d^2}{dr^2}+\frac{2Z}{r}-\frac{l(l+1)}{r^2}|5p\rangle$$

and the Coulomb interaction integrals

$$\langle nl4p|e^2/r_{12}|nl5p\rangle ,$$

where nl runs over all orbitals including the inner ones. Since the $4p$ orbital in this case was kept fixed the cancellation was allowed to take place explicitly. It is possible to cancel the $I(4p, 5p)$ integral directly[19] but this requires additional constraints on the inner orbitals.

The calculations were carried out with the inner-shell orbitals frozen in order to avoid complications due to lack of orthogonality between the inner orbitals in the calculation of the oscillator strengths. The HF orbitals for the ^1S state were used in both MCHF expansions. At the same time the frozen-core approximation saves a considerable amount of computation. It was verified, using a somewhat shorter MCHF expansion, that in the case of Ga II there is a negligible difference between the frozen core and completely variational calculations.

To investigate the importance of spin-orbit interaction a simple intermediate-coupling calculation was performed for the heavier ions by diagonalizing the 2×2 interaction matrix for the two $J = 1$ states of $4s4p$. The electrostatic energy difference between the two states was obtained as the difference between the total HF energies for $4s4p\,^1P$ and ^3P. The mean value of the spin-orbit parameters determined in the two calculations was used to calculate the off-diagonal matrix element and the spin-orbit parameter for the ^3P term used to determine the position of $^3P_1$ relative to the mean energy of the ^3P term. The diagonalization yields an approximate value for the energy separation between the two levels as well as their eigenvector compositions.

III. RESULTS

To give an indication of the quality of the wave functions we compare in Table II the observed and calculated values for the $4s^2\,^1S$-$4s4p\,^1P$ transition energies. The latter are computed as the difference between total energies. Also some transition energies calculated using different relativistic approximations are shown. The relativistically cor-

TABLE II. Observed and calculated $4s^2\,^1S$-$4s4p\,^1P$ transition energies in the Zn I isoelectronic sequence. Values in atomic units.

						$\frac{\text{Obs}}{\text{MCHF}}$ [c]	
	HF	MCHF	HFR[a]	RRPA[b]	Observed	Zn I sequence	Cu I[d] sequence
Zn I	0.1759	0.2024			0.2130*[e]	1.052	0.9753
Ga II	0.3011	0.3155		0.3077	0.3221*[e]	1.021	0.9879
Ge III	0.4016	0.4108		0.4093	0.4186*[e]	1.019	
As IV	0.4928	0.4989			0.5104*[e]	1.023	1.0095
Se V	0.5792	0.5834			0.6002*[e]	1.029	
Br VI	0.6629	0.6655	0.681	0.6886	0.6893*[e]	1.036	
Kr VII	0.7446	0.7460	0.770		0.7784*[f]	1.043	1.040
Mo XIII	1.215	1.213	1.32	1.3445	1.3365*[g]	1.102	1.102
Sn XXI	1.824	1.820	2.20*			1.21	
Xe XXV	2.125	2.120	2.74	2.7853	2.770*[h]	1.307	1.318
Sm XXXIII	2.725	2.720		4.1966*		1.543	
W XLV	3.622	3.617	7.57	7.5292*		2.082	2.033

[a] Cowan, Ref. 8.

[b] Shorer and Dalgarno, Ref. 9.

[c] Values marked with an asterisk are used as observed energies in the evaluation of the ratio; these values are used also in Table VI as explained in the text.

[d] Froese Fischer, Ref. 7.

[e] *Atomic Energy Levels*, Ref. 20.

[f] Fawcett *et al.*, Ref. 21.

[g] Reader and Acquista, Ref. 22.

[h] Hinnov, Ref. 23.

TABLE III. Differences between observed and MCHF $4s^2$-$4s4p\,^1P$ transition energies compared to approximate relativistic corrections to the $4s$-$4p$ transition energies. Values in atomic units.

	$E_{\mathrm{Obs}}-E_{\mathrm{MCHF}}$ [a]	Relativistic corrections[b]
Zn I	0.0106	0.0066
Ga II	0.0066	0.0110
Ge III	0.0078	0.0158
As IV	0.0115	0.0211
Se V	0.0168	0.0276
Br VI	0.0238	0.0356
Kr VII	0.0324	0.0443

[a] Values taken from Table II.

[b] Fraga *et al.*, Ref. 24. For the method of calculation see text.

rected HF (HFR) values due to Cowan[8] and the relativistic RPA (RRPA) results of Shorer and Dalgarno[9] are given together with the observed values.[20-23] Finally the ratios between the observed and the MCHF values in the Zn I as well as the Cu I sequence are tabulated. If no observed values are known the RRPA results, which agree well with the observed energy differences except for the first few atoms, have been used when available to determine the ratio. For Sn XXI, the HFR value has been used. The ratios for the Cu I sequence also are reported for the same atom using approximation ii of Ref. 7 (Table 9). Thus the value for Zn I, for example, in Table II is calculated from the $3d^{10}4s$-$3d^{10}4p$ transition energy in Zn II.

Table II shows that the calculated transition energies are smaller than observed. For large values of Z, this is due to relativistic effects since the relativistic correction associated with a $4s$ electron is larger than for a $4p_{3/2}$ electron and $4s_{1/2}4p_{3/2}$ is the largest component of the ^1P state. For low values of Z the difference can also be due to neglected correlation effects. In this region of Z, the observed transition energies are often used as approximations to the nonrelativistic energies needed for the calculation of nonrelativistic *gf* values. In order to determine whether the observed or the MCHF values are closer to the true nonrelativistic energies for low Z, Table III compares the differences between observed and MCHF values with approximate relativistic corrections to the transition energies derived from the tabulation by Fraga *et al.*[24] The latter are obtained by equating the $4s^2\,^1S$-$4s4p\,^1P$ relativistic correction with the $4s_{1/2}-(\frac{2}{3}4p_{3/2}+\frac{1}{3}4p_{1/2})$ correction (the *jj* composition of the $4s4p\,^1P$ term is $\frac{2}{3}4s_{1/2}4p_{3/2}+\frac{1}{3}4s_{1/2}4p_{1/2}$ and LS coupling is a good approximation up to Kr VII, the heaviest ion in the sequence considered in Ref. 24). The relativistic correction to the total energy for a $4s_{1/2}$ electron in Zn I, say, is approximated by the difference between the total relativistic corrections in Zn I $4s^2\,^1S$ and Zn II $4s\,^2S_{1/2}$ tabulated in Ref. 24. The relativistic correction for a $4p_{1/2}$ electron in Zn I is approximated by the difference between the total relativistic corrections in Ga I $4s^24p\,^2P_{1/2}$ and Ga II $4s^2\,^1S$, and the correction for a $4p_{3/2}$ electron by the correction for $4p_{1/2}-\frac{3}{2}\zeta_{4p}$. The estimated relativistic corrections shown in Table III are obviously fairly uncertain. If we assume that they are correct, the difference between the relativistic corrections and the "observed" values in Table III is equal to the discrepancy between the MCHF and the nonrelativistic energy. These differences are in all cases smaller than the relativistic corrections which, under the above assumption, means that the MCHF values are closer to the nonrelativistic energies than the observed. Hence in the absence of better evidence the MCHF energies have been used as the best approximation to the nonrelativistic energies.

From about Kr VII, the MCHF transition energies becomes slightly smaller than the HF ones (Table II). This is because the outer-shell correlation energy becomes larger in the ^1P than in the ^1S state with increasing ionization. This is somewhat surprising but is a result of the fact that the number of configurations belonging to the complex increases with n. For $n=2$, the correlation energy associated with the ^1S state is the larger for all Z but for $n=3$ the additional $3p3d$ component in the ^1P state picks up nearly as much correlation energy as the $3p^2$ and $3d^2$ components in the ^1S state together and the correlation energies for the two terms become rather similar with increasing Z. For $n=4$, more energy is picked up by adding a $4d4f\,^1P$ than a $4f^2\,^1S$ component and the MCHF transition energy becomes smaller than the HF one for large Z. The same behavior, although probably more pronounced, can be expected for $n=5$.

For Ga II and Ge III, the MCHF energies (Table II) are in better agreement with observation than the RRPA values but for Br VI the opposite is the case and from Mo XIII on the influence of relativity on the transition energies is obvious. It is interesting that the ratio between observed and MCHF energies is very close in the Zn I and Cu I sequences from about Kr VII where relativistic effects become important. For lower Z, the two sets of values are different due to differences in the amount of correlation energy picked up in the two calculations.

The nonrelativistic *gf* values are shown in Table IV. The MCHF transition energies are used in all calculations presented here in order to show the

TABLE IV. Nonrelativistic gf values for the Zn I isoelectronic sequence. In the rows headed HF and MCHF, the upper value is calculated in the dipole length, the lower in the dipole velocity approximation. The MCHF energies shown in Table II have been used to evaluate all gf values in the present work.

		MCHF						
	HF	Outer correlation	Full correlation	Coulomb approximation[a]	Helliwell[b]	Zilitis[c]	Warner[d]	Amusia *et al.*[e]
Zn I	1.92	1.68	1.49	1.5	1.77	1.95	1.95	1.50
	0.98	1.70	1.49					
Ga II	2.53	1.97	1.71		2.29	2.29	2.26	
	1.45	1.87	1.63					
Ge III	2.51	1.96	1.71			2.29	2.25	
	1.51	1.85	1.63					
As IV	2.40	1.90	1.67			2.24	2.20	
	1.50	1.80	1.61					
Se V	2.29	1.84	1.63			2.16		
	1.47	1.75	1.57					
Br VI	2.19	1.78	1.58			2.09		
	1.44	1.70	1.54					
Kr VII	2.10	1.72	1.54					
	1.40	1.65	1.50					
Mo XIII	1.69	1.42	1.30					
	1.20	1.39	1.29					
Sn XXI	1.35	1.15	1.07					
	1.00	1.15	1.08					
Xe XXV	1.22	1.05	0.98					
	0.92	1.05	1.00					
Sm XXXIII	1.03	0.89	0.85					
	0.79	0.90	0.86					
W XLV	0.84	0.73	0.70					
	0.65	0.74	0.72					

[a] Bates and Damgaard, Ref. 25.
[b] Helliwell, Ref. 27.
[c] Zilitis, Ref. 28.
[d] Warner, Ref. 29.
[e] Amusia *et al.*, Ref. 30.

differences in line strengths between different approximations. Three different results are shown in Table IV using both the dipole length and the dipole velocity approximations. To indicate the importance of correlation for this transition, HF results are shown. The MCHF expansions have been used to calculate two types of results. In the first, outer correlation only is taken into account whereas in the second, the core-polarization effect also has been included to first order.

Table IV shows the importance particularly of outer-shell correlation in this case. The amount of correlation increases from Zn I to Ga II and Ge III and decreases thereafter. Outer-shell correlation changes the length value 12.5% in Zn I and 22% in Ga II. Its influence is still 15% in Mo XIII and 13% in W XLV. The influence of core polarization is smaller, 11% in Zn I, 13% in Ga II, 10% in Mo XIII, and 4% in W XLV. Thus core polarization decreases more slowly than outer-shell correlation up to about Mo XIII but from there somewhat faster. It is interesting that the agreement between length and velocity values assuming outer-shell correlation only is nearly as good as when full correlation is included. Thus in Zn I, the length and velocity values are 1.68 and 1.70, respectively, assuming outer correlation only while the values including core polarization are 1.489 and 1.495. Thus the good agreement found between the length and velocity approximation when outer-shell correlation is included does not guarantee that core polarization is negligible.

It is seen (Table IV) that the velocity values are larger than the length ones for Zn I and for the ions heavier than approximately Sn. This would imply that the nonrelativistic energies used here are slightly too low especially for large Z. This corresponds to the remaining correlation energy being larger in the ^1S than in the ^1P state which is reasonable especially since correlation *in* the core has been neglected in the present work. The possibility of using the agreement between length and velocity values to determine the nonrelativistic energy[7] has been considered but abandoned since the velocity value for the line strength is believed to be less accurate than the length value as described

TABLE V. Contributions to the square root of the line strength for the $4s^2\,{}^1S$-$4s4p\,{}^1P$ transition arising from $3d \rightarrow 4f$ excitations compared to the square root of the total line strength $S^{1/2}$.

	Zn I		Ga II		Mo XIII		W XLV	
	Length	Velocity	Length	Velocity	Length	Velocity	Length	Velocity
a	−0.0707	−0.1988	−0.0830	−0.3081	−0.0329	−0.5520	−0.0069	−0.6344
b	−0.0546	+0.1623	−0.0635	+0.2492	−0.0268	+0.4591	−0.0061	+0.5595
a+b	−0.1253	−0.0365	−0.1465	−0.0589	−0.0597	−0.0929	−0.0130	−0.0749
$S^{1/2}$	3.3222	0.6735	2.8542	0.8796	1.2679	1.5344	0.5380	1.9754
$\frac{a+b}{S^{1/2}}$ (%)	3.8	5.4	5.1	6.7	4.7	6.1	2.4	3.8

[a] $3d^{10}4s^2\,{}^1S$-$3d^94f4s^2\,{}^1P$.

[b] $3d^94f4s4p\,{}^1S$-$3d^{10}4s4p\,{}^1P$.

later.

Only a few nonrelativistic calculations of these oscillator strengths have been carried out earlier. For Zn I, Bates and Damgaard[25] used the Coulomb approximation to obtain a value which is in good agreement with the MCHF value with full correlation included. However, Pinnington *et al.*[26] have used the same approximation to obtain *gf* values for ions up to Kr VII and their values appear to be in closer agreement with the MCHF values including outer-shell correlation only. Helliwell[27] has used a somewhat more complicated semiempirical approach and similar methods have been used by Zilitis[28] and Warner[29] but the results, while below the HF values, fail to take outer-shell correlation into account properly. Zilitis[28] also has carried out a HF calculation (not shown) which is in agreement with the present one except for different choices of transition energies. Finally, more recently Amusia *et al.*[30] have made an RPA calculation for Zn I including the interaction with the $3d$ shell which is in good agreement with the MCHF value including core polarization.

The question of the accuracy of the final results including core polarization is difficult to answer. The uncertainty in the energies gives some uncertainty in the *gf* values. The true nonrelativistic energies are, as mentioned already, likely to be somewhat larger than the energies used here. This will lead to an increase in the length and a decrease in the velocity values which means that the discrepancy between the two will increase in the region between Ga II and Sn XXI. The discrepancy in Table IV is slightly less than 5% in Ga II and Ge III (8% if the observed energies are used) which are the worst cases. The tests for Ga II described in the Appendix show that the neglected correlation with the $3p$ shell and approximations in the interactions which are included apparently can account for some of the discrepancy. The results of the tests when added together showed a decrease in the length value by approximately 0.02 to 1.69 and an increase in the velocity value by approximately 0.05 to 1.68 which reduces the discrepancy to 0.6% (5% if the observed energy is used). The discrepancy in the MCHF calculation for the Cu I sequence[7] is at best 2.5% for Zn II. Thus the accuracy in the present calculation has not quite reached that obtained in the Cu I sequence but would apparently come very close with a more consistent treatment of core polarization. However, the intrinsic accuracy of the Zn calculation is believed to be worse than for the Cu calculation since the latter includes a partial allowance for the effects of correlation *in* the core which have been neglected in the former. For Ga II, a very small contribution to the velocity matrix element can bring length and velocity values into agreement. The velocity value is the more unstable of the two which is reflected in the fact that additions to the MCHF expansions in the course of the calculations led to a steady decrease in the length value whereas the velocity value behaved irregularly.

The velocity value is strongly dependent on cancellation between contributions from the initial and final state and to obtain an accurate value it is necessary that the two states be improved in an equivalent way. This is demonstrated in Table V which shows the contributions to the length and velocity reduced matrix element ($S^{1/2}$) arising from the $3d^{10}4s^2\,{}^1S$-$3d^94f\,4s^2\,{}^1P$ and $3d^94f\,4s4p\,{}^1S$-$3d^{10}4s4p\,{}^1P$ transitions in a few ions. While the total contribution from the two channels is of the same order of magnitude in the length and in the velocity matrix element (less than 7% of the total value), the individual contributions are smaller than 3% of the total in the case of the length value but up to 36% of the total for the velocity value. If only one state is improved the length value would still be improved but the effect on the velocity value would be disastrous. Even when both states are improved the velocity value is rather sensitive to the precise cancellation between the two contributions. We therefore expect the length values to be the more accurate in Table IV particularly in the beginning of the isoelectronic sequence.

IV. APPROXIMATE RELATIVISTIC *gf* VALUES

As mentioned in the Introduction it has been observed that the main relativistic effect on the length oscillator strength for $\Delta n = 0$ resonance transitions in a number of one- and two-electron systems is to change the transition energy. This observation, if true for the Zn I sequence, allows us to obtain approximate relativistic *gf* values by scaling the nonrelativistic length values in the ratio between the observed and the nonrelativistic energy values. Some relativistic calculations have already been performed for the Zn I sequence which allow us to test the hypotheses and in addition give theoretical relativistic energies for ions for which no observations exist. Cowan[8] has made HFR calculations of both the $4s^2\,{}^1S$-$4s4p\,{}^1P$ and ${}^3P$ oscillator strengths (and energies) including some outer-shell correlation for a number of ions and Shorer and Dalgarno[9] have reported RRPA results. These include outer-shell correlation but not core polarization and consequently it is possible to compare the HFR and RRPA results with the MCHF

TABLE VI. Approximate relativistic *gf* values. The length values given in Table IV are scaled as described in the text. The energies used in the scaling are given in Table II.

		MCHF				
	HF	Outer correlation	Full correlation	HFR[a]	RRPA[b]	Experiment
Zn I	2.02	1.77	1.56		1.59	1.50 ± 0.05[c] 1.46 ± 0.04[d] 1.43 ± 0.15[e] 1.45 ± 0.15[f] 1.18 ± 0.14[g]
Ga II	2.58	2.01	1.75		1.97	1.39 ± 0.17[h]
Ge III	2.56	2.00	1.74		1.98	1.38 ± 0.22[h]
As IV	2.46	1.94	1.71			1.12 ± 0.11[h]
Se V	2.36	1.89	1.68			0.96 ± 0.18[h]
Br VI	2.27	1.84	1.64	1.91	1.84	0.82 ± 0.12[i] 0.82 ± 0.07[j]
Kr VII	2.19	1.79	1.61	1.85		0.81 ± 0.09[k] 0.94 ± 0.04[l] 0.81 ± 0.09[j]
Mo XIII	1.86	1.57	1.43	1.57	1.54	
		(1.54)[m]	(1.41)[m]			
Sn XXI	1.63	1.39	1.29	1.32		
		(1.31)	(1.22)			
Xe XXV	1.60	1.37	1.28	1.24	1.24	
		(1.25)	(1.17)			
Sm XXXIII	1.59	1.37	1.31		1.15	
		(1.17)	(1.12)			
W XLV	1.75	1.52	1.46	1.16	1.15	
		(1.19)	(1.15)			

[a] Cowan, Ref. 8.

[b] Shorer and Dalgarno, Ref. 9.

[c] Landman and Novick, Hanle effect, Ref. 31.

[d] Lurio *et al.*, Hanle effect, Ref. 32.

[e] Andersen and Sørensen, beam-foil, Ref. 33.

[f] Abjean and Johannin-Gilles, absorption in an atomic beam, Ref. 34.

[g] Bauman and Smith, phase-shift, Ref. 35.

[h] Sørensen, beam-foil, Ref. 36.

[i] Pinnington *et al.*, beam-foil, Ref. 26.

[j] Knystautas and Drouin, beam-foil, Ref. 37.

[k] Druetta and Buchet, beam-foil, Ref. 38.

[l] Irwin *et al.*, beam-foil, Ref. 39.

[m] For these values the spin-orbit interaction has been taken into account in an approximate way as explained in the text.

TABLE VII. Calculated $4s4p\,^1P_1$-$^3P_1$ separations (a.u.) and $4s^2\,^1S_0$-$4s4p\,^3P_1$ gf values.

	$4s4p\,^1P_1$-$4s4p\,^3P_1$ Separation			$gf\,(^3P)$ Present		
	Present	HFR[a]	Observed	Outer correlation	Full correlation	HFR[a]
Br VI		0.230	0.2043[b]			0.004
Mo XIII	0.459	0.408		0.016	0.015	0.026
Sn XXI	0.759	0.727		0.051	0.047	0.073
Xe XXV	0.978	0.977		0.075	0.070	0.098
Sm XXXIII	1.63			0.120	0.115	
W XLV	3.42	4.19		0.178	0.171	0.159

[a] Cowan, Ref. 8.
[b] *Atomic Energy Levels*, Ref. 20.

results with outer-shell correlation only included. Table VI shows the scaled HF and MCHF (length) values as well as the HFR and RRPA results. The relativistic energies, either observed or calculated, used in the scaling were indicated in Table II. For the ions Zn I to Kr VII observed gf values are also given in Table VI.

Comparison between the MCHF values with outer-shell correlation included and the HFR and RRPA results shows that in the beginning of the sequence (except for Zn I) there is good agreement between the RRPA and MCHF results. The small discrepancy between the two is probably partly due to the use of different transition energies. For Br VI, there is perfect agreement between the three methods but then the MCHF results slowly become larger than the others. The difference, it turns out, can be explained to a large degree by the neglect of spin-orbit interaction in the MCHF calculation. The simple intermediate-coupling calculation described earlier has been used to determine the actual amount of ^1P in the $J=1$ states of $4s4p$ for the ions Mo XIII to W XLV and the results used to correct the MCHF results in Table VI. The corrected values are given in parentheses. Comparison of the HFR and RRPA results with the corrected MCHF values show good agreement for Mo XIII, Sn XXI, and Xe XXV whereas for Sm XXXIII and W XLV the agreement is not quite as good. This might be due partly to the simplicity of the intermediate-coupling calculation. Nevertheless, it seems possible to conclude that the relativistically corrected MCHF values with core polarization included will give a reasonable approximation to the true oscillator strengths in this sequence.

The discrepancy between the MCHF results including outer-shell correlation and the RRPA result for Zn I is not understood.

Table VII shows the $4s4p\,^1P_1$-$^3P_1$ separations as well as the $4s^2\,^1S_0$-$4s4p\,^3P_1$ oscillator strengths obtained from the intermediate-coupling calculations. The energy for the $^1S_0$-$^3P_1$ transition was determined using the best values for the $^1P_1$ energy given in Table II together with the $^1P_1$-$^3P_1$ energy separations resulting from the diagonalization. The energy separations and oscillator strengths are compared with those calculated by Cowan.[8] Cowan's energy separations are smaller up to Xe XXV and larger thereafter. His value in Br VI is larger than observed which indicates that his values are the more accurate. However, the two methods do lead to $^1S_0$-$^3P_1$ transition probabilities which are in reasonable agreement.

V. COMPARISON WITH EXPERIMENT

In addition to the calculated values, Table VI gives observed gf values for the ions Zn I to Kr VII. For Zn I, there is good agreement between Hanle effect,[31,32], beam-foil,[33] and an absorption measurement using an atomic beam,[34] while a phase-shift measurement[35] gives a considerably smaller value. For the heavier atoms only the beam-foil method has been used[26,36-39] but there is good agreement between the different results for Br VI and Kr VII. As mentioned in the Introduction it was one of the purposes of this work to study whether the large discrepancy between observed and calculated values for this transition could be due to core polarization. Taking Ga II as an example it is seen (Table VI) that although core polarization does bring the calculated gf value down, in this case from 2.01 to 1.75, it is still considerably larger than the observed (1.39 ± 0.17). Since the length value has been decreasing steadily when additional configurations have been added to the MCHF expansions it is believed that the correct value can be somewhat smaller than the final values given in Table VI. However, an error of 10% in the neutral end would mean that there is good agreement between the MCHF value and the measurements in Zn I (except for the phase-shift result) while a considerable discrepancy still would exist with the beam-foil measurements for the heavier ions, a discrepancy which increases with increasing ionization and amounts to a factor of 2 in Br VI and Kr VII. The calculations are believed to become more accurate with increasing ionization which makes it difficult to ascribe the discrepancy to neglected core-polarization effects. The observed *gf* values are lower than the calculated which could be expected if cascade corrections are more important than has been anticipated in the evaluation of the measurements.

Younger and Wiese[40] recently have made a study of this problem for the Cu I sequence and have shown that cascade problems in general can be expected to be more severe for heavier atoms (and in particular for $\Delta n = 0$ transitions) and more specifically that, using what appears to be a reasonable model for the population of excited states following foil interaction, a two-exponential fit to the simulated decay curve for Kr VIII can reproduce the observed lifetime of about 0.36 ns even though the theoretical lifetime used in constructing the decay curve is only about 0.26 ns. Younger and Wiese studied also the $4s^2\,^1S$-$4s4p\,^1P$ transition for the Kr VII ion and obtained similar results which, however, are more uncertain due to difficulties in establishing the initial populations. It thus seems likely that a substantial part of the discrepancy can be due to difficulties in the evaluation of measurements and an experimental reinvestigation of these transitions seems called for at this point.

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APPENDIX

A number of additional calculations were made for Ga II for which the largest discrepancy between length and velocity values exists. One purpose was to determine the necessary number of orbitals for each *nl* value. In principle it is possible to pick up more correlation energy by allowing the orbitals in each correlating configuration to be determined variationally but not constrained to be the same as other orbitals of the same type in other configurations. However, the complexity of the calculation increases rapidly with the number of orbitals and the maximum number of correlation orbitals of any given type therefore was restricted to three. Calculations using unconstrained orbitals were performed to decide which orbitals could be made identical without substantial loss in correlation energy.

Since the main purpose is to determine the first-order correction to the oscillator strength it is essential that pair-correlation functions are able to describe the single-particle excitations which contribute to the oscillator strength. In the case, say, of the $(4f, 4p)$ correlation function, the interacting configuration in the ^1S state, $3d^94f4s4p$, can be viewed as being constructed from a $3d \rightarrow 4f$ excitation in the $3d^{10}4s4p\,^1P$ state. To account for the oscillator strength associated with the $3d \rightarrow f$ excitations it is necessary that the $4f$ correlation orbital be able to represent the total oscillator strength associated with the $3d^9f4s4p$ series, where f in principle includes all bound as well as continuum f orbitals. This will often be possible due essentially to Brillouin's theorem.[18] It was checked that this was achieved in the present case by performing calculations for $3d^{10}4s^2 + 3d^94f4s_14p_1\,^1S$ in which the $4s_1$ and $4p_1$ functions were taken from a HF calculation for $3d^{10}4s4p\,^1P$ and only the $4f$ orbital was varied. A similar calculation was made for the $3d^{10}4s4p + 3d^94f4s_1^2\,^1P$ state in which the $4s_1$ orbital was taken from a HF calculation for $3d^{10}4s^2\,^1S$ and only $4f$ varied. The $4f$ functions obtained were rather different from those found by allowing all the orbitals to be determined variationally and less correlation energy was picked up but the $3d \rightarrow 4f$ contributions to the oscillator strength were practically the same. A larger deviation was found for the $(4p, 4p)$ correlation function for the $(3d, 4s)$ pair in the ^1S state. The interacting configuration in this case is $3d^94s4p^2$ which can be thought of as being obtained by a $3d \rightarrow 4p$ excitation from the $3d^{10}4s4p\,^1P$ state. In this case the $4p$ orbital cannot at the same time be a correlation orbital and represent the $4p$ function in the $3d^{10}4s4p\,^1P$ state. If the $4s_1$ and $4p_1$ functions in the $3d^94s_14p_1^2$ configuration are frozen as HF functions for $3d^{10}4s4p\,^1P$ it is necessary to add the $3d^94s_14p_15p$ correlating configuration in order to include at least partially the interaction with the p series. It was found that the contribution to the oscillator strength, if this was done, was slightly different from that obtained when the $4s$ and $4p$ orbitals were allowed to vary but again less correlation energy was picked up. Thus in the final calculation the $3d \rightarrow 4p$ excitation was represented by the two configurations $3d^94s_14p_1^2$ and $3d^94s_14p_15p$.

In the ^1P state, the $(4p, 4p)$ correlation function is associated with the $3d^94p^3$ configuration. Calculations were made in which the $4p$ orbital was frozen and the $3d^94p^25p$ configuration was introduced but the difference in this case was smaller. However, this is not surprising since these configurations combine only with the second component of the ^1S state, $3d^{10}4p^2$, and have a smaller influence on the oscillator strength.

Finally it was checked that taking into account the interaction within the complex gives a good approximation to the correlation among the two outer electrons. $5s$ and $5p$ orbitals were added to the $4l$ orbitals describing the outer correlation and it was found that their influence on the oscillator strength (for Ga II) was small.

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