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Multiconfiguration Hartree-Fock calculations for singlet terms in neutral strontium

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Multiconfiguration Hartree-Fock (MCHF) calculations are presented for singlet terms in neutral strontium (Sr I) belonging to (perturbed) *sp*, *sd*, and *sf* Rydberg series. We discuss briefly some particularly difficult MCHF calculations and the steps taken to overcome the difficulties. The *ab initio* wave functions are used to calculate radiative lifetimes as well as individual transition rates for electric dipole and quadrupole radiation. The calculated lifetimes are compared to recent experimental results. The observed trends are well reproduced by the calculations. We compare our wave functions with wave functions obtained from multichannel quantum-defect theory (MQDT) in either of two different ways. One is based on semiempirical fitting to the observed energy levels and the other on a recent *ab initio* *R*-matrix calculation of MQDT parameters. We find good agreement with the wave functions obtained in the latter calculation, confirming earlier conjectures about the degree of reliability of semiempirical MQDT fits to perturbed Rydberg series [C. Froese Fischer and J. E. Hansen, Phys. Rev. A **24**, 631 (1981)].

I. INTRODUCTION

Some years ago, Hansen and Persson[1] predicted a strong mixing between the $4d5p\ ^1F^\circ$ term and the $5snf\ ^1F^\circ$ series in neutral strontium (Sr I). This interaction leads to cancellation in the transition integral from the lowest $^1F^\circ$ to the lower-lying $5s4d\ ^1D$ term in agreement with observations of the line intensities in emission spectroscopy.[1] Similarly, the $5snp\ ^1P^\circ$ series has been observed to interact strongly with the $4d5p\ ^1P^\circ$ term. This leads to some ambiguities in level designations[2] which form part of the motivation for the present work.

The study of interactions in Rydberg series has been given new impetus by the extensive experimental studies which have been carried out during the last few years using laser techniques. Recently, the lifetimes of a number of levels in the $^1P^\circ$ and $^1F^\circ$ series have been measured by Jönsson *et al.*[3] These measurements confirm the long lifetime of the lowest $^1F^\circ$ term but show otherwise a very regular variation with *n*. On the other hand, the $5snp\ ^1P^\circ$ series is characterized by a shortening of the lifetime between $n=7$ and 8 which presumably is due to the interaction with the doubly excited $4d5p\ ^1P^\circ$ state.

It is interesting to try to understand the variations in the lifetime trends as well as any deviation from the simple scaling law $\tau \sim (n^*)^3$ in terms of configuration-interaction (CI) effects. Approximate formulas have been used to interpret the decrease in lifetimes in the vicinity of doubly excited levels of two-electron systems.[4] These take into account the admixture of a short-lived perturber and involve the amount of perturber character in the particular level, which may be taken, for example, from a multichannel-quantum-defect-theory (MQDT) analysis[5] of the energy-level structure. As an alternative, we present here results of an *ab initio* multiconfiguration Hartree-Fock (MCHF) study of the observed lifetime trends.

A number of MQDT studies of the alkaline earths have been carried out starting with the work of Lu[6] and, in particular, Armstrong, Esherick, and Wynne.[7] To investigate the applicability of MQDT to the alkaline-earth spectra, Froese Fischer and Hansen[8] carried out MCHF calculations for the ^1S and ^1D series in Ca I and Sr I. Disagreements between MQDT and MCHF results with regard to eigenfunction compositions were found in all cases considered. The qualitative agreement between observed isotope shifts and theoretical values calculated from simplified MCHF wave functions, which was found by Aspect *et al.*,[9] supported the MCHF results. As a further check, Froese Fischer and Hansen[10] tested their MCHF wave functions by calculating lifetimes of the ^1S terms and found reasonable agreement with those observed. We are here extending these comparisons by investigating the perturbed $5snp\ ^1P^\circ$, $5snd\ ^1D$, and $5snf\ ^1F^\circ$ series in Sr I, using the MCHF approach to account accurately for the correlation between the two outer electrons but neglecting core-polarization and relativistic effects.

Recently, Aymar *et al.*[11] have published an *R*-matrix calculation of MQDT parameters for Sr I which supports the earlier MCHF results[8-10] for Ca I and Sr I. This calculation makes it interesting to report more extensive and more accurate MCHF wave functions.

We describe first the MCHF calculations. MCHF solutions for excited Rydberg states are often very difficult to obtain and we discuss in some detail a few cases which were particularly difficult. Section II discusses the eigenvector compositions in relation to experimental and MQDT results. We then compare the experimental oscillator strength values for the $5s^2\ ^1S-5snp\ ^1P^\circ$ series with the calculated, and report

TABLE I. Wave function expansions. Orbitals kept fixed in the variational process are underlined and orbitals with the same index are orthogonal. The first entry on each line is the label used to identify the expansion in the text.

$1\,^1S$	$\{5s^2,6s^2,7s^2,5p^2,6p^2,4d^2,5d^2,4f^2,5g^2\}$
$1\,^1P^\circ$	$\{5s5p_2,6s6p_2,7s7p_2,5p_14d_1,6p_15d_1,4d_24f_1,5d_25f_1,4f_25g_1\}$
$2\,^1P^\circ$	$\{5s6p_2,6s5p_2,7s7p_2,5p_14d_1,6p_15d_1,4d_24f_1,5d_25f_1,4f_25g_1\}$
$3\,^1P^\circ$	$\{5s_17p_2,6s_15p_2,7s_26p_2,5p_14d_1,6p_15d_1,4d_24f_1,5d_25f_1,4f_25g_1\}$
$4\,^1P^\circ$	$\{5s7p_2,6s5p_2,7s6p_3,5p_14d_1,6p_15d_1,4d_24f_1,5d_25f_1,4f_25g_1\}$
$5\,^1P^\circ$	$\{5s8p_2,6s5p_2,7s6p_3,5p_14d_1,6p_15d_1,4d_24f_1,5d_25f_1,4f_25g_1\}$
$1\,^1D$	$\{5s4d_1,6s5d_1,7s6d_1,5p_1^2,6p_1^2,4d_2^2,5d_2^2,5p_24f_1,6p_25f_1,4f_2^2,5g_1^2,4d_35g_2\}$
$2\,^1D$	$\{5s5d_1,6s4d_1,7s6d_1,5p_1^2,6p_1^2,4d_2^2,5d_2^2,5p_24f_1,6p_25f_1,4f_2^2,5g_1^2,4d_35g_2\}$
$3\,^1D$	$\{5s\underline{4d}_1,5s\underline{5d}_1,5s6d_1,6s4d_3,5p_1^2,6p_1^2,4d_2^2,5d_2^2,5p_24f_1,4f_2^2,5g_1^2,4d_45g_2\}$
$1\,^1F^\circ$	$\{4d_15p_1,5d_16p_1,5s4f_1,6s5f_1,4d_24f_2,5d_25f_2,5p_25g_1,6p_26g_1,4f_35g_2\}$
$2\,^1F^\circ$	$\{4d_15p_1,5d_16p_1,5s4f_1,6s5f_4,4d_24f_2,5d_25f_2,5p_25g_1,6p_26g_1,4f_35g_2\}$
$3\,^1F^\circ$	$\{5s\underline{4f}_1,5s\underline{5f}_1,5s6f_1,4d_15p_1,4d_24f_2,5p_25g_1,4f_35g_2\}$
$4\,^1F^\circ$	$\{5s6f_1,4d_15p_1,4d_24f_2,5p_25g_1,4f_35g_2\}$
$5\,^1F^\circ$	$\{5s\underline{4f}_1 5s\underline{5f}_1,5s\underline{6f}_1,5s7f_1,4d_15p_1,4d_24f_2,5p_25g_1,4f_35g_2\}$
$1\,^1G$	$\{5s5g_1,6s6g_1,4d_2^2,5d_2^2,4d_15g_2,5p_14f_1,6p_15f_1,4f_2^2,5g_3^2\}$

electric dipole and electric quadrupole transition probabilities for a number of transitions between the Rydberg states considered. In Sec. V the lifetime results for the $^1P^\circ$ and $^1F^\circ$ series are reported and compared with the recent experimental results of Jönsson *et al.*[3]

Since a consistent labeling of the different states is difficult we use the designations given by Garton and Codling[2] throughout this paper in order to facilitate the discussion.

II. MCHF CALCULATIONS

The multiconfiguration Hartree-Fock method is particularly well suited for a theoretical study of two-electron systems where correlation is important as is the case for the singlet terms in the alkaline earths. The general approach was described by Froese Fischer[12] and applied successfully to the study of alkaline earths and isoelectronic ions.[8,10,13–15] More recently, length and velocity oscillator strengths, differing by less than one unit in the fifth decimal place and bordering the exact nonrelativistic value, were obtained for the $2\,^3S-2\,^3P^\circ$ transition in Li II,[16] illustrating the high accuracy attainable with the reduced forms of the MCHF wave-function expansions. We are using the same approach here to account for the correlation between the two outer electrons in neutral Sr.

The reduced form is based on the reduction of the following (4×4) wave-function expansion:

$$\Phi^{\mathrm{MCHF}_4}(^1P^\circ)=\alpha\,|\,5s'5p'\rangle+\beta\,|\,5s'6p'\rangle+\gamma\,|\,6s'5p'\rangle+\delta\,|\,6s'6p'\rangle\ ,$$

where a closed-shell core is implied, to a diagonal (2×2) representation

$$\Phi^{\mathrm{MCHF}_2}(^1P^\circ)=c_1\,|\,5s5p\rangle+c_2\,|\,6s6p\rangle\ ,$$

which usually is presented as the result of the application of two different orthogonal transformations of the radial functions in each l space.[12,17] These transformations, which can be applied directly from the beginning in the multiconfigurational scheme, define the *reduced form* of the MCHF expansion. The equivalence follows from Brillouin's theorem[12,18] $\langle\Phi^{\mathrm{MCHF}_2}\,|\,H\,|\,\Phi_{i\rightleftharpoons j}\rangle=0$ formulated for the following perturbations:

$$P_{5s}\rightarrow P_{5s}+\epsilon P_{6s}\ ,$$

$$P_{6s}\rightarrow P_{6s}-\epsilon P_{5s}\ ,$$

and

$$P_{5p}\rightarrow P_{5p}+\epsilon' P_{6p}\ ,$$

$$P_{6p}\rightarrow P_{6p}-\epsilon' P_{5p}\ ,$$

which gives, respectively,

$$c_1\langle\Phi^{\mathrm{MCHF}_2}\,|\,H\,|\,6s5p\ ^1P^\circ\rangle=c_2\langle\Phi^{\mathrm{MCHF}_2}\,|\,H\,|\,5s6p\ ^1P^\circ\rangle$$

and

$$c_1\langle\Phi^{\mathrm{MCHF}_2}\,|\,H\,|\,5s6p\ ^1P^\circ\rangle=c_2\langle\Phi^{\mathrm{MCHF}_2}\,|\,H\,|\,6s5p\ ^1P^\circ\rangle\ .$$

These two equations are fulfilled for arbitrary sets (c_1,c_2) with c_1 different from c_2 if and only if

$$\langle\Phi^{\mathrm{MCHF}_2}\,|\,H\,|\,6s5p\ ^1P^\circ\rangle=\langle\Phi^{\mathrm{MCHF}_2}\,|\,H\,|\,5s6p\ ^1P^\circ\rangle=0\ ,$$

which shows that the configuration state functions $6s5p$ and $5s6p$ are implicitly included in the two-configuration expansion Φ^{MCHF_2}.

The MCHF expansion used in our calculations for Sr I are given in Table I. The subscripts on the orbitals designate the different orthogonal sets involved in the different angular couplings. For instance, for the lowest $^1P^\circ$ state, labeled $1\,^1P^\circ$ and described by the superposition

$$\{5s5p_2,6s6p_2,7s7p_2,5p_14d_1,6p_15d_1,4d_24f_1,5d_25f_1,4f_25g_1\}\ ,$$

the use of two different orthogonal sets $\{np_1; n=5,6\}$ and $\{np_2; n=5,6,7\}$ without radial constraints between the two sets, allows us to take advantage of the reduced forms for each angular coupling ($sp_2\ {}^1P^\circ$ and $p_1 d_1\ {}^1P^\circ$, respectively), while still keeping orthogonality between configuration state functions,

$$\langle 5s5p_2\ {}^1P^\circ \,|\, 6p_1 5d_1\ {}^1P^\circ \rangle = 0 \ .$$

From Brillouin's theorem,[12,18] the corresponding MCHF expansion can be shown to include, at least to first order, the complete $ns/\epsilon s\ 5p_2\ {}^1P^\circ$, $5s\ np_2/\epsilon p_2\ {}^1P^\circ$, $ns/\epsilon s\ 6p_2\ {}^1P^\circ$, $6s\ np_2/\epsilon p_2\ {}^1P^\circ, \ldots, np_1/\epsilon p_1\ 4d_1\ {}^1P^\circ, \ldots$ and $4f_2\ ng_1/\epsilon g_1\ {}^1P^\circ$ series where nl and ϵl designate excited bound and free electrons, respectively. This property makes the MCHF approach particularly powerful for the study of "two-electron" systems and extremely compact for investigating discrete-continuum interactions compared to conventional CI calculations.[19,20]

Previous MCHF calculations for alkaline earths have usually been performed using a frozen core with orbitals taken from the ion.[8,10] However, the sensitivity of the $3d$ orbital to the details of the screening has been illustrated in Ca where it is strong enough to change the relative position of the $3d4p\ {}^1P^\circ$ term in the $4snp\ {}^1P^\circ$ series.[10] This effect should be less important in Sr I than in Ca I since the collapse of the $4d$ orbital is less pronounced than the collapse of $3d$. However, in order to limit any basis set dependence of the $4d$ contraction, we systematically included all the core orbitals $(1s,2s,2p,3s,3p,3d,4s,4p)$ in the variational procedure. We thus automatically include correlation effects which are related to the relaxation of the core. For example, a completely variational calculation in the single-configuration Hartree-Fock approximation for $5s^2\ {}^1S$ would produce a wave function which cannot interact to first order with any configuration state function arising from a single-electron excitation from the core. For instance, we would have

$$\langle \Phi^{\mathrm{HF}}(4p^6 5s^2\ {}^1S) \,|\, H \,|\, 4p^5 5s^2\ np/\epsilon p\ {}^1S \rangle = 0$$

for any single-electron excitation $4p \rightarrow np/\epsilon p$ where the ket $|\,4p^5 5s^2\ np/\epsilon p\ {}^1S\rangle$ has been constructed from the Φ^{HF} orbitals, and the $np/\epsilon p$ orbital is orthogonal to all p orbitals in the Φ^{HF} wave function. This property is no more satisfied when valence correlation effects are included. By using a two-configuration MCHF approach

$$c_1\,|\,5s^2\ {}^1S\rangle + c_2\,|\,5p^2\ {}^1S\rangle \ ,$$

Brillouin's theorem is satisfied for a particular linear combination[12,18]

$$\alpha\,|\,4p^5 5s^2\ np/\epsilon p\ {}^1S\rangle + \beta\,|\,4p^5 5p^2\ np/\epsilon p\ {}^1S\rangle$$

but not for the individual components separately. Thus the configuration state functions $4p^5 5s^2\ np/\epsilon p\ {}^1S$, which were implicitly included in the Hartree-Fock approximation, are interacting with the zero-order MCHF_2 wave function even when the core is relaxed.

The MCHF calculations corresponding to the expansions given in Table I were performed in the following way. For the ${}^1S$ series we were interested in the ground level only. The expansion has a simple form for this symmetry and the calculation presented no problem. For the ${}^1P^\circ$ series, we wanted to obtain accurate wave functions describing the five lowest levels. This series is known to be perturbed by $4d5p\ {}^1P^\circ$. Moore's compilation[21] [referred to as AEL (atomic energy levels)] does not give a $4d5p\ {}^1P^\circ$ term, although Shenstone and Russell[22] suggested that the level given by Moore as $5s9p\ {}^1P^\circ$ might be labeled more appropriately as $4d5p\ {}^1P^\circ$. Garton and Codling[2] proposed that the fourth ${}^1P^\circ$ term, listed in AEL as $5s8p\ {}^1P^\circ$, should be identified as the $4d5p\ {}^1P^\circ$ perturber, although they realized that there probably is a severe mixing. The last proposal was supported by the MQDT analysis due to Esherick.[23]

In an *ab initio* treatment, the same MCHF expansion can be used to determine all bound members of a Rydberg series.[24] For instance, if we approximate the ${}^1P^\circ$ series by a MCHF expansion over the following three-configuration state function:

$$\Phi^{\mathrm{MCHF}_3}({}^1P^\circ) = c_1\,|\,5snp_2\ {}^1P^\circ\rangle + c_2\,|\,4d_1 5p_1\ {}^1P^\circ\rangle + c_3\,|\,4d_2 4f_1\ {}^1P^\circ\rangle \ ,$$

then in order to confirm that the MCHF solution has converged to a particular np level we must rely on the behavior[25] of the radial solution $P(r)$ which, in analogy with hydrogen, means that an np orbital is required to be positive near the origin and have $n-2$ nodes. The $5s$ and np_2 orbitals are then referred to as spectroscopic orbitals in contrast to the correlation orbitals ($4d_1$, $5p_1$, $4d_2$, and $4f_1$) which can be very different in form and for which node counting is not applied in the MCHF procedure.

The four MCHF eigenvectors obtained for $n=5-8$ and their position relative to the ionization limit are given in Table II. The MCHF solution for $n=8$ is in compara-

TABLE II. MCHF expansions $c_1\,|\,5snp_2\ {}^1P^\circ\rangle + c_2\,|\,4d_1 5p_1\ {}^1P^\circ\rangle + c_3\,|\,4d_2 4f_1\ {}^1P^\circ\rangle$ for the five lowest ${}^1P^\circ$ levels of Sr I. Also shown are the calculated and observed ionization energies.

Level[a]	c_1	c_2	c_3	I^{MCHF} (cm^{-1})	I^{obs} (cm^{-1})[b]
$n=5$	0.9038	0.4227	0.0123	23 374.7	24 233.62
$n=6$	0.9426	0.3313	0.0419	11 271.0	11 833.66
$n=7$	0.9297	-0.3620	0.0683	6702.0	7025.20
$4d5p$	0.8826	0.4598	0.0982	4161.6	4759.98
$n=8$	0.9245	-0.3716	0.0844	3326.8	3469.78

[a] Adopting the level notation of Garton and Codling (Ref. 2).

[b] Using the ionization potential $I_s = 45\,932.09$ from Baig and Connerade (Ref. 28), term values from Moore (Ref. 21) with the exception of the $5s8p$ and $4d5p$ terms from Garton and Codling (Ref. 2).

tively good agreement with the fifth experimental level. This correspondence would be confirmed if we could find another MCHF solution described by the same expansion and lying somewhere between the $n=7$ and 8 MCHF eigenvalues. Following Garton and Codling[2] we would expect this solution to be dominant in $4d5p\ {}^1P^\circ$. However, all attempts to find such a solution using the MCHF_3 expansion but with $5s$ and $5p_2$ as correlation orbitals has failed. To solve this stability problem we have instead introduced a fixed spectroscopic-orbital basis $(5s,\underline{5p}_2,\underline{6p}_2,\underline{7p}_2)$ for the lower $5snp_2$ states ($n=5-7$) and a variational and correlating orbital $8p_2$ for the rest of the series, i.e.,

$$\Phi^{\mathrm{MCHF}_6}({}^1P^\circ)=c_1\,|\,5s\underline{5p}_2\,{}^1P^\circ\rangle+c_2\,|\,5s\underline{6p}_2\,{}^1P^\circ\rangle+c_3\,|\,5s\underline{7p}_2\,{}^1P^\circ\rangle+c_4\,|\,4d_15p_1\,{}^1P^\circ\rangle+c_5\,|\,5s8p_2\,{}^1P^\circ\rangle+c_6\,|\,4d_25f_1\,{}^1P^\circ\rangle\ .$$

The underlined orbitals have been kept fixed in the variational process on orbital functions obtained for $5snp$ states in single-configuration HF calculations. By selecting the eigenfunction corresponding to the fourth eigenvalue at each iteration of the MCHF procedure we have obtained a stable solution for the fourth ${}^1P^\circ$ eigenvalue in this "explicit" representation. This way of circumventing such stability difficulties has been proposed and used by Froese Fischer.[26] We want to point out that the explicit (6×6) and reduced (3×3) forms are strictly equivalent only if the $5s$ is variational. The explicit solution has the following expansion coefficients: $c_1=0.1179$, $c_2=0.1881$, $c_3=0.7443$, $c_4=0.4598$, $c_5=-0.4192$, and $c_6=0.0982$, and it is lying 4161.6 cm^{-1} below the ionization limit.

We can obtain the "implicit" form from the "explicit" simply by constructing a p_2 radial distribution using the equation

$$P_{p_2}(r)=\left[\sum c_n^2\right]^{-1/2}\sum c_nP_{np_2}(r)\ , \tag{1}$$

and selecting the second eigenvector of the (3×3) representation $(5sp_2,4d_15p_1,4d_25f_1)$. The total energy is obviously invariant under this transformation and the corresponding eigenvector is given in Table II. It corresponds exactly to the MCHF solution we would get if the calculation using the reduced form would converge. The p_2 orbital built according to Eq. (1) has five nodes and therefore should be labeled $7p$. The diagonal matrix elements corresponding to $5sp_2$ and $4d_15p_1$ of the (3×3) interaction matrix are -3131.3946 and -3131.3948 a.u., respectively. This quasidegeneracy, which clearly makes this representation unstable, is lifted in the explicit representation or when additional terms are added to the expansion.

By analyzing the variational conditions corresponding to the MCHF_6 expansion, it is easy to show that too many degrees of freedom are available if all np_2 radial distributions are variational. One can show that the same solution is obtained by varying one (arbitrary) np_2 orbital in the MCHF_6 expansion, the mixing coefficients being such that in all cases the same p_2 orbital is obtained by the transformation (1). If all np_2 orbitals are varied, the correct MCHF solution has the surprising property that all diagonal Lagrange multipliers $\epsilon(np_2,np_2)$ are equal $[\epsilon(5p_2,5p_2)=\epsilon(6p_2,6p_2)=\epsilon(7p_2,7p_2)=\epsilon(8p_2,8p_2)=9635.1\ \mathrm{cm}^{-1}$ in the present case]. This property can be derived from the MCHF equations (see Appendix) and can be used to test whether the variational conditions are applied correctly in an explicit MCHF calculation. Cases where a rotation of the orbital basis leaves the total wave function and energy unchanged usually require the use of large accelerating factors in the MCHF procedure and are therefore not computationally attractive, but the analysis of them may provide insight into the structure of the solution,[25] in particular into the values of the off-diagonal Lagrange multipliers. For the example just given, we can show that the solution consisting of setting the off-diagonal Lagrange multipliers to zero, in order to remove the extra degrees of freedom and make the solution unique, corresponds to the reduced representation, i.e., $c_2=c_3=c_5=0$.

The MCHF_3 expansion reported in Table II has been extended by adding more components and using the reduced forms (see Table I). For the two highest eigenvalues, we included a $7s6p_3$ component, without any orthogonality constraint between the $6p_3$ and p_2 radial distributions. A similar approach has been used for the wave function of $3\ {}^1P^\circ$, including a $7s_26p_2$ component. These representations somewhat complicate the Hamiltonian matrix elements but allowed us to achieve better convergence while satisfying the orthogonality requirement between configuration state functions.

It was particularly difficult to obtain converged MCHF solutions for the higher members of the ${}^1D$ series. The wave functions for $1\ {}^1D$ and $2\ {}^1D$ were calculated using the same reduced forms. However, for the third eigenstate an explicit form was used in which the $4d_1$ and $5d_1$ orbitals were kept fixed while the $6d_1$ orbital was variational and represents the rest of the $5s\,nd_1/\epsilon d_1$ series. When adding a further component having the same angular coupling, it is important to relax some orthogonality constraints if an explicit representation is chosen for the other states with this coupling. For example, the $4d_3$ orbital of the new component $6s4d_3$ appearing in the $3\ {}^1D$ expansion is not required to be orthogonal to the $\underline{4d}_1$, $\underline{5d}_1$, and $6d_1$ orbitals. This degree of freedom is necessary for the equivalence between the explicit

$$\{5s\underline{4d}_1,5s\underline{5d}_1,5s6d_1,6s4d_3\}$$

and implicit

$$\{5s6d_1,6s4d_1\}$$

representations.

Similar stability problems occurred for the ${}^1F^\circ$ series and we did not succeed in adding a further sf component in the MCHF expansion of $3-5\ {}^1F^\circ$.

Concluding this section, we note that although HF calculations now in most cases can be carried out in a routine manner, convergence problems still exist for MCHF calculations for excited states which are not the lowest of a given symmetry. However, referring to earlier studies,[27] in which no states higher than the second lowest was attempted, it is clear that progress has been made in choosing expansions for which convergence is easier to obtain. Explicit forms have usually been found to be more stable than implicit representations: starting with implicit forms obtained from the variational solution of the explicit form using Eq. (1), the MCHF program often diverges even when large acceleration factors are used.

We report the final eigenvector compositions in Table III. The accuracy of the results is evaluated by comparing the MCHF and observed ionization energies[2,21,28] (Table IV). The lowest ^1S and $^1P^\circ$ terms have earlier been calculated by Hansen[29] using (5×5) and (3×3) MCHF expansions. The eigenvector compositions are very similar in the two calculations and the total energies have been lowered by only 160 and 170 cm^{-1}, respectively.

TABLE III. Eigenvector compositions of the MCHF expansions (Table I) for ^1S, $^1P^\circ$, ^1D, $^1F^\circ$, and ^1G terms in Sr I.

$1\,^1S$		$1\,^1P^\circ$		$2\,^1P^\circ$		$3\,^1P^\circ$	
$5s^2$	0.959 11	$5s5p_2$	0.899 18	$5s6p_2$	0.914 40	$5s_17p_2$	0.916 12
$6s^2$	−0.037 16	$6s6p_2$	−0.028 31	$6s5p_2$	0.169 94	$6s_15p_2$	−0.137 58
$7s^2$	−0.003 23	$7s7p_2$	−0.002 92	$7s7p_2$	−0.008 02	$7s_26p_2$	−0.003 49
$5p^2$	0.272 77	$5p_14d_1$	0.435 37	$5p_14d_1$	0.363 29	$5p_14d_1$	−0.369 57
$6p^2$	0.008 98	$6p_15d_1$	0.029 94	$6p_15d_1$	0.029 15	$6p_15d_1$	−0.023 73
$4d^2$	−0.064 18	$4d_24f_1$	0.013 13	$4d_24f_1$	0.045 29	$4d_24f_1$	0.067 30
$5d^2$	−0.003 42	$5d_25f_1$	0.004 63	$5d_25f_1$	0.004 94	$5d_25f_1$	0.006 47
$4f^2$	0.008 67	$4f_25g_1$	−0.005 38	$4f_25g_1$	0.005 17	$4f_25g_1$	0.008 14
$5g^2$	−0.004 20						
$4\,^1P^\circ$		$5\,^1P^\circ$		$1\,^1D$		$2\,^1D$	
$5s7p_2$	0.912 25	$5s8p_2$	0.929 65	$5s4d_1$	0.916 45	$5s5d_1$	0.882 37
$6s5p_2$	−0.093 16	$6s5p_2$	−0.050 79	$6s5d_1$	0.071 84	$6s4d_1$	−0.156 17
$7s6p_3$	−0.001 69	$7s6p_3$	0.002 26	$7s6d_1$	−0.004 28	$7s6d_1$	0.012 13
$5p_14d_1$	−0.390 11	$5p_14d_1$	−0.356 19	$5p_1^2$	0.367 71	$5p_1^2$	−0.303 22
$6p_15d_1$	−0.025 08	$6p_15d_1$	0.028 58	$6p_1^2$	0.002 51	$6p_1^2$	0.043 69
$4d_24f_1$	−0.078 49	$4d_24f_1$	0.073 16	$4d_2^2$	−0.084 73	$4d_2^2$	−0.307 77
$5d_25f_1$	0.007 70	$5d_25f_1$	0.007 31	$5d_2^2$	0.008 18	$5d_2^2$	0.035 32
$4f_25g_1$	0.009 41	$4f_25g_1$	0.008 69	$5p_24f_1$	0.109 18	$5p_24f_1$	−0.082 08
				$6p_25f_1$	−0.009 60	$6p_25f_1$	−0.005 23
				$4f_2^2$	0.003 07	$4f_2^2$	−0.013 73
				$5g_1^2$	0.000 34	$5g_1^2$	0.001 27
				$4d_35g_2$	−0.021 31	$4d_35g_2$	0.010 47
$3\,^1D$		$1\,^1F^\circ$		$2\,^1F^\circ$		$3\,^1F^\circ$	
$5s\underline{4d}_1$	0.250 16	$4d_15p_1$	0.733 68	$4d_15p_1$	0.585 51	$5s\underline{4f}_1$	−0.005 03
$5s\underline{5d}_1$	−0.428 41	$5d_16p_1$	0.043 58	$5d_16p_1$	0.036 99	$5s\underline{5f}_1$	0.965 88
$5s6d_1$	−0.160 13	$5s4f_1$	−0.671 70	$5s4f_1$	0.804 72	$5s6f_1$	−0.066 59
$6s4d_3$	0.036 66	$6s5f_1$	−0.028 61	$6s5f_4$	−0.021 69	$4d_15p_1$	0.243 19
$5p_1^2$	−0.528 27	$4d_24f_2$	−0.071 50	$4d_24f_2$	−0.070 43	$4d_24f_2$	−0.031 60
$6p_1^2$	0.016 96	$5d_25f_2$	0.006 74	$5d_25f_2$	0.006 74	$5p_25g_1$	0.049 69
$4d_2^2$	−0.658 46	$5p_25g_1$	−0.050 95	$5p_25g_1$	0.052 15	$4f_35g_2$	0.003 89
$5d_2^2$	0.094 35	$6p_26g_1$	0.003 95	$6p_26g_1$	0.002 14		
$5p_24f_1$	0.062 57	$4f_35g_2$	0.006 76	$4f_35g_2$	0.006 46		
$4f_2^2$	−0.033 33						
$5g_1^2$	0.004 37						
$4d_45g_2$	0.005 33						
$4\,^1F^\circ$		$5\,^1F^\circ$		$1\,^1G$			
$5s6f_1$	0.989 31	$5s\underline{4f}_1$	−0.009 41	$5s5g_1$	−0.033 98		
$4d_15p_1$	0.138 17	$5s\underline{5f}_1$	−0.015 82	$6s6g_1$	−0.003 20		
$4d_24f_2$	−0.026 43	$5s\underline{6f}_1$	−0.032 05	$4d_2^2$	0.957 09		
$5p_25g_1$	0.038 34	$5s7f_1$	0.994 09	$5d_2^2$	−0.198 45		
$4f_35g_2$	−0.002 26	$4d_15p_1$	0.095 32	$4d_15g_2$	−0.027 88		
		$4d_24f_2$	−0.020 23	$5p_14f_1$	−0.202 58		
		$5p_25g_1$	0.030 30	$6p_15f_1$	0.009 29		
		$4f_35g_2$	−0.001 67	$4f_2^2$	0.038 69		
				$5g_3^2$	−0.005 66		

TABLE IV. Binding energies (cm^{-1}).

Level[a]	MCHF	Obs.[b]	Δ (cm^{-1})
$5s^2\,{}^1S$	43 536.4	45 932.1	2395.7
$5s5p\,{}^1P^{\circ}$	23 550.1	24 233.6	683.5
$5s6p$	11 897.3	11 833.7	−63.6
$5s7p$	7083.4	7025.2	−58.2
$4d5p$	4769.1	4760.0	−9.1
$5s8p$	3437.7	3469.8	32.1
$5s4d\,{}^1D$	25 188.4	25 782.4	594.0
$5s5d$	11 078.4	11 204.6	126.2
$5p^2$	9374.7	8971.2	−403.5
$4d5p\,{}^1F^{\circ}$	8285.4	7924.1	−361.3
$5s4f$	6510.7	6393.1	−117.6
$5s5f$	4366.4	4413.2	46.8
$5s6f$	3063.0	3092.7	29.7
$5s7f$	2255.8	2276.0	20.2
$4d^2\,{}^1G$	5492.9		

[a] Adopting the level notation of Garton and Codling (Ref. 2).

[b] Using the ionization potential $I_s = 45\,932.09$ from Baig and Connerade (Ref. 28), term values from Moore (Ref. 21) with the exception of the $5s8p$ and $4d5p$ terms from Garton and Codling (Ref. 2).

The present calculations for the higher ${}^1P^{\circ}$ terms illustrate the strong dispersion of the $4d5p\,{}^1P^{\circ}$ perturber which effectively disappears, in a similar way[10] as for Ca I, leaving two ${}^1P^{\circ}$ states (the third and the fourth) having $5s7p$ as their main eigenvector component. The MCHF and MQDT results are compared in Sec. III. In order to discuss the validity of the MQDT approach, Froese Fischer and Hansen[8] calculated the lowest ${}^1D$ term using a more limited MCHF$_5$ expansion. The present calculation confirms their results. However, the present results disagree somewhat with the MCHF$_5$ wave-function composition obtained by Aspect *et al.*[9] for the third eigenstate. The comparison of these two eigenvectors shows a transfer from d^2+p^2 to sd character, the weights associated with the p^2, d^2, and sd basis states changing from 35%, 61%, and 3.5% to 28%, 44%, and 27%, respectively. Our expansion is much more complete and is fully variational, while their $5s$ orbital was frozen in the MCHF procedure. The eigenvector compositions for the three lowest ${}^1D$ terms illustrate the importance of the perturbers $5p^2$, $4d^2$, and even $5p4f$, the last two having been neglected in the MQDT analysis by Esherick.[23] For the ${}^1F^{\circ}$ series, the perturber $4d5p$ is spread over several members of the $5snf$ series. However, it is predominantly mixed into the lowest states conventionally labeled $4d5p$ (54%) and $5s4f$ (34%), respectively. These eigenvector compositions support the labeling predicted[1] for the lowest ${}^1F^{\circ}$ term on the basis of more limited MCHF$_4$ expansions. The completely variational MCHF$_9$ calculation for the lowest ${}^1G$ term predicts an ionization energy of 5493 cm^{-1} and an eigenvector composition of $4d^2$ (92%), $5p4f$ (4%), and $5d^2$ (4%). This term has not been observed experimentally as mentioned later.

III. COMPARISON BETWEEN MQDT AND MCHF

In a very interesting recent paper, Aymar *et al.*[11] have made *ab initio* *R*-matrix calculations of MQDT parameters for the ${}^{1,3}S$, ${}^{1,3}P^{\circ}$, and ${}^{1,3}D$ series in Sr I. Their paper gives also a discussion of earlier semiempirical fits to the observed energy levels in Sr I as well as a comparison with earlier MCHF results[8,10] for Sr and Ca. The main conclusion is that additional configurations (collision channels) must be included in most cases compared to what has been done in the semiempirical treatments and that these additional configurations can substantially change the previous MQDT parameters bringing MQDT and MCHF predictions of, for example, wave-function compositions into much closer agreement. It is therefore interesting to compare this treatment with our improved MCHF calculations. We will discuss the series separately with the main emphasis on the ${}^1P^{\circ}$ series for which we present new MCHF results.

A. ${}^1P^{\circ}$ series

The $5s\,np/\epsilon p$ series is perturbed by the $4d\,np/\epsilon p$ series in such a way that it is not immediately obvious where the lowest member of the latter series, $4d5p$, is located, as mentioned earlier. In 1968, Garton and Codling[2] concluded on the basis of extrapolations of the observed energy-level values of the autoionizing $4dnp\,{}^1P^{\circ}$ series, which they identified above the $5s$ threshold from $n=6$, that the lowest member, $4d5p$, should be identified with the $5s8p\,{}^1P^{\circ}$ term in AEL. This identification was also based on the observed quantum defects and intensities of ground-state transitions but in the presence of strong CI none of these criteria is entirely unambiguous. A similar situation for the ${}^1P^{\circ}$ series in Ca I was discussed by Froese Fischer and Hansen[10] and the two series have many similarities as the following discussion will show.

The identification of $4d5p\,{}^1P^{\circ}$ by Garton and Codling[2] was later justified by the two-channel MQDT treatments due to Esherick[23] and Armstrong *et al.*,[30] who concluded that $4d5p$ interacts with a relatively small number of $5snp$ series members in such a way that no particular level has primarily $4d5p$ character. However, the largest amount of $4d5p$ was found for the level identified as $4d5p$ by Garton and Codling.[2] This conclusion was based on the following arguments.

In the MQDT analysis it is possible to calculate the contribution to a particular state from a particular "collision channel" which is defined as all states with the core in a particular state, for example, $4p^64d$, coupled with an outer electron np or ϵp to a particular symmetry such as ${}^1P^{\circ}$. The precise quantum number of the p electron is not specified but Seaton[31] has for the equivalent situation in Ca argued that, since in that case, the total $3dp$ character in an energy region comprising a number of low $4snp$ states is approximately equal to 1, the $3dp$ amplitude should be interpreted as belonging to the lowest state $3d4p$. In fact, the summed character is slightly larger than 1 for the eight lowest ${}^1P^{\circ}$ states[10] showing that some amplitude must be coming from $3d\,np/\epsilon p(n>4)$. It is seen that this argument depends crucially on the fact that a summed character of approximately 1 can be found in a reasonably small energy interval in the vicinity of the position where the level would be found in a single-configuration calculation. For Ca and Sr such a calculation predicts that only the lowest member of the *dp* ${}^1P^\circ$ series will be located below the first ionization limit, and on this basis Esherick[23] concluded that all *dp* amplitude in the bound 5*snp* series in Sr I is due to 4*d*5*p*, while the MQDT calculation as such only shows that the amplitude has 4*dp* character. Esherick found a maximum of "4*d*5*p*" character (18%) in the level identified as 4*d*5*p* ${}^1P^\circ$ by Garton and Codling.[2] He also found that the sum of 4*dp* ${}^1P^\circ$ character in the bound spectrum excluding the lowest state 5*s*5*p* is 0.89, and he concluded that the latter must contain the remaining 4*d*5*p* character (0.11), an argument based on the assumption that all amplitude in the bound region must be due to 4*d*5*p* alone.

In their recent paper, Aymar *et al.*[11] have shown that a two-channel MQDT description of the ${}^1P^\circ$ series in Sr in fact "does not achieve close agreement with the experimental data; in particular the value of μ_2 appears too small, indicating that the perturber 4*d*5*p* is located too high." Aymar *et al.* finds that adding 4*dnf* configurations in the *R*-matrix procedure leads to a substantial increase in μ_2 and a further increase is found by adding additional configurations $5pnl+4d'\epsilon l$ where $4d'$ is supposed to take core relaxation effects into account (the calculations use a frozen Sr^{++} core). From this it can be concluded that the more complete calculation gives a larger 4*d*5*p* percentage for the lower ${}^1P^\circ$ states than the two-level calculation. It is interesting to compare this result with the MCHF calculations in different stages of completeness. This development is shown in Table V, which contains the amount of *dp* character in the lowest ${}^1P^\circ$ levels in different MCHF approximations. These numbers are obtained by adding all contributions of the type *dp* in the MCHF expansions, which means that the quoted values have a similar interpretation to the MQDT results; they correspond, due to Brillouin's theorem, to adding all contributions from a 4*dp* collision channel but also, unlike the MQDT results, all contributions from *ndp* ($n>4$) channels plus contributions from *npd* collision channels. These levels are further away from the 5*snp* series and can be expected to have a smaller effect on this series than the 4*dp* channel.

In Table V are shown the results of three types of MCHF expansions, a 2×2 $\{5snp+4dnp\}$ expansion, a 3×3 expansion, which contains in addition a 4*dnf* series, and the final expansion described in Sec. II. We see the same effect described by Aymar *et al.*;[11] the amount of *dp* character in the lower levels increases when additional configurations are added to the MCHF expansion except for the lowest state, which is rather stable against addition of configurations. In the 3×3 expansion the largest amount of *dp* character is found in the fourth ${}^1P^\circ$ state in agreement with the proposal of Garton and Codling[2] and in agreement with the two-channel MQDT result due to Esherick.[23] However, in the final calculation, the maximum amount of *dp* character is found in the lowest ${}^1P^\circ$ state with a smaller secondary maximum for the fourth ${}^1P^\circ$ state. The situation in the ${}^1P^\circ$ series in Ca is similar except that the second local maximum is absent in the MCHF calculations of Froese Fischer and Hansen.[10] The agreement with the MQDT composition due to Esherick[23] is not very good for any of the MCHF results. It is perhaps in somewhat better agreement with the 3×3 expansion than with any of the others. The "eigenvector composition" found in the *R*-matrix calculation by Aymar *et al.*[11] was not given in the paper but Dr. Aymar has kindly supplied this information which is included in Table V. We give in Table V the *W* coefficients for the 4*dnp* channel. These coefficients are defined by the relation $W_i=Z_i^2/\sum_k(Z_k)^2$, where the Z_i are defined by Seaton.[31] Dr. Aymar supplied the Z^2 coefficients for the 5*snp* and 4*dnp* channels. Seaton states that the W_i values will give a reasonable value for the amount of channel *i* in a particular highly excited state. The use of the *W* values for low-lying states is therefore somewhat doubtful, but we observe that there is good agreement between the *W* values and the results of our final calculation, except for the lowest state where the *W* value is much larger than

TABLE V. The amount of *dp* character in percent in the ${}^1P^\circ$ series in Sr I obtained using different MCHF approximations. Also, results of *R*-matrix calculations and MQDT fits are included.

Level[a]	2×2[b]	MCHF 3×3[c]	Final[d]	*R*-matrix[e]	MQDT[f]
5*s*5*p*	18.5	17.9	19.0	42.0[g]	11[h]
5*s*6*p*	8.9	11.0	13.3	12.0	
5*s*7*p*	7.4	13.1	13.7	13.9	15
4*d*5*p*	12.5	21.1	15.3	15.9	18
5*s*8*p*		13.8	12.8	13.6	16

[a] Adopting the level notation of Garton and Codling (Ref. 2).

[b] $5snp_2+4d_15p_1$ (fixed core).

[c] $5snp_2+4d_15p_1+4d_24f$ (fixed core).

[d] Relaxed core and final MCHF expansions (see Table III).

[e] Private communication from M. Aymar (see also Ref. 11).

[f] MQDT analysis of Esherick (Ref. 23).

[g] The significance of this number is discussed in the text.

[h] Obtained by subtracting the calculated amount of 4*dp* character over the bound states (except the lowest one) from 100 (see text).

the MCHF result. For the higher states the sum of the Z^2 values is 1 ± 0.03, whereas for the lowest state the sum is 1.56. This result, in combination with the expectation that the W_i are reliable measures of eigenvector composition only for high members of Rydberg series, means that there is no obvious disagreement between MCHF and R-matrix calculations. Since core-polarization effects are included in the R-matrix calculations to some extent it is not surprising that the two sets of results are slightly different.

B. ^1S and ^1D series

For the ^1S series we are not presenting new results in this paper, but we note that the isotope shift investigation due to Aspect *et al.*[9] confirmed the importance of a $4d^2$ component in the perturber which conventionally has been labeled $5p^2$. A similar conclusion was reached by Aymar *et al.*,[11] although they found a weak coupling between the $5sns$ series and the perturbing channels which made the wave-function composition of the perturber very sensitive to small changes in the MQDT parameters.

For the ^1D series, the situation is now clearer. The three-channel model of Esherick,[23] $5snd+4d6s+5p^2$, predicted that the bound $5snd$ series was not perturbed by $4d^2$, while the MCHF calculations of Froese Fischer and Hansen[8] for the lowest ^1D term and by Aspect *et al.*[9] for the perturber showed that the latter had more $4d^2$ than $5p^2$ character. Our improved calculations for the three lowest ^1D terms show that $4d^2$ is more important than $5p^2$ for the second and third ^1D term and a similar conclusion was reached by Aymar *et al.*,[11] who found that the $5snd$-$4dnd$ mixing is stronger than the $5snd$-$5pnp$ mixing below the Sr^+ $5s$ threshold, while the situation is reversed over the threshold.

C. $^1F^\circ$ series

There is no MQDT analysis available for the $^1F^\circ$ series, but Rubbmark and Borgström[32] found that it is possible to get an acceptable description of this series by use of Langer's formula[33] and including in the fit the $4d5p$ $^1F^\circ$ term as a perturber. An equally good fit to Langer's formula was obtained by interchanging the designations of $4d5p$ $^1F^\circ$ and $5s4f$ $^1F^\circ$, illustrating that the designation of the perturber is somewhat arbitrary due to strong CI as predicted by Hansen and Persson.[1] Our MCHF eigenvector composition confirms this configuration mixing for the five lowest $^1F^\circ$ members. The $4d5p$ perturber has a shorter-range effect in the $^1F^\circ$ series than in the $^1P^\circ$ series. However, it is somewhat surprising that Langer's formula, which can be derived[34] from perturbation theory assuming that the interaction is small compared to the distance between adjacent series members, works so well for a strongly perturbed series as is the case here.

IV. OSCILLATOR STRENGTHS

We have calculated electric dipole ($E1$) and electric quadrupole ($E2$) oscillator strengths for the transitions involving the terms $1\,^1S$, $n\,^1P^\circ$ ($n=1$–5), $n\,^1D$ ($n=1$–3), $n\,^1F^\circ$($n=1$–5), and $1\,^1G$. Length (L) and velocity (V) values were obtained using theoretical and observed wavelength values. For comparison with experiment we use the transition probabilities calculated using the observed transition energies.

A. Electric dipole transitions

The $E1$ results are reported in Tables VI and VII. Table VI gives the oscillator strengths, transition probabilities, and transition energies for all the transitions considered. The general agreement between length and velocity forms is quite satisfactory. Strong cancellation due to destructive interference between the different contributions to the line strength $S^{1/2}$ occurs for $5s^2\,^1S-5s6p\,^1P^\circ$, $5s4d\,^1D-5s5p\,^1P^\circ$, and $5s4d\,^1D-4d5p\,^1F^\circ$. The last two transitions have been discussed previously by Hansen[29] and Hansen and Persson,[1] respectively, using shorter expansions. These three lines are clearly affected by the perturbers $5p^2\,(^1S,^1D)$, $4d^2\,(^1S,^1D)$, and $4d5p\,(^1P^\circ,^1F^\circ)$.

B. $5s^2\,^1S-^1P^\circ$ series

Parkinson *et al.*[35] have measured f values for the $5s^2\,^1S_0-(5snp+4d5p)\,^1P_1^\circ$ transitions for n up to 26 using the Hook method. Less extensive measurements have also been reported by Penkin and Shabanova.[36] The absolute values of the oscillator strengths in the work of Parkinson *et al.*[35] were obtained by calibrating to the measured lifetime of the lowest $^1P^\circ$ level as measured by Lurio *et al.*[37] A later lifetime measurement by Kelly *et al.*[38] gave the same f value within the stated error limits but assuming a branching ratio of 5% for the only other decay (to $5s4d\,^1D_2$) from $5s5p\,^1P^\circ$. Hansen[29] noted that this branching ratio corresponds to a gf value of 19 for the $5s4d\,^1D-5s5p\,^1P^\circ$ transition which lies in the infrared. With a more reasonable gf value the branching ratio is less than $\frac{1}{2}\%$, which is confirmed in the present calculation, and this leads to a f value 6% larger than that used by Parkinson *et al.*[35] All of the measured gf values should therefore in principle be increased by 6%. However, the error limits on the experimental values are larger than 10% except for the two lowest levels, and we have therefore chosen to retain the original gf values.[35] An additional reason for this is that Jönsson *et al.*[3] have found that the measurements by Kelly *et al.*[38,39] for the higher $^1P^\circ$ states are less accurate than stated in the paper as mentioned later. For the lowest $^1P^\circ$ state, Jönsson *et al.*[3] have confirmed the value due to Kelly *et al.*[38] but with a larger error so that it is not possible to conclude that the latter value is better than the value from Lurio *et al.*[37]

We show the results of two MCHF approximations in Table VII in both cases using the experimental energy differences to calculate the gf values, namely, results from a (3×3) $^1P^\circ$ expansion in combination with a (5×5) ^1S expansion and the results using the final MCHF expansions. These results are compared to the experimental results from Parkinson *et al.*[35] and from Penkin and Shabanova.[36] The minimum in gf value for the second $^1P^\circ$ state is reproduced in the calculation and the agreement is generally better than 20% except for the weak

TABLE VI. Electric dipole oscillator strengths gf and transition probabilities A (sec^{-1}) using the length (L) and velocity (V) forms and using the calculated and observed transition energies.

	$\lvert gf \rvert$		ΔE (calc.)	ΔE (obs.)	A (sec^{-1})	
	ΔE (calc.)	ΔE (obs.)	(cm^{-1})		ΔE (calc.)	ΔE (obs.)
$5s^2\,{}^1S \rightarrow 5s5p\,{}^1P^\circ$	L 1.9536	L 2.1210	19 986.3	21 698.5	L 1.735×10^8	L 2.220×10^8
	V 1.8459	V 1.7002			V 1.639×10^8	V 1.780×10^8
$5s^2\,{}^1S \rightarrow 5s6p\,{}^1P^\circ$	L 0.0048	L 0.0051	31 639.1	34 098.3	L 1.059×10^6	L 1.326×10^6
	V 0.0030	V 0.0028			V 6.670×10^5	V 7.188×10^5
$5s^2\,{}^1S \rightarrow 5s7p\,{}^1P^\circ$	L 0.0186	L 0.0198	36 453.0	38 906.9	L 5.483×10^6	L 6.666×10^6
	V 0.0191	V 0.0179			V 5.653×10^6	V 6.034×10^6
$5s^2\,{}^1S \rightarrow 4d5p\,{}^1P^\circ$	L 0.0419	L 0.0445	38 767.4	41 172.1	L 1.400×10^7	L 1.677×10^7
	V 0.0399	V 0.0376			V 1.334×10^7	V 1.417×10^7
$5s^2\,{}^1S \rightarrow 5s8p\,{}^1P^\circ$	L 0.0407	L 0.0431	40 098.8	42 462.3	L 1.456×10^7	L 1.729×10^7
	V 0.0376	V 0.0355			V 1.343×10^7	V 1.422×10^7
$5s4d\,{}^1D \rightarrow 5s5p\,{}^1P^\circ$	L 0.0080	L 0.0075	1638.3	1548.8	L 4.760×10^3	L 4.022×10^3
	V 0.1212	V 0.1282			V 7.233×10^4	V 6.838×10^4
$5s4d\,{}^1D \rightarrow 5s6p\,{}^1P^\circ$	L 0.3281	L 0.3443	13 291.1	13 948.7	L 1.289×10^7	L 1.490×10^7
	V 0.4542	V 0.4328			V 1.784×10^7	V 1.872×10^7
$5s4d\,{}^1D \rightarrow 5s7p\,{}^1P^\circ$	L 0.2514	L 0.2605	18 105.0	18 757.1	L 1.832×10^7	L 2.038×10^7
	V 0.2997	V 0.2893			V 2.184×10^7	V 2.263×10^7
$5s4d\,{}^1D \rightarrow 4d5p\,{}^1P^\circ$	L 0.2103	L 0.2166	20 419.4	21 022.5	L 1.950×10^7	L 2.128×10^7
	V 0.2269	V 0.2204			V 2.104×10^7	V 2.166×10^7
$5s4d\,{}^1D \rightarrow 5s8p\,{}^1P^\circ$	L 0.1374	L 0.1410	21 750.8	22 312.6	L 1.446×10^7	L 1.561×10^7
	V 0.1374	V 0.1340			V 1.446×10^7	V 1.483×10^7
$5s5d\,{}^1D \rightarrow 5s5p\,{}^1P^\circ$	L 0.2798	L 0.2924	12 471.8	13 028.9	L 5.807×10^6	L 6.621×10^6
	V 0.1903	V 0.1822			V 3.949×10^6	V 4.125×10^6
$5s5d\,{}^1D \rightarrow 5s6p\,{}^1P^\circ$	L 0.4615	L 0.3545	818.9	629.1	L 4.129×10^4	L 1.871×10^4
	V 0.8703	V 1.1330			V 7.787×10^4	V 5.981×10^4
$5s5d\,{}^1D \rightarrow 5s7p\,{}^1P^\circ$	L 0.2979	L 0.3117	3995.0	4179.4	L 1.057×10^6	L 1.210×10^6
	V 0.4082	V 0.3902			V 1.448×10^6	V 1.515×10^6
$5s5d\,{}^1D \rightarrow 4d5p\,{}^1P^\circ$	L 0.0845	L 0.0863	6309.3	6444.7	L 7.477×10^5	L 7.969×10^5
	V 0.1115	V 0.1092			V 9.867×10^5	V 1.008×10^6
$5s5d\,{}^1D \rightarrow 5s8p\,{}^1P^\circ$	L 0.0366	L 0.0371	7640.7	7734.8	L 4.756×10^5	L 4.934×10^5
	V 0.0436	V 0.0431			V 5.664×10^5	V 5.734×10^5
$5p^2\,{}^1D \rightarrow 5s5p\,{}^1P^\circ$	L 2.6479	L 2.8509	14 175.4	15 262.4	L 7.098×10^7	L 8.859×10^7
	V 2.7063	V 2.5136			V 7.255×10^7	V 7.811×10^7
$5p^2\,{}^1D \rightarrow 5s6p\,{}^1P^\circ$	L 0.4302	L 0.4882	2522.6	2862.5	L 3.652×10^5	L 5.336×10^5
	V 0.2692	V 0.2372			V 2.285×10^5	V 2.593×10^5
$5p^2\,{}^1D \rightarrow 5s7p\,{}^1P^\circ$	L 0.4014	L 0.3409	2291.3	1946.0	L 4.686×10^5	L 2.871×10^5
	V 0.3111	V 0.3662			V 3.631×10^5	V 3.084×10^5
$5p^2\,{}^1D \rightarrow 4d5p\,{}^1P^\circ$	L 0.0430	L 0.0393	4605.6	4211.3	L 2.027×10^5	L 1.549×10^5
	V 0.0245	V 0.0268			V 1.157×10^5	V 1.058×10^5
$5p^2\,{}^1D \rightarrow 5s8p\,{}^1P^\circ$	L 0.0077	L 0.0071	5937.0	5501.4	L 6.022×10^4	L 4.791×10^4
	V 0.0030	V 0.0033			V 2.362×10^4	V 2.189×10^4
$5s4d\,{}^1D \rightarrow 4d5p\,{}^1F^\circ$	L 0.0093	L 0.0098	16 903.1	17 858.3	L 2.532×10^5	L 2.986×10^5
	V 0.0563	V 0.0533			V 1.532×10^6	V 1.619×10^6
$5s4d\,{}^1D \rightarrow 5s4f\,{}^1F^\circ$	L 0.7280	L 0.7557	18 677.7	19 389.3	L 2.420×10^7	L 2.707×10^7
	V 0.5490	V 0.5288			V 1.825×10^7	V 1.895×10^7

TABLE VI. (*Continued*).

	$\lvert gf \rvert$		ΔE (calc.)	ΔE (obs.)	A (sec^{-1})	
	ΔE (calc.)	ΔE (obs.)	(cm^{-1})		ΔE (calc.)	ΔE (obs.)
$5s4d\ ^1D \rightarrow 5s5f\ ^1F^\circ$	L 0.4335	L 0.4449	20 822.1	21 369.2	L 1.791×10^7	L 1.936×10^7
	V 0.3615	V 0.3522			V 1.493×10^7	V 1.533×10^7
$5s4d\ ^1D \rightarrow 5s6f\ ^1F^\circ$	L 0.2391	L 0.2452	22 125.4	22 689.7	L 1.115×10^7	L 1.203×10^7
	V 0.2051	V 0.2000			V 9.569×10^6	V 9.813×10^6
$5s4d\ ^1D \rightarrow 5s7f\ ^1F^\circ$	L 0.1439	L 0.1475	22 932.6	23 506.4	L 7.209×10^6	L 7.764×10^6
	V 0.1244	V 0.1214			V 6.234×10^6	V 6.390×10^6
$5s5d\ ^1D \rightarrow 4d5p\ ^1F^\circ$	L 1.7943	L 2.1075	2793.0	3280.5	L 1.334×10^6	L 2.161×10^6
	V 1.9530	V 1.6627			V 1.452×10^6	V 1.705×10^6
$5s5d\ ^1D \rightarrow 5s4f\ ^1F^\circ$	L 1.6932	L 1.7836	4567.6	4811.5	L 3.366×10^6	L 3.935×10^6
	V 1.5803	V 1.5002			V 3.142×10^6	V 3.309×10^6
$5s5d\ ^1D \rightarrow 5s5f\ ^1F^\circ$	L 0.1371	L 0.1387	6712.0	6791.4	L 5.886×10^5	L 6.098×10^5
	V 0.1553	V 0.1535			V 6.666×10^5	V 6.745×10^5
$5s5d\ ^1D \rightarrow 5s6f\ ^1F^\circ$	L 0.0124	L 0.0126	8015.3	8111.9	L 7.593×10^4	L 7.871×10^4
	V 0.0154	V 0.0152			V 9.420×10^4	V 9.534×10^4
$5s5d\ ^1D \rightarrow 5s7f\ ^1F^\circ$	L 0.0012	L 0.0012	8822.5	8928.6	L 8.670×10^3	L 8.986×10^3
	V 0.0019	V 0.0019			V 1.420×10^4	V 1.437×10^4
$5p^2\ ^1D \rightarrow 4d5p\ ^1F^\circ$	L 0.0831	L 0.0799	1089.3	1047.1	L 9.399×10^3	L 8.348×10^3
	V 0.0227	V 0.0236			V 2.567×10^3	V 2.467×10^3
$5p^2\ ^1D \rightarrow 5s4f\ ^1F^\circ$	L 1.3830	L 1.2450	2864.0	2578.1	L 1.081×10^6	L 7.885×10^5
	V 1.9651	V 2.1830			V 1.536×10^6	V 1.383×10^6
$5p^2\ ^1D \rightarrow 5s5f\ ^1F^\circ$	L 0.0057	L 0.0052	5008.3	4558.0	L 1.359×10^4	L 1.024×10^4
	V 0.0509	V 0.0559			V 1.216×10^5	V 1.107×10^5
$5p^2\ ^1D \rightarrow 5s6f\ ^1F^\circ$	L 0.0026	L 0.0025	6311.7	5878.5	L 9.994×10^3	L 8.074×10^3
	V 0.0041	V 0.0044			V 1.561×10^4	V 1.454×10^4
$5p^2\ ^1D \rightarrow 5s7f\ ^1F^\circ$	L 0.0042	L 0.0040	7118.9	6695.2	L 2.033×10^4	L 1.691×10^4
	V 0.0004	V 0.0005			V 2.063×10^3	V 1.940×10^3
$4d^2\ ^1G \rightarrow 4d5p\ ^1F^\circ$	L 0.8694		2792.4		L 5.024×10^5	
	V 1.0386				V 6.002×10^5	
$4d^2\ ^1G \rightarrow 5s4f\ ^1F^\circ$	L 0.1418		1017.8		L 1.089×10^4	
	V 0.2775				V 2.131×10^4	
$4d^2\ ^1G \rightarrow 5s5f\ ^1F^\circ$	L 0.0249		1126.6		L 3.006×10^3	
	V 0.0023				V 2.780×10^2	
$4d^2\ ^1G \rightarrow 5s6f\ ^1F^\circ$	L 0.0141		2429.9		L 7.941×10^3	
	V 0.0054				V 3.054×10^3	
$4d^2\ ^1G \rightarrow 5s7f\ ^1F^\circ$	L 0.0080		3237.1		L 7.978×10^3	
	V 0.0040				V 3.947×10^3	

transition to the second $^1P^\circ$ state where the deviation is 42%. It is interesting to compare these results with the situation in the $^1P^\circ$ series in Ca where Parkinson *et al.*[35] also found a (more pronounced) minimum for the second $^1P^\circ$ state. This minimum was not reproduced by the MCHF calculations due to Froese Fischer and Hansen[10] which generally show larger discrepancies with experiment than the Sr results. An increase of 6% in the experimental gf values for Sr, as suggested by the lifetime due to Kelly *et al.*,[38] would give better agreement between the length value and experiment for the lowest and third lowest $^1P^\circ$ states, while the agreement would be somewhat worse for the other transitions.

Kelly *et al.*[39] deduced from their lifetime measurements for the $5s6p\ ^1P^\circ$ state ($\tau = 3.64 \pm 0.14$ nsec) the weighted oscillator strength $gf = 6.3 \pm 0.25$ for

TABLE VII. Calculated gf values for $5s^2\,{}^1S$–$5snp\,{}^1P^\circ$ transitions in Sr I. Observed transition energies are used and length (L) and velocity (V) values are given.

	This work		
Transition[a]	I[b]	II[c]	Observed
$5s^2\,{}^1S$–$5s5p\,{}^1P^\circ$	L	2.1210	1.92±0.06[d,e]
	V	1.7002	
$5s^2\,{}^1S$–$5s6p\,{}^1P^\circ$	L 0.0129	0.0051	0.007 24±0.0011[d]
	V 0.0100	0.0028	0.006 46±0.0010[e]
$5s^2\,{}^1S$–$5s7p\,{}^1P^\circ$	L 0.0090	0.0198	0.0158±0.0019[d]
	V 0.0080	0.0179	0.0135±0.0006[e]
$5s^2\,{}^1S$–$4d5p\,{}^1P^\circ$	L 0.0837	0.0445	0.0447±0.0066[d]
	V 0.0563	0.0376	0.0323±0.0015[e]
$5s^2\,{}^1S$–$5s8p\,{}^1P^\circ$	L 0.0486	0.0431	0.0457±0.0068[d]
	V 0.0355	0.0355	0.0417±0.0020[e]

[a] Adopting the level notation of Garton and Codling (Ref. 2).

[b] Using $\{5s^2,4p^2,4d^2,4f^2,5g^2\,{}^1S\}$ and $\{5snp_2,4d_15p_1,4d_24f\,{}^1P^\circ\}$ MCHF expansions.

[c] Using the final MCHF expansions of Table III.

[d] Hook method from Parkinson *et al.* (Ref. 35); absolute scale for the f values derived from zero-field level-crossing measurement of the $5s5p\,{}^1P^\circ$ lifetime by Lurio *et al.* (Ref. 37) and assuming no branching to $5s4d\,{}^1D$.

[e] Hook measurements from Penkin and Shabanova (Ref. 36); same absolute scale as in footnote d.

$5s4d\,{}^1D$–$5s6p\,{}^1P^\circ$, which disagrees with our value ($gf_l=0.3443$) by a factor of 20. Taking the more recent lifetime determination by Jönsson *et al.*[3] ($\tau=65\pm5$ nsec) and the Hook oscillator strength of Parkinson *et al.*[35] ($gf=0.007\,24$) corresponding to a transition probability $A=1.87\times10^6$ sec^{-1} for the $5s^2\,{}^1S$–$5s6p\,{}^1P^\circ$ transition, we obtain $gf=0.3124$ for $5s4d\,{}^1D$–$5s6p\,{}^1P^\circ$, which agrees well with our calculated value.

In both the Ca and Sr calculations it is found that there is better agreement between length and velocity values when calculated energies are used instead of the observed as we have done in this paper.

We conclude that the MCHF calculations for Sr seem more accurate than those[10] for Ca. This is perhaps because it is possible to give a better description of the $4d$ orbital in Sr I than of the $3d$ orbital in Ca I which is very sensitive to the exact details of screening and coupling.

C. Electric quadrupole transitions

We report, in Table VIII, oscillator strengths and the corresponding transition probabilities for $5s^2\,{}^1S$–$n\,{}^1D$ ($n=1$–3), $5s5p\,{}^1P^\circ$–$n\,{}^1F^\circ$ ($n=1$–5), $5s6p\,{}^1P^\circ$–$5s4f\,{}^1F^\circ$, $5s4d\,{}^1D$–$4d^2\,{}^1G$, and for some transitions between ${}^1D$ states obtained using both observed and calculated transition energies. All the other $E2$ transition probabilities connecting the terms considered in Table I are at least one order of magnitude smaller than the ones given in Table VIII. The agreement between length and velocity values is systematically better than for the $E1$ transitions.

The $E2$ transitions $3s^2\,{}^1S$–$(3s3d+3p^2)\,{}^1D$ have been observed in the spark spectra of Mg-like ions.[40] The equivalent transition $4s^2\,{}^1S$–$4s3d\,{}^1D$ appears in the emission spectra[41] of Ca I and the corresponding transition probability has been measured recently.[42] In Sr I, a very weak absorption line from the ground state has been identified by Rubbmark and Borgström[32] as the electric quadrupole transition $5s^2\,{}^1S$–$5s4d\,{}^1D$ but no measurement of the transition probability is available.

We compare our $1\,{}^1S$–$1\,{}^1D$ transition probability with other recent theoretical results in Table IX. FOTOS many-electron calculations have been performed by Beck and Nicolaides[43] which give an $E2$ transition rate 35% larger than the value calculated more recently by Bauschlischer *et al.*[44] using elaborate CI techniques in Gaussian-type orbital (GTO) basis sets. Both calculations include valence and some core-valence correlation effects. Relativistic effects were considered by Bauschlischer *et al.*[44] using a relativistic effective-core potential, but these affect the final transition rates by 9% only. The huge core-valence effects on the $E2$ transition rate (a decrease of 37%) found by Bauschlischer *et al.*[44] are somewhat surprising. These authors found a similar reduction in Ca I, obtaining a very good agreement with the recent experimental value.[42] The reduction of 13% due to core-valence correlation found by Beck and Nicolaides[43] is more in line with other results. For example, Glass[45] has recently reported that the static polarizability of Ca I is only slightly affected by the inclusion of core and core-valence effects. Moreover, core-polarization effects were estimated to be less than 10– 15% on some electric dipole transition probabilities[46,47] in Zn I for which the $3d$ orbital is expected to be more polarizable than in Sr.

Our values are not relativistic and do not include core-valence correlation effects. They agree very well with the "valence-CI" (VCI) results of Bauschlischer *et al.*[44] which point to the completeness of their Gaussian basis set for the valence problem. The single-configuration FOTOS results[43] seem to differ strongly from our value, but Beck and Nicolaides used the radial functions from a MCHF calculation to evaluate the transition probability in the single-configuration approximation. The use of the final MCHF instead of the HF radial functions induces in our calculations an increase of 18% and 59% in the length and velocity forms of the radial quadrupole integral $\langle 5s\|Q^2\|4d\rangle$, bringing our "HF" values to 68.2 and 62.7 $\sec^{-1}$, respectively. Valence correlation does not modify very much the final transition rate; the $5p^2\,{}^1S-{}^1D$ contribution to the $E2$ (L) line strength $S^{1/2}$ for the $5s^2\,{}^1S-5s4d\,{}^1D$ transition is 11%.

V. LIFETIMES

The theoretical lifetimes obtained using length (L) and velocity (V) oscillator strengths and the observed transition energies for all the decay channels are reported in Table X. For the ${}^1P^{\circ}$ and ${}^1F^{\circ}$ series our length values agree quite well with the radiative lifetimes measured by Jönsson *et al.*[3] using pulse-modulated laser spectroscopy (PUMOLS) techniques. Our lifetime values confirm that the Hanle-effect measurements of Kelly *et al.*[38,39] are unreliable for $5s6p$, $5s7p$, and $5s8p\,{}^1P^{\circ}$. For the ${}^1F^{\circ}$ series, our velocity values are too high except for the perturber $4d5p$, and our length values are systematically closer to the measurements of Jönsson *et al.* than to the time resolved decay measurements of Gornik.[48] There are no experimental lifetime values for the low-lying ${}^1D$ terms

TABLE VIII. Electric quadrupole oscillator strengths gf and transition probabilities A $(\sec^{-1})$ using the length (L) and velocity (V) forms and using the calculated and observed transition energies.

	$\lvert gf\rvert\times10^{-6}$		ΔE (calc.)	ΔE (obs.)	A $(\sec^{-1})$	
	ΔE (calc.)	ΔE (obs.)	(cm^{-1})		ΔE (calc.)	ΔE (obs.)
$5s^2\,{}^1S\rightarrow5s4d\,{}^1D$	L 0.9645	L 1.2774	18 348.0	20 149.7	L 4.332×10^1	L 6.919×10^1
	V 1.0123	V 1.1117			V 4.546×10^1	V 6.021×10^1
$5s^2\,{}^1S\rightarrow5s5d\,{}^1D$	L 1.9336	L 2.3682	32 458.1	34 727.5	L 2.718×10^2	L 3.810×10^2
	V 1.8544	V 1.9841			V 2.606×10^2	V 3.192×10^2
$5s^2\,{}^1S\rightarrow5p^2\,{}^1D$	L 0.1804	L 0.2285	34 161.7	36 960.9	L 2.809×10^1	L 4.165×10^1
	V 0.1869	V 0.2022			V 2.909×10^1	V 3.685×10^1
$5s5p\,{}^1P^{\circ}\rightarrow4d5p\,{}^1F^{\circ}$	L 1.4374	L 1.7532	15 264.8	16 309.5	L 3.192×10^1	L 4.444×10^1
	V 1.3866	V 1.4815			V 3.079×10^1	V 3.755×10^1
$5s5p\,{}^1P^{\circ}\rightarrow5s4f\,{}^1F^{\circ}$	L 0.8036	L 0.9223	17 039.4	17 840.5	L 2.223×10^1	L 2.797×10^1
	V 0.8156	V 0.8539			V 2.256×10^1	V 2.590×10^1
$5s5p\,{}^1P^{\circ}\rightarrow5s5f\,{}^1F^{\circ}$	L 0.8267	L 0.9118	19 183.8	19 820.4	L 2.899×10^1	L 3.413×10^1
	V 0.8457	V 0.8737			V 2.966×10^1	V 3.271×10^1
$5s5p\,{}^1P^{\circ}\rightarrow5s6f\,{}^1F^{\circ}$	L 0.4779	L 0.5251	20 487.1	21 140.9	L 1.911×10^1	L 2.236×10^1
	V 0.4938	V 0.5096			V 1.975×10^1	V 2.170×10^1
$5s5p\,{}^1P^{\circ}\rightarrow5s7f\,{}^1F^{\circ}$	L 0.2842	L 0.3116	21 294.3	21 957.6	L 1.228×10^1	L 1.432×10^1
	V 0.2944	V 0.3036			V 1.272×10^1	V 1.395×10^1
$5s6p\,{}^1P^{\circ}\rightarrow5s4f\,{}^1F^{\circ}$	L 1.6787	L 1.7298	5386.6	5440.6	L 4.641	L 4.879
	V 1.6540	V 1.6706			V 4.573	V 4.712
$5s4d\,{}^1D\rightarrow4d^2\,{}^1G$	L 2.9241		19 695.5		L 8.407×10^1	
	V 2.9806				V 8.569×10^1	
$5s5p\,{}^1P^{\circ}\rightarrow5s6p\,{}^1P^{\circ}$	L 0.5461	L 0.6580	11 652.8	12 399.9	L 1.649×10^1	L 2.250×10^1
	V 0.5596	V 0.5955			V 1.689×10^1	V 2.035×10^1
$5s5p\,{}^1P^{\circ}\rightarrow5s7p\,{}^1P^{\circ}$	L 0.0872	L 0.0995	16 466.7	17 208.4	L 5.255	L 6.550
	V 0.0947	V 0.0990			V 5.708	V 6.515
$5s5p\,{}^1P^{\circ}\rightarrow4d5p\,{}^1P^{\circ}$	L 0.0148	L 0.0165	18 781.1	19 473.7	L 1.160	L 1.390
	V 0.0184	V 0.0191			V 1.444	V 1.610
$5s6p\,{}^1P^{\circ}\rightarrow5s7p\,{}^1P^{\circ}$	L 0.3759	L 0.3746	4813.9	4808.5	L 1.937	L 1.926
	V 0.3771	V 0.3767			V 1.943	V 1.936
$5s4d\,{}^1D\rightarrow5s5d\,{}^1D$	L 0.6705	L 0.7394	14 110.1	14 577.8	L 1.781×10^1	L 2.096×10^1
	V 0.6937	V 0.7167			V 1.843×10^1	V 2.032×10^1
$5s4d\,{}^1D\rightarrow5p^2\,{}^1D$	L 0.2882	L 0.3462	15 813.7	16 811.2	L 9.614	L 1.305×10^1
	V 0.3027	V 0.3218			V 1.010×10^1	V 1.213×10^1

TABLE IX. Electric quadrupole transition rates (in $\sec^{-1}$) for Sr I $5s4d\ ^1D-5s^2\ ^1S$ (L=length; V=velocity).

		L	V
	FOTOS[a]	68.0	60.6
	b	60.6	57.3
	CI[c] VCI	69.2	
	CVCI	43.5	
	MRCVCI	44.7	
This work	HF	49.0	24.8
	MCHF	69.2	60.2

[a] Beck and Nicolaides (Ref. 43): single configuration using radial functions from a MCHF calculation.

[b] FOTOS from Beck and Nicolaides (Ref. 43).

[c] GTO calculations by Bauschlicher *et al.* (Ref. 44) using a relativistic effective-core potential. VCI means valence-CI; CVCI means core-valence-CI; MRCVCI means multireference core-valence-CI calculations.

except for the third one for which our theoretical values support the Hanle-effect values of Kelly and Mathur[49] in comparison to the two other experimental values.[48,50]

The ^1G term has not been observed. A limited MCHF expansion

$$\{5s6h_1, 4d_1 4f_1, 5p_1 5g_1, 4f_2 5g_2\ ^1H^\circ\}$$

calculation gives the lowest $^1H^\circ$ term lying 2437 cm^{-1} above the $4d^2\ ^1G$ term which in this situation can only decay to the lowest $^1F^\circ$ level. We then predict a long lifetime ($\tau \simeq 2\ \mu$sec) which is consistent with the situation in Ba I where the corresponding $5d^2\ ^1G$ term has been found recently and appears to have an even longer lifetime.[51] This reflects the fact that the lowest $^1F^\circ$ term in Ba I is above $5d^2\ ^1G$.

The observed deviations from the expected simple scaling law $\tau \sim (n^*)^3$ are reproduced perfectly by our calculations for the $^1P^\circ$ series (see Fig. 1). In the length form, the decay channels to $5s^2\ ^1S$ and to $5s4d\ ^1D$ contribute (100%,0%), (8%,92%), (23%,71%), (43%,55%), and (52%,47%) to the lifetimes of the five lowest members of the $^1P^\circ$ series, respectively. The effect of the perturber $4d5p\ ^1P^\circ$ on the oscillator strength of the $5s^2\ ^1S-{}^1P^\circ$ series was discussed in Sec. IV. For the $5s4d\ ^1D-{}^1P^\circ$ series, the $4d5p\ ^1P^\circ$ perturber contributes $\approx 45\%$ (in the length form) to the corresponding $S^{1/2}$ value.

The situation is much clearer for the $^1F^\circ$ series. The calculated lifetime values reproduce the observed lifetime trend very well (see Fig. 2). The deexcitation channel $n\ ^1F^\circ \rightarrow 5s4d\ ^1D$ is clearly dominant for all members of the series, except for the lowest one ($4d5p$) for which the decay to $5s5d\ ^1D$ contributes 88% (in the length form) to the lifetime. The $n\ ^1F^\circ \rightarrow 5s4d\ ^1D$ decay rates are strongly affected by the $4d5p\ ^1F^\circ$ and $5p^2\ ^1D$ perturbers which contribute to the $S^{1/2}$ values (60%,19%) and (30%,10%) for $n=4$ and 7, respectively. Our calculations then show that the smoothness of an observed lifetime trend, such as the one depicted in Fig. 2, does not imply the absence of perturbations.

TABLE X. Lifetimes (nsec) of Rydberg levels in Sr I.

	MCHF				
Level	Length	Velocity	Experimental		
$5s5p\ ^1P^\circ$	4.50	5.62	4.68(10)[a]	4.97(15)[b]	
$5s6p$	61.63	51.44	3.64(14)[a]	65(5)[c]	
$5s7p$	35.03	32.80	4.93(32)[a]	39.2(20)[c]	
$4d5p$	25.64	27.05		23.4(23)[c]	
$5s8p$	29.90	33.73	5.46(17)[a]	27.1(13)[c]	
$5s4d\ ^1D$	14.45×10^6	16.61×10^6			
$5s5d$	150.61	238.96			
$5p^2$	11.22	12.76	9.53(10)[d]	23.8(13)[e]	25(3)[f]
$4d5p\ ^1F^\circ$	405.19	300.62		296(22)[c]	
$5s4f$	31.45	42.30	33.5(12)[e]	31.3(9)[c]	34.2(4)[g]
$5s5f$	50.04	62.05	33.6(13)[e]	45.0(21)[c]	
$5s6f$	82.48	100.75	98.5(12)[e]	78.0(3)[c]	
$5s7f$	128.37	156.10	126(5)[h]	120(5)[c]	
$4d^2\ ^1G$	1948.0	1609.0			

[a] Hanle measurements of Kelly *et al.* (Refs. 38 and 39).

[b] Hanle measurements of Lurio *et al.* (Ref. 37).

[c] PUMOLS measurements of Jönsson *et al.* (Ref. 3).

[d] Hanle measurements of Kelly and Mathur (Ref. 49).

[e] Time resolved measurement of Gornik (Ref. 48).

[f] Delayed coincidence measurements due to Erdevdi and Shimon (Ref. 53).

[g] Time resolved decay measurement of Andrä *et al.* (Ref. 52).

[h] PUMOLS measurements of Grafström *et al.* (Ref. 50).

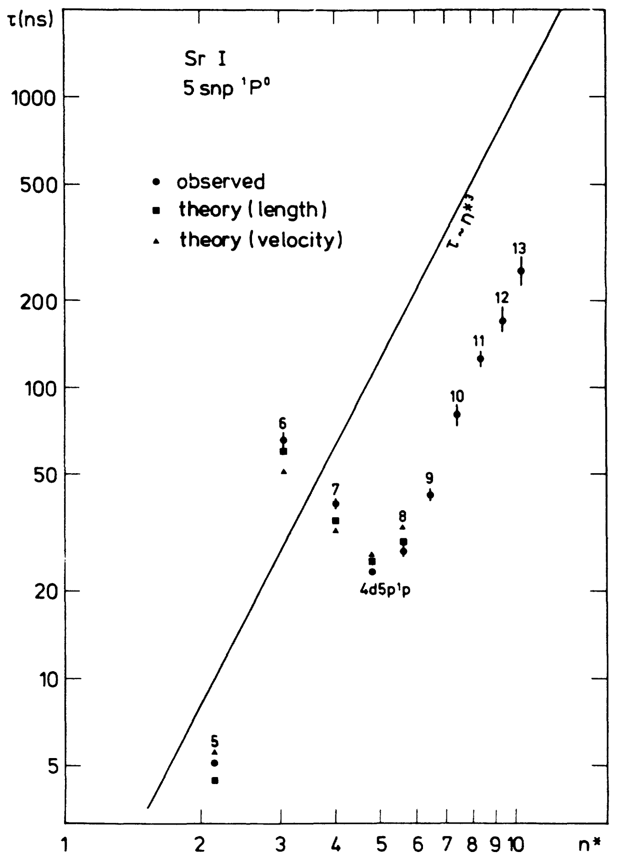

FIG. 1. Experimental lifetimes from Jönsson *et al.* (Ref. 3) (●) compared with theory (length ■ and velocity ▲) for the $5snp\ ^1P^\circ$ series and for $4d5p\ ^1P^\circ$ plotted vs the effective principal quantum number (log-log scale). The $(n^*)^3$ dependence expected for unperturbed Rydberg series is indicated by the solid line.

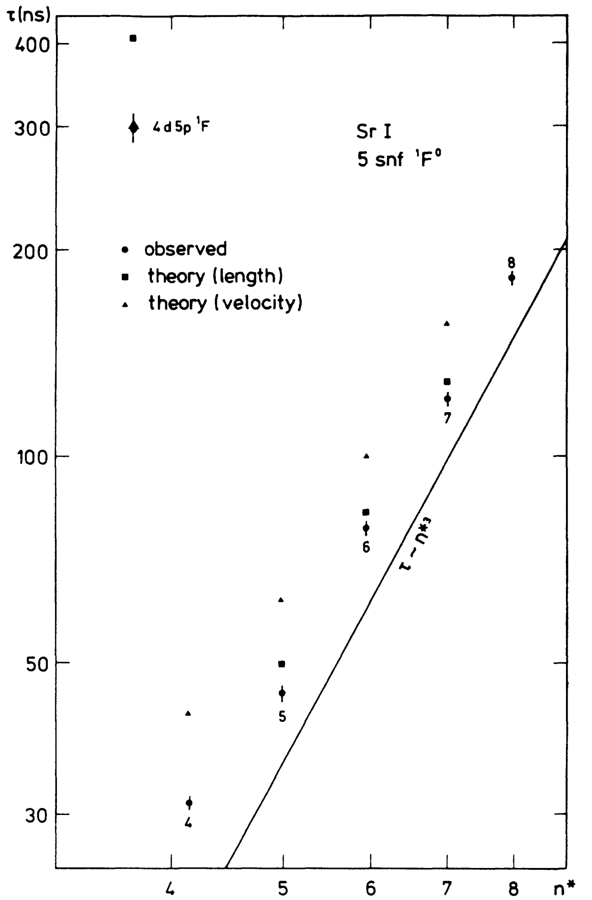

FIG. 2. Experimental lifetimes from Jönsson *et al.* (Ref. 3) (●) compared with theory (length ■ and velocity ▲) for the $5snf\ ^1F^\circ$ series and for $4d5p\ ^1F^\circ$ plotted vs the effective principal quantum number (log-log scale). For $n=4$, the (length) value is equal to the observed lifetime and is not explicitly indicated on the figure. The $(n^*)^3$ dependence expected for unperturbed Rydberg series is indicated by the solid line.

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APPENDIX

Let a two-configuration multiconfiguration Hartree-Fock wave function

$$\Psi^{\mathrm{MCHF}_2}=a_1\,|\,\gamma_c nln'l'LS\,\rangle+a_2\,|\,\gamma_c nln''l'LS\,\rangle \qquad \text{(A1)}$$

describe a two-electron system. γ_c stands for the set of closed shells. The two configurations are assumed to differ only in the n value of one electron. The corresponding MCHF equations can be derived[12] by requiring the total energy

$$E=\langle\,\Psi^{\mathrm{MCHF}_2}\,|\,H\,|\,\Psi^{\mathrm{MCHF}_2}\,\rangle$$

to be stationary with respect to variations in the radial functions,

$$\begin{aligned}LP_{n'l'}=&\;A(n'l')+(a_2/a_1)A(n''l')-(a_2/a_1)LP_{n''l'}\\&+\epsilon(n'l',n'l')P_{n'l'}+\sum_{i\in l'}\epsilon(n'l',n_il')P_{n_il'}\;,\end{aligned} \qquad \text{(A2)}$$

$$\begin{aligned}LP_{n''l'}=&\;A(n''l')+(a_1/a_2)A(n'l')-(a_1/a_2)LP_{n'l'}\\&+\epsilon(n''l',n''l')P_{n''l'}+\sum_{i\in l'}\epsilon(n''l',n_il')P_{n_il'}\;,\end{aligned} \qquad \text{(A3)}$$

with

$$A(n_il_i)=\sum_c \left[(4l_c+2)(2/r)Y^0(n_cl_c,n_cl_c)P_{n_il_i}-[l_i]^{-1}\sum_k (l_c\|C^k\|l_i)^2(2/r)Y^k(n_cl_c,n_il_i)P_{n_cl_c}\right]$$
$$+\sum_k[\alpha^k(2/r)Y^k(nl,nl)P_{n_il_i}\pm\beta^k(2/r)Y^k(nl,n_il_i)P_{nl}]\ . \tag{A4}$$

The one-electron operator L and the function $Y^k(i,j)$ are defined by Froese Fischer.[12] The + and − signs refer to singlet and triplet terms, respectively, and the α^k and β^k coefficients are given by

$$\begin{aligned}\alpha^k&=(-1)^{l+l'+L}(l\|C^k\|l)(l'\|C^k\|l')\begin{Bmatrix} l & l' & L\\ l' & l & k\end{Bmatrix}\ ,\\ \beta^k&=(l\|C^k\|l')^2\begin{Bmatrix} l & l' & L\\ l & l' & k\end{Bmatrix}\ .\end{aligned} \tag{A5}$$

The four quantities $\epsilon(n'l',n'l')$, $\epsilon(n'l',n''l')$, $\epsilon(n''l',n'l')$, and $\epsilon(n''l',n''l')$ can be evaluated from the MCHF equations (A2) and (A3) as

$$\epsilon(i,i)=L_{i,i}+KL_{i,j}-\sum_c\left[(4l_c+2)[F^0(c,i)+KR^0(c,j;c,i)]-[l_i]^{-1}\sum_k(l_c\|C^k\|l_i)^2[G^k(c,i)+KR^k(c,j;i,c)]\right]$$
$$-\sum_k\{\alpha^k[F^k(nl,i)+KR^k(nl,i;nl,j)]\pm\beta^k[G^k(nl,i)+KR^k(nl,i;j,nl)]\}\ , \tag{A6}$$

$$\epsilon(j,i)=L_{i,j}+K^{-1}L_{i,i}-\sum_c\left[(4l_c+2)[R^0(c,i;c,j)+K^{-1}F^0(c,i)]-[l_i]^{-1}\sum_k(l_c\|C^k\|l_i)^2[R^k(c,i;j,c)+K^{-1}G^k(c,i)]\right]$$
$$-\sum_k\{\alpha^k[R^k(nl,i;nl,j)+K^{-1}F^k(nl,i)]\pm\beta^k[R^k(nl,i;j,nl)+K^{-1}G^k(nl,i)]\}\ , \tag{A7}$$

with

$$\begin{aligned}K&=(a_2/a_1)\ \text{ if } i=n'l'\ ,\quad j=n''l'\ ,\\ K&=(a_1/a_2)\ \text{ if } i=n''l'\ ,\quad j=n'l'\ .\end{aligned} \tag{A8}$$

By comparing (A6) and (A7), we see that

$$\epsilon(i,i)=K\epsilon(j,i)\ . \tag{A9}$$

On the other hand, the quantities $\epsilon(i,j)$ and $\epsilon(j,i)$ are related[12] by

$$q_i\epsilon(i,j)=q_j\epsilon(j,i)=\lambda\ , \tag{A10}$$

where q_i and q_j are the occupation numbers of the (n_il_i) and (n_jl_j) orbitals, respectively. In our two-configuration approximation (A1), this gives

$$a_2^2\epsilon(n''l',n'l')=a_1^2\epsilon(n'l',n''l')\ . \tag{A11}$$

Equations (A9) and (A11) are compatible only if the diagonal Lagrange multipliers are identical, i.e.,

$$\epsilon(n'l',n'l')=\epsilon(n''l',n''l')\ . \tag{A12}$$

This property is independent of the term considered and applies also to more extended multiconfiguration expansions.

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[1] J. E. Hansen and W. Persson, J. Phys. B **10**, L363 (1977).

[2] W. R. S. Garton and K. Codling, J. Phys. B **1**, 106 (1968).

[3] G. Jönsson, C. Levinson, A. Persson, and C.-G. Wahlström, Z. Phys. A **316**, 225 (1984).

[4] M. Aymar, J. Opt. Soc. Am. B **1**, 239 (1984).

[5] M. J. Seaton, Proc. Phys. Soc. London **88**, 815 (1966); K. T. Lu and U. Fano, Phys. Rev. A **2**, 81 (1970).

[6] K. T. Lu, Phys. Rev. A **4**, 579 (1971); C. M. Lee and K. T. Lu, *ibid.* **8**, 1241 (1973).

[7] J. A. Armstrong, P. Esherick, and J. J. Wynne, Phys. Rev. A **15**, 180 (1977); J. J. Wynne and J. A. Armstrong, IBM J. Res. Dev. **23**, 490 (1979).

[8] C. Froese Fischer and J. E. Hansen, Phys. Rev. A **24**, 631 (1981).

[9] A. Aspect, J. Bauche, A. L. A. Fonseca, P. Grangier, and G. Roger, J. Phys. B **17**, 1761 (1984).

[10] C. Froese Fischer and J. E. Hansen, J. Phys. B **18**, 4030 (1985).

[11] M. Aymar, E. Luc-Koenig, and S. Watanabe, J. Phys. B **20**, 4385 (1987).

[12] C. Froese Fischer, *The Hartree-Fock Method for Atoms* (Wiley, New York, 1977).

[13] C. Froese Fischer and K. M. S. Saxena, Phys. Rev. A **9**, 1498 (1974).

[14] C. Froese Fischer and M. Godefroid, Nucl. Instrum. Methods **202**, 307 (1982); Phys. Scr. **25**, 394 (1982).

[15] J. E. Hansen, Phys. Rev. A **15**, 810 (1977).

[16] C. Froese Fischer, in Proceedings of the Symposium on Atomic Spectroscopy and Highly Ionized Atoms, Lisle, Illinois, 1987, edited by H. G. Berry, R. Dunford, and L. Young [Nucl. Instrum. Methods B **31**, 265 (1988)].

[17] C. Froese Fischer, J. Comput. Phys. **13**, 508 (1973).

[18] M. Godefroid, J. Lievin, and J. Y. Metz, J. Phys. B **20**, 3283 (1987).

[19] R. D. Cowan and J. E. Hansen, J. Opt. Soc. Am. **71**, 60 (1981).

[20] H. Smid and J. E. Hansen, J. Phys. B **16**, 3339 (1983).

[21] C. E. Moore, *Atomic Energy Levels,* Natl. Bur. Stand. (U.S.) Circ. No. 467 (U.S. GPO, Washington, D.C., 1952), Vol. II.

[22] A. G. Shenstone and H. N. Russell, Phys. Rev. **39**, 415 (1932).

[23] P. Esherick, Phys. Rev. A **15**, 1920 (1977).

[24] C. Froese Fischer, Phys. Scr. **21**, 466 (1980).

[25] C. Froese Fischer, Comput. Phys. Rep. **3**, 275 (1986).

[26] C. Froese Fischer, J. Opt. Soc. Am. **69**, 118 (1979).

[27] P. McCavert and E. Trefftz, J. Phys. B **7**, 1270 (1974).

[28] M. A. Baig and J. P. Connerade, J. Phys. B **17**, L271 (1984).

[29] J. E. Hansen, J. Phys. B **11**, L579 (1978).

[30] J. A. Armstrong, J. J. Wynne, and P. Esherick, J. Opt. Soc. Am. **69**, 211 (1979).

[31] M. J. Seaton, Rep. Prog. Phys. **46**, 167 (1983).

[32] J. R. Rubbmark and S. A. Borgström, Phys. Scr. **18**, 196 (1978).

[33] R. Langer, Phys. Rev. **35**, 649 (1930).

[34] U. Fano, Phys. Rev. **124**, 1866 (1961).

[35] W. H. Parkinson, E. M. Reeves, and F. S. Tomkins, J. Phys. B **9**, 157 (1976).

[36] N. P. Penkin and L. N. Shabanova, Opt. Spectrosk. **12**, 3 (1962) [Opt. Spectrosc. (USSR) **12**, 1 (1962)].

[37] A. Lurio, R. Dezafra, and R. J. Goshen, Phys. Rev. **134**, A1198 (1964).

[38] F. M. Kelly, T. K. Koh, and M. S. Mathur, Can. J. Phys. **52**, 795 (1974).

[39] F. M. Kelly, T. K. Koh, and M. S. Mathur, Can. J. Phys. **51**, 1653 (1973).

[40] M. Godefroid, C. E. Magnusson, P. O. Zetterberg, and I. Joelsson, Phys. Scr. **32**, 125 (1985).

[41] G. Risberg, Ark. Fys. **37**, 231 (1968).

[42] K. Fukuda and K. Ueda, J. Phys. Chem. **86**, 676 (1982).

[43] D. R. Beck and C. A. Nicolaides, J. Phys. B **16**, L627 (1983).

[44] C. W. Bauschlischer, Jr., S. R. Langhoff, R. L. Jaffe, and H. Partridge, J. Phys. B **17**, L427 (1984).

[45] R. Glass, J. Phys. B **20**, 4649 (1987).

[46] C. Froese Fischer and J. E. Hansen, Phys. Rev. A **17**, 1956 (1978); **19**, 1819 (1979).

[47] P. Shorer, Phys. Rev. A **18**, 1060 (1978).

[48] W. Gornik, Z. Phys. A **283**, 231 (1977).

[49] F. M. Kelly and M. S. Mathur, Can. J. Phys. **57**, 657 (1979).

[50] P. Grafström, Jiang Zhan-Kui, G. Jönsson, C. Levinson, H. Lundberg, and S. Svanberg, Phys. Rev. A **27**, 947 (1983).

[51] W. Wassen, E. Bente, and W. Hogervorst, J. Phys. B **20**, 2383 (1987).

[52] H. J. Andrä, H.-J. Plöhn, W. Wittman, A. Gaup, John O. Stoner, Jr., and M. Gaillard, J. Opt. Soc. Am. **65**, 1410 (1975).

[53] N. M. Erdevdi and L. L. Shimon, Opt. Spektrosk. **40**, 771 (1976) [Opt. Spectrosc. (USSR) **40**, 443 (1976)].