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Core-valence and core-core correlation effects on hyperfine-structure parameters and oscillator strengths in Tl II and Tl III

Tomas Brage and David S. Leckrone
Code 681, NASA/Goddard Space Flight Center, Greenbelt, Maryland 20771

Charlotte Froese Fischer
Department of Computer Science, Box 1679B, Vanderbilt University, Nashville, Tennessee 372 35

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We report on large-scale *ab initio* multiconfiguration Dirac-Fock calculations of hyperfine-structure parameters and oscillator strengths for the lowest few levels in Tl II and Tl III. The effect of both core-valence and core-core correlation on these properties is investigated, probing effects of all core subshells. The agreement with most experiments is excellent. These data are of vital interest for the interpretation of recent spectra of the chemically peculiar star χ Lupi.

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I. INTRODUCTION

There has recently been an increased interest in large-scale, accurate calculations for atomic properties, using fully relativistic methods. The reasons for this can be found from different branches of atomic physics. Measured hyperfine structure and isotope shifts may serve as important probes of different properties of the nucleus, but only if the electronic structure of the ions is represented accurately in the atomic model. The possibility of observing parity violation in atoms is of great importance, but again a careful treatment of the atomic structure is needed. There is also an interest from basic atomic structure to better understand which contributions are important and need to be included when determining different atomic properties. Tl II and Tl III are excellent test cases, since they represent relatively simple two- and one-electron systems.

Heavy elements are also important in different branches of astrophysics. Peculiar stars show an overabundance of all elements heavier than the iron group, compared to their solar abundance. In addition, isotope anomalies are observed, where the isotopic admixture appears to be very different from the one observed in the solar system ([1], and references given therein).

The research presented in this paper was initiated by recent results from the Goddard High Resolution Spectrograph (GHRS) on board the Hubble Space Telescope. In the GHRS spectra of the peculiar, HgMn star χ Lupi the $6s^2\ {}^1S_0$-$6s6p\,{}^3P_1$ transition of Tl II was observed [2]. This is not only the first time thallium has been observed in a star other than our Sun, but it also is the first time hyperfine structure has been resolved in an ultraviolet stellar spectrum. To analyze this spectrum, a detailed knowledge of different atomic parameters is necessary, parameters that are usually not available in the literature. We have therefore initiated a careful study of different ionization stages of thallium, and this paper presents our first results. Parallel to this theoretical work, experimental studies are performed in Lund to determine hyperfine-structure splittings and isotope shifts [3].

We use the multiconfiguration Dirac-Fock (MCDF) method for all our calculations, in the form of the GRASP94 package, a version modified for large-scale computation based on GRASP (general purpose relativistic atomic structure package) [4,5] and GRASP92 [6]. We aim at designing a systematic method, which makes it possible not only to get accurate results, but to estimate the uncertainty in our results. By defining different sorts of restricted approaches, based on the definition of different types of correlation and the concept of restricted active spaces, we hope to be able to design an efficient and reliable method for calculations of hyperfine-structure parameters and oscillator strengths.

The most sophisticated calculation for Tl II and Tl III to date is the relativistic configuration interaction calculation by Beck and Cai [7], where the effect of core-valence correlation is included in a similar way as in the present work. Other works, by Migdalek and co-workers [8–10], use core polarization potentials to represent this important contribution. In some other, quite recent works, the effect of core polarization has been completely neglected [11,12]. As we will show this is not a valid approximation. To the best of our knowledge no attempt has been made to treat core-core correlation.

II. THEORY

A. The MCDF method

The MCDF method [4] is based on an expansion of the atomic state function in a linear combination of configuration state functions (CSF's), $\Phi(\alpha_i J)$,

$$\Psi(\gamma J)=\sum_i c_i\Phi(\alpha_i J). \tag{1}$$

The CSF's are in turn antisymmetric functions, constructed from products of spin orbitals of the form

$$u(n\kappa j m_j;\vec{q})=\frac{1}{r}\begin{pmatrix} P(n\kappa;r)\Omega_{\kappa m}(\theta,\varphi) \\ iQ(n\kappa;r)\Omega_{-\kappa m}(\theta,\varphi)\end{pmatrix}, \tag{2}$$

where $\Omega_{\kappa m}(\theta,\varphi)$ denotes a two-component angular-dependent spin-orbit function [13]. The α_i represents all one-electron and intermediate quantum numbers needed to define the CSF's. The γ is a label, usually chosen as the α_i of the CSF with largest weight $|c_i|$. The quantum number κ is given by

$$\kappa=\pm(j+\tfrac{1}{2}). \tag{3}$$

In this paper we are mainly interested in radiative transitions between bound states, and hyperfine structure.

The transition properties are represented by the electric dipole, oscillator strength, in two different gauges [5] — the Babushkin, gf_l, and the Coulomb, gf_v, gauges. These correspond to the length and velocity forms, respectively, in the nonrelativistic limit.

The only hyperfine-structure parameter of interest here is the magnetic dipole constant [14,15]

$$A_J=\frac{\mu_I}{I}\frac{1}{[J(J+1)]^{1/2}}\langle\gamma J||\mathbf{T}^{(1)}||\gamma J\rangle \tag{4}$$

since the nuclear spin quantum number, I, for both thallium isotopes is 1/2 (the higher-order magnetic and electric moments of the nucleus are therefore zero). The operator $\mathbf{T}^{(1)}$ is given by

$$\mathbf{T}^{(1)}=-i\alpha\sum_{j=1}^{N}[\alpha(j)\cdot\mathbf{l}(j)\mathbf{C}^{(1)}(j)]r_j^{-2}. \tag{5}$$

The hyperfine-structure energy of a given level is given by

$$E_{\mathrm{hfs}}(J)=\tfrac{1}{2}A_J[F(F+1)-J(J+1)-I(I+1)], \tag{6}$$

which gives us the measurable quantity.

The two sets of unknowns are the radial functions $P(n\kappa j;r)$ and $Q(n\kappa j;r)$, and the c_i coefficients in Eq. (1). These are determined in an iterative, self-consistent field procedure for the integrodifferential equations of the MCDF procedure [4,5]. The functional that defines the energy on which the orbitals are optimized can be defined according to different schemes. We will use what is commonly known as the extended optimal level scheme, where a linear combination of a few eigenstates is used to define the energy expression.

Thallium has two different isotopes, with slightly different measured hyperfine-structure constants. This is completely due to a difference in the magnetic dipole moment of the nucleus, and is not an atomic structure effect. We will therefore completely concentrate on the isotope ^{203}Tl, with moment, $\mu_I=1.6223$ nuclear magnetons.

B. The restricted active space (RAS)

The main task in a multiconfiguration calculation is to find an algorithm for the generation of the CSF's in Eq. (1). There are many different ways of doing this, but in this paper we are aiming for a systematic approach. In the case of multiconfiguration Hartree-Fock (MCHF) calculations we have found an "orbital-driven" method [16] based on the notion of restricted active spaces (RAS) [17,18] of CSF's to be very efficient. To describe it, we need clear definitions of two central concepts, different types of correlation and active sets of orbitals.

The RAS is spanned by all CSF's that can be generated from a given active set (AS) of orbitals, with some constraints. The constraints are derived from the notions of different types of correlations. Let us use the two-electron system of Tl II as an example, with the ground level of

$$1s^22s^2\ldots4f^{14}5s^25p^65d^{10}6s^2(J=0). \tag{7}$$

We denote the two outer electrons as belonging to valence subshells and the rest as occupying core subshells. The valence correlation (VC) is then represented by the RAS defined by the constraint of closed core subshells, and varying valence subshells. If the active set of orbitals is given by AS $=\{6s,6p,6p_-,6d,6d_-,5f,5f_-,5g,5g_-\}$, we can describe the CSF's that span the VC-AS RAS as

$$\ldots5d^{10}\mathrm{AS}^2=\ldots5d^{10}\{6spd5fg\}^2=5d^{10}\{6s,6p,6d,5f,5g\}^2. \tag{8}$$

We use the notation of only giving the last filled subshell. All subshells before, in this case, the $5d$ one, are assumed to be filled. We also abbreviate our notation, implying both forms when writing nl (both nl and nl_-).

The active set will be increased in a systematic fashion, to get a better and better approximation of the full RAS. We will discuss this in detail below.

The next type of RAS-defining correlation will be of core-valence (CV) type. According to this we include CSF's with excitations from a given core subshell. As an example, the CV$_{5d}$ RAS is defined as the union of VC and the space spanned by CSF's of the form

$$\ldots5p^65d^9\mathrm{AS}^3. \tag{9}$$

We will also discuss the core-valence correlation of more inner shells, and as an example we define the CV$_{4f}$ RAS as the union of VC and the space spanned by CSF's of the form

$$\ldots4d^{10}4f^{13}\ldots5d^{10}\mathrm{AS}^3, \tag{10}$$

i.e., only allowing a hole in the $4f$ core subshell.

A final type of model would include core-core (CC) correlation, which represents correlation within the core. In the case of correlation within the $5d$ subshell we would define a CC$_{5d}$ RAS as the union of the VC, the CV$_{5d}$, and the space spanned by CSF's of the form

$$\ldots5d^8\mathrm{AS}^4. \tag{11}$$

The definition of these subspaces of the full CSF space is just the first step in finding a working and efficient method. If the calculations are unrestricted, the number of CSF's will grow very fast with the size of the active set. We will therefore use some further approximations to limit the size of the different RAS that is included.

C. Limiting the size of CSF expansions

Even the restricted forms of active spaces described above might sometimes be too large, and a large part of it does not contribute to the properties of interest. We will use two different methods to limit the size of the included part of the RAS.

It has been shown [19] that a large part of the contribution to the hyperfine-structure parameters arises from only single substitutions of orbitals from the main CSF's. We will utilize this when we include CV effects from inner subshells.

A more elaborate way of limiting the size of our calculations is based on first-order calculations and condensation techniques, techniques used successfully in convergence studies of the total energy for Be and Li^- [20]. The first step is to define a zero-order set of CSF's, including only the most important CSF's. The rest constitutes the first-order set. When setting up the interaction matrix to be used in the MCDF calculation, we only include interactions within the zero-order set, and between the zero- and first-order set. The interaction within the first-order set is ignored, which explains the label. After the orbitals are optimized, we condense the set of CSF's to only include the ones with a weight, $|c_i|$ in Eq. (1), larger than a certain cutoff. For this condensed set a full interaction matrix, configuration interaction (CI) calculation is performed without reoptimization of the orbitals.

D. Systematic approach

The systematic approach used is twofold and aims for convergence in the properties of interest. First we define a set of models, including more and more correlations based on the ideas of RAS and different types of correlations as described above. Second, within each model we increase the active set step by step. This procedure should not only let us determine a final answer, within the best model, but also estimate the accuracy of the result.

III. CORE-VALENCE CORRELATION IN TL II

In our first set of calculations, we look at valence and core-valence correlation in Tl II and their effect on oscillator strengths and hyperfine-structure parameters. The three atomic states of interest are in most literature represented by LS coupling designation as

$$6s^{2}\,{}^1S_0, \quad 6s6p\,{}^3P_1, \quad 6s6p\,{}^1P_1. \tag{12}$$

The interesting properties are the gf value for transitions from the ground level to each of the excited $J=1$ levels, and the hyperfine-structure A constant for the two odd levels ($A=0$ for the ground state, since $J=0$).

The calculations are divided into two distinct parts. First, we will perform all order, full RAS calculations for valence correlation and core-valence correlation of the $5d$ subshell. Then, we use the single substitution to include core-valence correlations for all other, important core subshells. We frequently use the first-order, condensation techniques to limit the sizes of our calculations.

An estimate of the importance of different core subshells is obtained from first-order calculations (described below).

TABLE I. Estimate, from first-order calculations described in the text, of contributions to the hyperfine-structure parameters for $6s6p\,{}^3P_1$ and $6s6p\,{}^1P_1$ of Tl II.

Correlation type		Relative contribution $A({}^3P_1)$	$A({}^1P_1)$
Valence correlation	VC	$+0.66\%$	$+33.27\%$
Core-valence $5d$	CV_{5d}	$+13.25\%$	$+42.19\%$
Core-valence $5s$	CV_{5s}	$+3.58\%$	$+6.72\%$
Core-valence $5p$	CV_{5p}	$+0.34\%$	$+2.50\%$
Core-valence $4f$	CV_{4f}	$+0.08\%$	-5.79%
Core-valence $4d$	CV_{4d}	-0.03%	$+0.06\%$
Core-valence $4s$	CV_{4s}	-0.02%	$+0.00\%$
Core-valence $1s$	CV_{1s}	-0.00%	$+0.02\%$

In Table I we list the estimated size of the contributions to the hyperfine-structure constant.

A. Dirac-Fock and valence correlation

The first model is what we label Dirac-Fock. In reality it is an extended average level calculation [4,5] for the three main configurations. All orbitals are optimized in this model, and the core ones are kept fixed for the rest of the calculations.

Next we move to the valence correlation RAS, VC. The active set is increased in three steps

$$\begin{aligned} \mathrm{AS}_1 &= \{6s,6p,6d,5f,5g\}, \\ \mathrm{AS}_2 &= \mathrm{A}S_1+\{7s,7p,7d\}, \\ \mathrm{AS}_3 &= \mathrm{AS}_2+\{8s,8p,8d\}, \end{aligned} \tag{13}$$

and as can be seen in Tables II and III convergence seems to be reached.

TABLE II. Tl II: Hyperfine-structure A parameters, in 10^{-3} cm^{-1} (=29.979 25 MHz), for the $6s6p\,{}^3P_1$ and ${}^1P_1$ levels of Tl II, from models only including valence and core-valence correlation.

Model[a]	Active set[a]	A parameter ${}^3P_1$	${}^1P_1$
Present			
DF		2065	-346
VC	AS_1	2079	-381
	AS_2	2085	-465
	AS_3	2079	-461
CV_{5d}	AS_1	2251	-449
	AS_2	2333	-607
	AS_3	2352	-607
$\cup\mathrm{CV}_{5s}$	AS_4	2437	-637
$\cup\mathrm{CV}_{5p}$	AS_4	2444	-644
$\cup\mathrm{CV}_{4f}$	AS_5	2433	-638
Experiment, $A=\frac{2}{3}\Delta E_{\mathrm{HFS}}$:			
FTS[b]		2469 ± 1	-648 ± 6

[a] See text.

[b] Fourier transform spectroscopy, Johansson *et al.* [3].

TABLE III. Tl II: Wavelengths in Å and oscillator strengths in Babushkin/length (gf_l) and Coulomb/velocity (gf_v) form [5], for the $6s^2\,{}^1S_0$-$6s6p\,{}^3P_1$ and $6s^2\,{}^1S_0$-$6s6p\,{}^1P_1$ transitions in Tl II. Results from models including only core-valence correlation.

Model[a]	Active set[a]	${}^1S_0$-${}^3P_1$ λ	gf_l/gf_v	gf[b]	${}^1S_0$-${}^1P_1$ λ	gf_l/gf_v	gf[b]
Present							
DF		2389	0.0452/0.0322	0.0566	1394	2.625/1.985	2.768
VC	AS_1	2220	0.0362/0.0609	0.0421	1375	2.291/2.332	2.383
	AS_2	2154	0.0403/0.0420	0.0455	1364	2.326/2.198	2.400
	AS_3	2151	0.0405/0.0416	0.0456	1364	2.306/2.178	2.379
CV_{5d}	AS_1	2042	0.0333/0.0479	0.0356	1345	1.314/1.617	1.339
	AS_2	1915	0.0421/0.0553	0.0422	1315	1.382/1.641	1.375
	AS_3	1909	0.0448/0.0573	0.0448	1320	1.380/1.611	1.378
$\cup CV_{5s}$	AS_4	1910	0.0449/0.0574	0.0449	1322	1.374/1.601	1.374
$\cup CV_{5p}$	AS_4	1918	0.0450/0.0579	0.0452	1327	1.365/1.594	1.370
$\cup CV_{4f}$	AS_5	1919	0.0449/0.0579	0.0451	1327	1.364/1.594	1.369
Experiment							
FTS[c]		1909			1322		
BFS[d]							1.21 ± 0.20
Other theories							
RCI[e]		1671	0.0222/0.0115	0.0222	1196	1.362/1.249	1.362
MCDF-CP[f]				0.0449			1.359
CI-CP[g]				0.0411			1.37
MCDF[h]				0.0203			2.37
MCRRPA[i]		2141		0.0374	1339		2.307

[a] See text.

[b] Recommended gf value, computed using gf_l and experimental λ.

[c] Fourier transform spectroscopy, Johansson *et al.* [3] for ^{203}Tl, λλ = 1321.6519,1321.6350 and λλ = 1908.5725,1908.7087.

[d] Beam-foil spectroscopy, Andersen *et al.* [21].

[e] Beck and Cai [7], including core polarization. The authors label this method MCDF+Corr.

[f] Migdalek and Baylis [8], MCDF using core polarization potentials.

[g] Migdalek and Bojara [9], relativistic CI using core polarization potentials.

[h] Das and Idrees [11], only limited valence correlation included.

[i] Chou and Huang [12], multiconfiguration relativistic random-phase approximation, with only valence correlation included.

B. Core-valence correlation of 5*d*

The next model is based on the CV_{5d} RAS. We use the same size AS's, and the convergence seems to be good (see Tables II and III). In the first step, CV_{5d}–AS_1 we include all CSF's, and optimize all orbitals outside the $5d$.

When increasing the active set to AS_2 we use first-order, condensation techniques. The zero-order set is defined as all CSF's in CV_{5d}–AS_1 with weight larger than 0.001 and is labeled CV_{5d}–$AS_1(0.001)$. The first-order set consists of the rest of the CSF's in the CV_{5d}–AS_2 set. After the $n=7$ orbitals are optimized, we condense the set to 0.000 05. As a test, for future references, we compare this to an "uncondensed" calculation and find that the condensation changes the interesting properties by less than one per thousand.

To represent the CV_{5d}–AS_3 space, which consists of 9297 CSF's, we start with a zero-order set of CV_{5d}–$AS_2(0.01)$. After performing first-order calculations, the set is condensed to only include CSF's with weights larger than 0.0001. This is compared to an approach with the same condensation as for the AS_2 set, 0.000 05. The change in gf values and hyperfine parameters is much smaller than 1%. We therefore conclude that the 0.0001 level is an appropriate condensation.

This final set, which could be labeled CV_{5d}–$AS_3(0.0001)$, is used to represent the core-valence correlation of $5d$, and is our approximation of the full CV_{5d} RAS.

C. Core-valence correlation of inner subshells

The next step is to include an approximation of the core-valence correlation of inner subshells. Based on the experiences gained in the calculations for Sc II and Y II [19] we will represent this by only including the part of the full CV RAS that is obtained by single excitations from the three main CSF's.

We start with an approximation for the $CV_{5d}\cup CV_{5s}$ RAS, by using the CV_{5d}–$AS_2(0.01)$ as a zero-order set. We include all CSF's belonging to the CV_{5d}–$AS_3(0.0001)$, together with the ones in CV_{5s} obtained by single substitutions from the three main CSF's, to the set of orbitals defined by

$$AS_4 = AS_3 + \{9s,9p,9d\} \tag{14}$$

and the new $n=9$ orbitals are optimized. After condensing the CSF set to 0.0001 we do a full CI on the remaining CSF's.

A similar model is used to include core-valence correlation of $5p$. To the set of CSF's already used, we add CSF's obtained from single substitions from the valence and $5p$ subshells to the AS_4 set. The $n=9$ orbitals are reoptimized, in a first-order calculation using the same zero-order set as for the $5s$ core-valence calculation. After condensation to 0.0001 a CI calculation gives us our representation of the subspace $\mathrm{CV}_{5d} \cup \mathrm{CV}_{5s} \cup \mathrm{CV}_{5p}$.

For subshells inside the $n=5$ shell, we use the same philosophy, adding the single substitution CSF's from, in turn, $4f$, $4d$, $4s$, and $1s$. The estimated contributions from the different subshells are all given in Table I. For the s shells we add a set of $10s, 10p$, and $10d$ to the AS_4 active set, while for the d and f shells we use an active set of

$$\mathrm{AS}_5 = \mathrm{AS}_4 + \{10s, 10p, 10d, 6f, 6g, 6h\}. \tag{15}$$

Again we use the same zero-order set, $\mathrm{CV}_{5d-}\mathrm{AS}_2(0.01)$, and perform a first-order calculation. The results from the different first-order calculations are given in Table I, as estimates of the contribution to the total hyperfine-structure parameters from different types of correlations. It is clear that core-valence correlation contributes significantly to the A parameters all the way down to the $4f$ subshell. The contributions from $4d$, $1s$, and $4s$ are negligible, however. Since these three subshells define the extreme n and l quantum numbers of the remaining subshells, below $4f$, it seems fair to assume that the rest of the inner subshells does not contribute (that is all with $n=1$, 2, and 3, and the $n=4$ ones, except for $4f$).

The results from full order calculations, as described above, are given in Table II for hyperfine structure parameters, and Table III for oscillator strengths. In both cases the results agree very well with recent experiments. From Table III it is also clear that the oscillator strengths are virtually not affected at all by any correlation below the $5d$ subshell.

D. Breit interaction

So far we have only used the Dirac-Coulomb operator to define our method. To investigate the corrections to this, in the form of the zero-frequency limit of the Breit interaction, we included this operator in a final CI calculation. The effect on the hyperfine-structure parameters and oscillator strengths was less than 0.5%. We will therefore ignore the effect of corrections to the Dirac-Coulomb approach for the rest of this paper.

We will return to a discussion of the results for Tl II after we have described the calculations for Tl III.

IV. CORE-VALENCE CORRELATION IN TL III

Tl III is considerably simpler than Tl II to treat with the types of methods described here. The three levels of interest are again usually denoted by LS designations in the literature

$$6s^2\,{}^2S_{1/2}, \quad 6p\,{}^2P_{1/2}, \quad 6p\,{}^2P_{3/2}. \tag{16}$$

TABLE IV. Tl III: Hyperfine-structure parameter, in 10^{-3} cm^{-1} (=29.979 25 MHz), for the $6s\,{}^2P_{1/2}$, $6p\,{}^2P_{1/2}$, and ${}^2P_{3/2}$ levels of Tl III. Results from models including only valence and core valence correlation.

Model[a]	Active set[a]	Hyperfine parameter, A ${}^2S_{1/2}$	${}^2P_{1/2}$	${}^2P_{3/2}$
DF		5286	1045	88.19
CV_{5d}	AS_1	5295	1134	109.61
	AS_2	5586	1101	97.80
	AS_3	5571	1128	99.24
	AS_4	5595	1121	98.63
	$\mathrm{AS}_{4'}$	5632	1129	98.43
$\cup\mathrm{CV}_{5s}$	AS_4	5855	1115	104.37
$\cup\mathrm{CV}_{5p}$	AS_4	5935	1181	109.04
$\cup\mathrm{CV}_{4f}$	AS_5	6104	1226	111.38
Experiment				
JR[b]		6060	1630	160

[a] See text.

[b] "Suggested tentative values," Joshi and Raassen [22].

In a one-electron system like this, there is no valence correlation, and the first correction to our "Dirac-Fock" approach is core-valence correlation. The number of CSF's is therefore reduced substantially, and we do not need to apply the same limitations to the generations as we did for Tl II.

We will use the experience gained from the calculations for Tl II, and include core-valence correlation of the $n=5$ and $4f$ subshells, but assume that all others do not contribute.

A. Core-valence correlation of 5*d*

Due to the lesser complexity of Tl III, we do not need to use any first-order and condensation techniques to represent core-valence correlation of the $5d$ subshell. We use four different active sets, $\mathrm{AS}_n, n=1,2,3,4$, defined as for Tl II. The results are given in Tables IV and V, where it is clear that the change from $\mathrm{CV}_{5d-}\mathrm{AS}_3$ to $\mathrm{CV}_{5d-}\mathrm{AS}_4$ is less than 1%. We will therefore use the former to represent the CV_{5d} RAS.

It might seem as a serious limitation of our models that only one orbital is included for each $l \geqslant 3$. We therefore investigate this restriction, by using the model $\mathrm{CV}_{5d-}\mathrm{AS}_{4'}$, where

$$\mathrm{AS}_{4'} = \mathrm{AS}_4 + \{6f, 6g\}. \tag{17}$$

As can be seen in Tables IV and V the resulting change in all properties of interest is much less than 1%, the only exception being the velocity (Coulomb) form of the oscillator strength. This form is only used as an accuracy test of our calculations, however, as we will discuss in the Conclusion. This supports the assumption that one high-l orbital, of each symmetry, is enough.

It is clear from the discussion above that it is sufficient to use the AS_3 active set to represent the core-valence correlation of $5d$, so for the rest of the calculations we use $\mathrm{CV}_{5d-}\mathrm{AS}_3$ as our representation of the CV_{5d} RAS.

TABLE V. Tl III: Wavelengths in angstroms and oscillator strengths in Babushkin/length (gf_l) and Coulomb/velocity (gf_v) form [5], for the $6s^2S_{1/2}$-$6p^2P_{1/2}$ and $6s^2S_{1/2}$-$6p^2P_{3/2}$ transitions in Tl III. Results from models including only valence and core-valence correlation.

		$^2S_{1/2}$-$^2P_{1/2}$			$^2S_{1/2}$-$^2P_{3/2}$		
Model[a]	Active set[a]	λ	gf_l/gf_v	gf[b]	λ	gf_l/gf_v	gf[b]
Present							
DF		1637	0.751/0.716	0.789	1339	1.792/1.693	1.895
CV_{5d}	AS_1	1629	0.400/0.473	0.418	1317	1.026/1.199	1.060
	AS_2	1558	0.401/0.474	0.401	1266	1.019/1.182	1.019
	AS_3	1557	0.400/0.477	0.399	1265	1.013/1.189	1.012
	AS_4	1557	0.399/0.477	0.398	1264	1.011/1.189	1.010
	$AS_{4'}$	1556	0.402/0.483	0.401	1263	1.015/1.202	1.013
$\cup CV_{5s}$	AS_4	1556	0.399/0.474	0.398	1263	1.011/1.190	1.009
$\cup CV_{5p}$	AS_4	1542	0.391/0.484	0.387	1251	0.989/1.190	0.977
$\cup CV_{4f}$	AS_5	1530	0.385/0.495	0.378	1240	0.977/1.216	0.957
Experiment							
JR[c]		1559			1266		
BFS[d]							1.28±0.14
Other theories							
RHF-CP[e]				0.362			0.944

[a] See text.

[b] Recommended gf value, computed using gf_l and experimental λ.

[c] Joshi and Raassen [22], classical spectroscopy, $\lambda\lambda = 1558.828, 1558.670$ and $\lambda\lambda = 1266.288, 1266.194$.

[d] Andersen *et al.* [21], Beam-foil spectroscopy, from lifetime of $^2P_{3/2}$ (0.75±0.08 ns).

[e] Migdalek and Baylis [10], relativistic Hartree-Fock, using core-polarization potentials.

B. Core-valence correlation of the 5*s* and 5*p* subshells

We use all CSF's based on the active set AS_4, to represent the CV_{5s} RAS. The $n=9$ orbitals are optimized in a model including the CSF-space $CV_{5d-}AS_3 \cup CV_{5s-}AS_4$.

For the core-valence correlation of $5p$ we use the $CV_{5d-}AS_3 \cup CV_{5s-}AS_4 \cup CV_{5p-}AS_4$, and reoptimize the $n=9$ orbitals. The results for these models are also given in Tables IV and V.

It might be a matter of concern that while we performed a systematic calculation for CV_{5d}, increasing the size of the active set step by step, we only optimize one extra set on the $5s$ and $5p$. This makes it hard to estimate any convergence in the results. To investigate the uncertainties, we therefore perform a separate calculation, labeled CV_{5spd}, where from the beginning we use the RAS $CV_{5d} \cup CV_{5s} \cup CV_{5p}$. The active set is stepwise increased up to AS_4, and the results are given in Table VI. It is obvious that the difference between this model and the one in Tables IV and V is negligible, and the "single orbital set" approach for core-valence correlation of $5s$ and $5p$ is a good approximation.

C. Core-valence correlation of the 4*f* subshell

Just as for Tl II, we use the active set AS_5 to include the core-valence correlation of the $4f$ subshell. This time we include all CSF's in the set $CV_{5d-}AS_3 \cup CV_{5s-}AS_4 \cup$

TABLE VI. Tl III: Results from the alternative CV_{5spd} model, as described in the text, for the same properties as in Tables IV and V.

		hyperfine A			$6s^2S_{1/2}$-$6p^2P_{1/2}$		$6s^2S_{1/2}$-$6p^2P_{3/2}$	
Model[a]	Active set[a]	$^2S_{1/2}$	$^2P_{1/2}$	$^2P_{3/2}$	λ	gf_l/gf_v	λ	gf_l/gf_v
Present								
CV_{5spd} [b]	AS_1	5321	1144	104.6	1624	0.394/0.480	1313	1.007/1.186
	AS_2	5790	1134	108.1	1546	0.394/0.481	1255	0.999/1.178
	AS_3	5880	1183	113.5	1542	0.392/0.483	1251	0.993/1.189
	AS_4	5941	1181	109.5	1541	0.391/0.484	1250	0.990/1.190
From Tables IV and V								
$\ldots \cup CV_{5p}$ [c]	AS_4	5935	1181	109.04	1542	0.391/0.484	1251	0.989/1.190

[a] See text.

[b] This implies that $CV_{5d} \cup CV_{5s} \cup CV_{5p}$ is used all through the calculations.

[c] This implies the $CV_{5d\_}AS_3 \cup CV_{5p\_}AS_4 \cup CV_{5s\_}AS_4$ model, as described in the text.

TABLE VII. Tl III: Hyperfine-structure parameters (in cm^{-1}) from models including core-core correlation in the $5d$ subshell for Tl III.

Model[a]	Active set[a]	hyperfine A $^2S_{1/2}$	$^2P_{1/2}$	$^2P_{3/2}$
Present				
DF		5286	1045	88.19
CC_{5d}	AS_1	5573	1210	106.74
	AS_2	5590	1132	97.40
	AS_3	5607	1148	97.77
	AS_4	5611	1144	97.73
$\cup\mathrm{CV}_{5s}\cup\mathrm{CV}_{5p}$	AS_4	5915	1185	108.98
$\cup\mathrm{CV}_{4f}$	AS_5	6068	1216	113.18
+triple excitations[b]		6064	1215	113.21
From Table IV[c]				
$\ldots\cup\mathrm{CV}_{4f}$	AS_5	6104	1226	111.38
Experiment				
JR[d]		6060	1630	160

[a] See text.
[b] Including triple excitations to AS_1.
[c] Only including core-valence correlation.
[d] Joshi and Raassen [22].

$\mathrm{CV}_{5p}-\mathrm{AS}_4\cup\mathrm{CV}_{4f}-\mathrm{AS}_5$, and optimize the $10s$, $10p$, $10d$, $6f$, and $6g$ orbitals. The results are again given in Tables IV and V.

It is clear that there are similarities between Tl II and Tl III. The effect on oscillator strengths for inner subshells are minor [about (1–2)%], while the effect on the hyperfine-structure parameter is much larger [(8–13)%]. We will return to a more general discussion of this in the Conclusion section.

We have so far concentrated on the core-valence correlation effect. The next step would be to include also correlation within the core. We will here investigate one such model, for Tl III, including the core-core correlation of $5d$.

V. CORE-CORE CORRELATION IN Tl III

Including core-core correlation increases the complexity of the model substantially. We do not only open up two holes in the core, but we also increase the number of "outer" electrons by two compared to the VC model. We will only attempt to construct a model that includes the correlation within the $5d$ subshell, and assume that the rest of the subshells do not contribute substantially.

In earlier work, using the MCHF method, we have developed a model that we labeled CCP [23] and similar methods were used for intercombination lines in small systems [24,25]. In this we recognize the fact that the most important effect of including core-core correlation is indirect. We therefore only include the core-core correlation in the first step, and then concentrate on the more important core-valence correlation. For Tl III this approach implies that we include CSF's with $5d^8$ core when using the AS_1 active set, by allowing single and double excitations from the three main CSF's to AS_1. This is our representation of $\mathrm{CC}_{5d}-\mathrm{AS}_1$. After that we use the union of this space and the $\mathrm{CV}_{5d}-\mathrm{AS}_n$, $n=2,3$. We also include the core-valence correlation of inner core subshells, by including the $\mathrm{CV}_{5s}-\mathrm{AS}_4\cup\mathrm{CV}_{5p}-\mathrm{AS}_4$ set, and finally the $\mathrm{CV}_{4f}-\mathrm{AS}_5$, as for the core-valence correlation model above. The results are given in Table VII for hyperfine-structure parameters and Table VIII for oscillator strengths.

To improve our CCP model, where core-core correlation is only included in a very restricted way, we finally perform a CI calculations where we use the same orbitals, but include the full set $\mathrm{CC}_{5d}-\mathrm{AS}_1$, that is we allow for triple excitations to the AS_1 active set. The difference in the results is very small for the hyperfine-structure parameters, and about 1.5% for oscillator strengths.

It is clear from a comparison of Tables VII and VIII, with Tables IV and V that the effect of including core-core correlation is small for hyperfine-structure parameters [about (0.5–1)%]. The oscillator strength changes by almost 30%, however, and the agreement between the two forms is im-

TABLE VIII. Tl III: Wavelengths in angstroms and oscillator strengths in Babushkin/length (gf_l) and Coulomb/velocity (gf_v) form [5], for transitions in Tl III, from models including core-core correlation of the $5d$ subshell.

Model[a]	Active set[a]	$^2S_{1/2}$-$^2P_{1/2}$ λ	gf_l/gf_v	gf[b]	$^2S_{1/2}$-$^2P_{3/2}$ λ	gf_l/gf_v	gf[b]
Present							
DF		1637	0.751/0.716	0.789	1339	1.792/1.693	1.895
CC_{5d}	AS_1	1618	0.518/0.550	0.538	1319	1.285/1.415	1.339
	AS_2	1570	0.525/0.546	0.529	1283	1.292/1.367	1.309
	AS_3	1569	0.525/0.548	0.528	1282	1.293/1.372	1.309
	AS_4	1568	0.525/0.548	0.528	1281	1.292/1.370	1.308
$\cup\mathrm{CV}_{5s}\cup\mathrm{CV}_{5s}$	AS_4	1552	0.518/0.551	0.516	1267	1.275/1.365	1.268
$\cup\mathrm{CV}_{4f}$	AS_5	1540	0.512/0.555	0.506	1256	1.264/1.377	1.254
+ triple excitations[c]		1539	0.505/0.553	0.499	1255	1.247/1.370	1.236
From Table IV[d]							
$\ldots\cup\mathrm{CV}_{4f}$	AS_5	1530	0.385/0.495	0.378	1240	0.977/1.216	0.957

[a] See text.
[b] Recommended gf value, computed using gf_l and experimental λ.
[c] Including triple excitations to AS_1.
[d] Only including core-valence correlation.

TABLE IX. Summary of results for Tl II and Tl III, from different models. Hyperfine structure, *A* parameter, in 10^{-3} cm^{-1}.

	A parameters				
	Tl III			Tl II	
Model[a]	$^2S_{1/2}$	$^2P_{1/2}$	$^2P_{3/2}$	$^3P_1$	$^1P_1$
DF	5286	1045	88.2	2065	−346
VC				2079	−413
CV_{5d}	5571	1128	99.2	2352	−607
$\cup\mathrm{CV}_{5s}$	5855	1115	104.4	2437	−637
$\cup\mathrm{CV}_{5p}$	5935	1181	109.0	2444	−644
$\cup\mathrm{CV}_{4f}$	6104	1226	111.4	2433	−638
$\cup\mathrm{CC}_{5d}$	6064	1215	113.2		
Expt.	(6060)[a]	(1630)[a]	(160)[a]	2469 ± 1[b]	-648 ± 6[b]

[a] Joshi and Raassen [22].

[b] Johansson *et al.* [3].

proved substantially. The final value for the $^2S_{1/2}$-$^2P_{3/2}$ transition is in excellent agreement with the experimental result of Andersen, Kirkegård Nielsen, and Sorensen [21].

VI. CORE-CORE CORRELATION FOR Tl II

The inclusion of core-core correlation in Tl II is a formidable task. We have started an attempt to include these CSF's, but in this paper we will only report on preliminary results. By again using a CCP model, allowing for single and double substitutions from the main CSF's to the AS_1, and then including the $\mathrm{CV}_{5d-}\mathrm{AS}_{2,3}$ RAS we find that the resulting oscillator strengths for the resonance transition ($6s^{2}\,{}^1S_0$-$6s6p\,{}^1P_1$) increase by 30%, compared to the corresponding model with only core-valence correlation included. At the same time, the results for the length form of the oscillator strength for the intercombination line ($6s^2\ {}^1S_0$-$6s6p\,{}^3P_1$) hardly change at all. Again, the agreement between length and velocity forms improved substantially for both transitions. This suggests that the final oscillator strengths in Table III should be increased for the resonance line, $6s^2\ {}^1S_0$-$6s6p\,{}^1P_1$ to 1.82, while the intercombination line is almost unchanged (possibly reduced by 0.001 to 0.0441). It is interesting to observe that the "intercombination transition," which is weak and exhibits major cancellations in the transition matrix element, is much more stable when we change our model, while the resonance transition seems to be very much affected by the core-core correlation.

VII. CONCLUSIONS

The aim of this paper was to investigate the dependence of different properties on different types of correlations. We summarize our results in Tables IX and X. If we start by looking at the hyperfine-structure parameters, we observe, for Tl II, that models that only include core-valence correlation represent the hyperfine structure very satisfactorily and are in excellent agreement with recent experiments (to within a few percent). To obtain this we needed to include correlation with subshells as deep as $4f$.

For Tl III no accurate experimental hyperfine-structure splitting is available, but only measurements where the line width is larger than the hyperfine structure splitting [22]. The fitted values for the A parameters, using these spectra, are probably only reliable for the ground level, $6s\ {}^2S_{1/2}$. The trend in our calculations for this is similar as for Tl II, and the result after including the $4f$ core-valence correlation is in agreement with the experiment.

For Tl III we also showed that the inclusion of core-core correlation had virtually no effect on the computed hyperfine structure parameters. This is very encouraging for future calculations, since it implies that core-valence correlation is sufficient for an accurate treatment of hyperfine structure.

The results are less encouraging for oscillator strengths. It is true that we do see only limited contributions from deeper subshells, and only need to worry about the correlation with and within the outermost $5d$ core subshell (as long as we do not aim for an accuracy better than a few percent). But the result from our core-valence correlation models shows a disturbing discrepancy (ranging from 15% to almost 30% for the transitions considered here) between results using the length and velocity form of the transition operator. The situation is drastically improved when including core-core correlation (to less than 10%), and the gf value for the transi-

TABLE X. Oscillator strengths in Babushkin/length (gf_l) and Coulomb/velocity (gf_v) form, and the recommended value.

	Tl III				Tl II			
	$^2S_{1/2}$-$^2P_{1/2}$		$^2S_{1/2}$-$^2P_{3/2}$		$^1S_0$-$^3P_1$		$^1S_0$-$^1P_1$	
Model[a]	gf_l/gf_v	gf[b]	gf_l/gf_v	gf[b]	gf_l/gf_v	gf[b]	gf_l/gf_v	gf[b]
DF	0.751/0.716	0.789	1.792/1.693	1.895	0.0452/0.0322	0.0566	2.625/1.985	2.768
VC					0.0405/0.0416	0.0456	2.306/2.178	2.379
CV_{5d}	0.400/0.477	0.399	1.013/1.189	1.012	0.0448/0.0553	0.0448	1.380/1.611	1.378
$\cup\mathrm{CV}_{5s}$	0.399/0.484	0.398	1.011/1.190	1.009	0.0449/0.0574	0.0449	1.374/1.601	1.374
$\cup\mathrm{CV}_{5p}$	0.391/0.484	0.387	0.989/1.190	0.977	0.0450/0.0579	0.0452	1.365/1.594	1.370
$\cup\mathrm{CV}_{4f}$	0.385/0.495	0.378	0.977/1.216	0.957	0.0449/0.0579	0.0451	1.364/1.594	1.369
$\cup\mathrm{CC}_{5d}$	0.505/0.553	0.499	1.247/1.370	1.236				
Expt.[c]				1.28 ± 0.14				1.21 ± 0.20

[a] See text.

[b] Recommended gf value, computed using gf_l and experimental λ.

[c] Beam-foil spectroscopy, Andersen *et al.* [21].

tion involving ${}^2P_{3/2}$ is brought into agreement with experiment, but at a high cost. Opening up two holes in the $5d$ core subshell increases the number of CSF's dramatically. Our results imply, however, that such a model is necessary, and further improvement of the core-core correlation model for Tl II is in progress.

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