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Ab initio calculations of the $^2P_{\frac{1}{2}}$-$^2P_{\frac{3}{2}}$ splitting in the thallium atom

Ulf Wahlgren[2], Merethe Sjøvoll[1], Hilde Fagerli[1], Odd Gropen[1], Bernd Schimmelpfennig[2]

[1] Institute of Mathematical and Physical Science, University of Tromsø, N-9037 Tromsø, Norway
[2] Institute of Physics, Stockholm University, P.O. Box 6730, S-11385 Stockholm, Sweden

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Abstract. The splitting between the $^2P_{\frac{3}{2}}$ and the $^2P_{\frac{1}{2}}$ terms in the thallium atom has been calculated at the perturbation theory level and by spin-orbit CI calculations, using both the Breit-Pauli and the no-pair form of the microscopic spin-orbit Hamiltonian. The importance of the spin-other-orbit contribution to the spin-orbit splitting is investigated, and it is also shown that an averaging procedure of the kinematic factors in the expression for the spin-other-orbit integrals in the no-pair spin-orbit Hamiltonian yields highly accurate results. A slightly modified version of a previously proposed mean-field spin-orbit method is shown to have an accuracy of a few wave numbers. Perturbation theory is found to give a term-splitting which is too low by more than 1000 cm^{-1}, while spin-orbit CI with the no-pair form of the spin-orbit operator with the averaged spin-other-orbit term, and the no-pair mean-field operator, gives results in good agreement with experimental data.

Key words: $^2P_{\frac{1}{2}}$-$^2P_{\frac{3}{2}}$ splitting – Thallium atom – Spin-orbit effects

1 Introduction

One of the first studies of the spin-orbit effect in TlH was done by Pitzer [1] in 1975. Pitzer pointed out that due to the admixture of π character in the $P_{\frac{1}{2}}$ spinor the Tl—H bond is weakened considerably compared to the usual σ bond in the LS picture. The TlH problem was further studied by Pyper [2], Pitzer and Christiansen [3], and Christiansen et al. [4]. In Ref. [4] a spin-orbit splitting in Tl of 7400 cm^{-1} was obtained at the ECP level using the spin-orbit approach suggested by Ermler [5] and a singles and doubles CI from the 6s and 6p shells.

Several calculations of the $^2P_{\frac{1}{2}}$-$^2P_{\frac{3}{2}}$ splitting have been reported recently in the literature. Using the spin-orbit RECP method of Ermler et al. [5] Ross et al. obtained an SCF value of 7324 [6] and in a later study 7424 cm^{-1} [7]. Balasubramanian and Tao [8] obtained 6930 cm^{-1} at the RECP-CI level, and Li et al. [9] 6457 cm^{-1} in a perturbation calculation using RECPs and MRD-CI wave functions. Küchle et al. report values of 7383 cm^{-1} at the HF-RECP level and 7397 cm^{-1} using a two-component approach [10]. Desclaux has reported a DF splitting of 7693 cm^{-1} [11]. The experimental value in 7793 cm^{-1} [12]. In his thesis, Rakowitz [13] investigated the spin-orbit effects in the Tl atom using the full microscopic no-pair spin-orbit Hamiltonian and four-component calculations. At the perturbation level he obtained results in the range of 6100–6500 cm^{-1}. At the four-component SCF level he obtained a value of 7640 cm^{-1}, which is in agreement with experimental results and with results previously reported by Desclaux. However, with a small four-component CI calculation, using averaged valence orbitals, Rakowitz obtained a lowering of the splitting of 800 cm^{-1}, which is in agreement with the previous two-component perturbation theory results. Shortly thereafter Rakowitz and Marian obtained a splitting which agreed with experimental data from a similar four-component CI using completely optimized valence orbitals [14]. The reason for the failure of the perturbation method in the case of Tl is the different shapes of the two spin-orbit split atom p orbitals (spinors); Desclaux has reported $r_{\max}$ values for the atomic spinors $P_{\frac{3}{2}}$ and $P_{\frac{1}{2}}$ of 3.2 and 2.8, respectively [15].

The complications arising from the differences in radial extension of the atomic p-type spinors, such as the failure of perturbation theory methods, make Tl ideally suited as a test system for spin-orbit CI methods.

Calculations of fine-structure splittings can be done using either the full microscopic spin-orbit Hamiltonian or simpler operators such as projection-type operators used in RECP calculations.

The simplest of the full microscopic spin-orbit Hamiltonians is the Breit-Pauli operator. The Breit-Pauli operator is obtained from an approximate decoupling of the Dirac equation in the presence of external fields. The Foldy-Wouthuysen transformation yields

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Correspondence to: U. Wahlgren

highly singular operators and the Breit-Pauli operator suffers from the same type of variational instabilities as the spin-free first-order perturbation operators (the mass-velocity and Darwin terms).

A variationally stable spin-orbit Hamiltonian is obtained from a full blocking of the Dirac equation in the absence of external fields. The results, the no-pair form of the Breit-Pauli operator (below simply called the no-pair SO operator), differs from the original Breit-Pauli operator by the occurrence of p-dependent multiplicative factors. These kinematic factors remove the r^{-3} dependence close to the origin, but make the operator considerably more difficult to handle.

The no-pair spin-orbit operator contains, just like the Breit-Pauli Hamiltonian, two types of two-electron operators: the spin-same-orbit (SSO) operator and the spin-other-orbit (SOO) operator. While the kinematic factors enter in a symmetric way in the SSO operator and therefore are reasonably easy to handle the asymmetric form of the SOO operator complicates the situation. It is therefore desirable to simplify the expression for the SOO operator.

Albeit simpler than the no-pair spin-orbit operator the Breit-Pauli operator is still quite difficult to use, e.g. the number of integrals becomes very large since there are three distinct operators (of the general type $s_x l_x$, $s_y l_y$ and $s_z l_z$) and there is a loss of symmetry due to the half-integer spin. Recently, a mean-field approach, involving Fock-like spin-orbit operators and a one-centre approximation for the two-electron spin-orbit operators has been suggested. We have used a simplified form of the mean-field operator in Ref. [16] where all orbitals and integrals used in the calculations are strictly atomic.

In the present study we have calculated the fine-structure splitting between the $^2P_{\frac{1}{2}}$ and $^2P_{\frac{3}{2}}$ states of the Tl atom using a simplified form of the no-pair spin-orbit Hamiltonian with an averaged SOO operator, the Breit-Pauli Hamiltonian and the mean-field Hamiltonian with full account of the SOO integrals. The calculations were done both at the perturbation theory and spin-orbit CI levels.

The results show that while the Breit-Pauli operators give too large splittings both the no-pair spin orbit operator with only SSO terms and with an approximate treatment of the SOO integrals give results in good agreement with experimental values at the spin-orbit CI level. Our perturbation theory results are in agreement with previously published results, i.e. too low by more than 1000 cm^{-1}. Furthermore, we show that the mean-field approximation, in its completely atomic form, give results in excellent agreement with the full microscopic spin-orbit Hamiltonian.

2 Theory

This section is divided into three parts: the term energies, the full microscopic spin-orbit Hamiltonian and the mean-field spin-orbit operator.

2.1 The term energies

The two basic methods to calculate the term energies are perturbation theory [17–20] or by solving the spin-orbit CI problem [21–24].

The starting point for perturbation calculations is a limited set of LS-coupled wave functions generated at the spin-free level. A spin-orbit Hamiltonian matrix is calculated in this basis, and the term energies are obtained by diagonalization. The quality of the results clearly depends on the quality of the basis used. An LS-coupled basis is normally generated from large spin-free relativistic CI calculations.

Perturbation methods work well if the molecular orbitals (or molecular spinors) are not changed appreciably by the spin-orbit interaction. This is normally the case for lighter elements and also for transition metals where the spin-orbit splitting originates from the d-shells. In cases where the molecular orbitals change significantly other methods must be used.

One possibility is certainly to solve the Fock-Dirac equation, at the SCF, or to include the spin-orbit operator already in a two-component SCF procedure (a subsequent CI should of course be done in both cases). One can also solve the spin-orbit CI problem in a relativistic spin-free many-electron basis.

In spin-orbit CI calculations the orbital basis will often not be optimal for the state under study: the different multiplets may be described by orbitals (spinors) with significantly different radial extents, or low-lying states which do not interact with the ground state in the LS scheme may become important in the reference state due to strong spin-orbit interactions. This problem can certainly be overcome by making a triples or quadruples CI, but this would be an expensive procedure. A simpler route is to use the multireference CI procedure and to make a careful selection of the orbitals used for the CI expansion.

In the present study term energies have been calculated using both perturbation theory in a space spanned by the sp or the spd manifold of LS-coupled states, and by a multireference spin-orbit CI procedure [25].

2.2 The microscopic spin-orbit Hamiltonian

Several strategies have been pursued for evaluating spin-orbit matrix elements. In the simplest approaches a model spin-orbit Hamiltonian is extracted from the difference potential for $l+1/2$ and $l-1/2$ orbitals obtained from atomic Dirac-Fock [5, 26] or Wood-Boring calculations [27]. Another possibility is to employ an effective one-electron, one-centre spin-orbit operator

$$\mathscr{H}^{\mathrm{eff}}_{\mathrm{SO}} = \frac{1}{2c^2}\sum_i \sum_\alpha \frac{Z^{\mathrm{eff}}_\alpha}{r^3_{\alpha i_\alpha}} \vec{l}_{\alpha i_\alpha} \vec{s}_{i_\alpha} \ . \tag{1}$$

In this operator the effective nuclear charge Z^{eff}_α is parametrized to fit experimental fine-structure splittings of one or several specific states on atom α.

The most rigorous approach is to use a full microscopic spin-orbit Hamiltonian, which is obtained from a transformation of the many-electron Dirac-Breit equation to a two-component form. However, such a transformation cannot be done exactly except for the non-interacting electron case (or more precisely in the absence of a scalar potential), and approximative transformation methods must be used.

Two different microscopic spin-orbit Hamiltonians have been considered in the present study, the Breit-Pauli operator [28] and the no-pair spin-orbit operator obtained by the free-particle Foldy-Wouthuysen transformation [29, 30, 24].

The Breit-Pauli spin-orbit Hamiltonian has the following form:

$$\mathscr{H}^{\mathrm{SO}}\mathrm{BP} = \frac{e^2\hbar}{2m^2c^2}\left\{\sum_i\sum_\alpha Z_\alpha i\left(\frac{\vec{r}_{i\alpha}}{r_{i\alpha}^3}\times\vec{p}_i\right) - \sum_{i\neq j}\left(\frac{\vec{r}_{ij}}{r_{ij}^3}\times\vec{p}_i\right)\cdot\left(\vec{s}_i+2\vec{s}_j\right)\right\} , \tag{2}$$

and the no-pair Hamiltonian can be written as:

$$\mathscr{H}^{\mathrm{SO}}_{\mathrm{NP}} = \frac{e^2\hbar}{2m^2c^2}\times\left\{\sum_i\sum_\alpha Z_\alpha\frac{A_i}{E_i+m}\vec{s}_i\left(\frac{\vec{r}_{i\alpha}}{r_{i\alpha}^3}\times\vec{p}_i\right)\frac{A_i}{E_i+m} - \sum_{i\neq j}\left(Q_{ij}^i\left(\frac{ij}{r_{ij}^3}\times\vec{p}_i\right)\cdot\vec{s}_iQ_{ij}^i + Q_{ij}^i\left(\frac{\vec{r}_{ij}}{r_{ij}^3}\times\vec{p}_i\right)\cdot 2\vec{s}_jQ_{ij}^j\right)\right\} , \tag{3}$$

where $Q_{ij}^i = \frac{A_iA_j}{E_i+m}$, $Q_{ij}^j = \frac{A_iA_j}{E_j+m}$, $A_i = \sqrt{\frac{E_i+m}{2E_i}}$ and $E_i = \sqrt{p_i^2+m^2}$ [24].

The Breit-Pauli Hamiltonian and the no-pair Hamiltonian differ by the presence of kinematic factors bracketing the microscopic one- and two-electron operators in the no-pair operator; the role of the kinematic factors is to dampen the interactions at small r. Neither Eq. (2) nor Eq. (3) is symmetric in the electron indices i and j.

The effect of the two-electron term is to screen the nucleus, and the one- and two-electron contributions to the spin-orbit splitting are of opposite sign. Since the effect of the kinematic factors is to dampen the interactions at small r, the no-pair spin-orbit Hamiltonian will in general give a smaller spin-orbit splitting than the Breit-Pauli Hamiltonian.

The first term in the two-electron part of the SO-Hamiltonian describes the SSO interaction and the second term the SOO interaction [30]. The SSO term arises in the transformation of the Dirac-Coulomb operator [31], while the SOO interaction stems from the Breit term in the Dirac-Coulomb-Breit operator [31].

Unfortunately, the kinematic factors appearing in the two-electron part of Eq. (3) do not enter symmetrically in the SSO and SOO operators. The effect of this asymmetry makes it difficult to calculate the SSO and SOO integrals at the same time (unless the primitive integrals are stored on disk in an intermediate step). If, on the other hand, the kinematic factors in the two-electron part of $\mathscr{H}^{\mathrm{SO}}_{\mathrm{NP}}$ (Eq. 3) can be modified such that the term can be rewritten as

$$\sum_{i\neq j} Q_{ij}^x\left(\frac{\vec{r}_{ij}}{r_{ij}^3}\times\vec{p}_i\right)\cdot(\vec{s}_i+2\vec{s}_j)Q_{ij}^y , \tag{4}$$

only one set of integrals need to be calculated. It can be further shown that in a local approximation the effect of the kinematic factors can be accounted for simply by modifying the contraction coefficients in the molecular basis set [32].

The two-electron terms contribute about 10–20% to the spin-orbit splitting for the third-row transition elements (but more for the lighter elements due to the $\frac{1}{r^3}$ dependence). Taking into account that the SSO term arises from the Dirac-Coulomb operator and the SOO term from the Breit correction we would expect the SOO term to contribute little to the spin-orbit splitting. In order to simplify the calculations one might consider averaging the kinematic factors in the two-electron operator or simply to drop the SSO term. Since both the SSO and SOO terms describe a screening of the nucleus, one would expect slightly too large spin-orbit splittings if the latter term is omitted.

In the present calculations we have used both the no-pair form of the spin-orbit operator with averaged kinematic factors in the two-electron operator and have dropped the SOO term altogether. The averaging was done by putting all the kinematic factors in the two-electron term equal to $\frac{1}{2}(Q_{ij}^i+Q_{ij}^j)$. Other schemes, such as replacing the rightmost Q_{ij}^j in Eq. (3) with Q_{ij}^i, are also conceivable.

2.3 The mean-field spin-orbit operator

The two-electron spin-orbit integrals contribute to the spin-orbit matrix element between Slater determinants which are singly or doubly excited relative to one another. The matrix element between singly excited determinants can, just like in the Hartree-Fock equations, be written as a pseudo one-electron integral. One of the key aspects of a mean-field theory is to neglect interactions between doubly excited states and to include all two-electron integrals in pseudo one-electron integrals.

A mean-field theory for spin-orbit interactions has recently been published [16], and we will only give a brief outline of the method here.

The matrix element of the spin-orbit operator between a pair of Slater determinants differing by a single valence spin orbital excitation $i \longrightarrow j$ is given by

$$H_{ij}^{\mathrm{SO}} = \langle i|\mathscr{H}^{\mathrm{SO}}(1)|j\rangle + \frac{1}{2}\sum_k n_k\left\{\langle ik|\mathscr{H}^{\mathrm{SO}}(1,2)|jk\rangle - \langle ik|\mathscr{H}^{\mathrm{SO}}(1,2)|kj\rangle - \langle ki|\mathscr{H}^{\mathrm{SO}}(1,2)|jk\rangle\right\} , \tag{5}$$

where n_k denotes the occupancy of orbitals common to the determinants on the left- and right-hand sides. k runs over all occupied spin orbitals common to the two determinants.

The pseudo one-electron operator which gives rise to these matrix elements has the form

$$
\begin{aligned}
H_{ij}^{\mathrm{mf-SO}} = {} & \langle i|\mathscr{H}^{\mathrm{SO}}(1)|j\rangle \\
& + \frac{1}{2}\sum_{M}^{\mathrm{mf-orbs}} occ(M)\Big\{ \langle i(M\alpha)|\mathscr{H}^{\mathrm{SO}}(1,2)|j(M\alpha)\rangle \\
& + \langle i(M\beta)|\mathscr{H}^{\mathrm{SO}}(1,2)|j(M\beta)\rangle \\
& - \langle i(M\alpha)|\mathscr{H}^{\mathrm{SO}}(1,2)|(M\alpha)j\rangle \\
& - \langle i(M\beta)|\mathscr{H}^{\mathrm{SO}}(1,2)|(M\beta)j\rangle \\
& - \langle (M\alpha)i|\mathscr{H}^{\mathrm{SO}}(1,2)|j(M\alpha)\rangle \\
& - \langle (M\beta)i|\mathscr{H}^{\mathrm{SO}}(1,2)|j(M\beta)\rangle \Big\} \;. \qquad (6)
\end{aligned}
$$

In [16] the orbitals $|k>$ were taken from spin-free molecular calculations.

Based on the short-range character of the spin-orbit operator (which is r_{ij}^{-3} at long distances), it was assumed in [16] that all two-electron integrals between basis functions centred on different centres could be neglected. This assumption is necessary in order to make the mean-field method efficient.

An atomic program which calculates all one- and two-electron integrals, including the two-electron SOO integrals, and forms the proper mean-field integrals has recently been written by one of us [33]. In molecular applications this amounts to the somewhat stronger assumption compared to [16] that *all* two-centre integrals can be neglected, and that the orbitals $|k>$ can be taken from atomic calculations. This approximation has been used with success in applications on PtH_2^+ and on NbO. These calculations will be presented in future publications.

In the present work we have carried out mean-field spin-orbit calculations on the thallium atom both at the perturbation theory level and using a spin-orbit CI program [25].

3 Details of the calculation

The spin-orbit calculations were done both as perturbation calculations and as spin-orbit CI calculations. The variational space used in the perturbation calculations consisted of all states generated, by distributing three electrons in the 6*s* and 6*p* shells. The basis vectors were generated by spin-free relativistic multireference SDCI calculations.

We used the Douglas-Kroll no-pair operators [34, 35] to account for relativistic effects at the spin-free level. Molecular spin-free calculated using the Hermit integral code [36], modified to include relativistic one-electron no-pair integrals, and the MCSCF program Sirius [37] was used for the orbital optimization. The program used both for the perturbation and spin-orbit CI calculations was based on a RASCI [38] formalism, extended to enable the inclusion of one- and two-electron spin-orbit terms [25]. The spin-orbit integrals over the full molecular basis set were generated by a modified version of the Hermit integral program [36].

A newly developed atomic program was used for the mean-field spin-orbit integral calculations [33].

All calculations were for practical reasons carried out in the D_{2h} point group. With our choice of coordinate axis the p_x orbital transformed as B_{3u}, p_y as B_{2u} and P_x as B_{1u}. The one-electron basis used in both the perturbation and spin-orbit CI calculations was generated as follows. SCF calculations were carried out on the three (degenerate) states ${}^2P_x$, ${}^2P_y$ and ${}^2P_z$. The orbitals used in the CIs (occupied and virtual) of A_g, B_{1g}, B_{1u} and A_u symmetry were taken from the ${}^2P_z$ state, those of B_{2g} and B_{2u} symmetry from the ${}^2P_y$ state and finally those of B_{1g} and B_{1u} symmetry from the ${}^2P_x$ state. This is the same choice as in Ref. [13].

In the RASCI formalism, reference states are generated by distributing electrons in three subspaces usually labelled RAS1, RAS2 and RAS3. The reference state is generated by all configurations arising from a complete redistribution of the electrons assigned to the RAS1 and RAS2 subspaces, specifying a minimum number of electrons in RAS1. The multireference CI is generated by excitations out of RAS1 and RAS2 (normally all single and double excitations) into virtual space (RAS3).

At the spin-free level our smallest CI calculation, henceforth labelled INT, was a full three-electron CI in the 6*s* and 6*p* orbitals, i.e. a RAS1 space with three electrons in the 6*s* and 6*p* orbitals, no RAS2 space and no excitations into RAS3. At the second level we used INT as the reference space for a full singles and doubles CI (CI3). At the third level all single excitations from the 5*d* shell into the virtual space were added to CI3 (CI3CV), i.e. a RAS1 space with 9–10 electrons in the 5*d* orbitals, a RAS2 space with 1–2 electrons in the 6*s* and 6*p* orbitals and finally a RAS3 space with 0–2 electrons. At the fourth level, CI13(A), the RAS1 space consisted of the 5*d* and 6*s* shells, with an occupation ranging from 10 to 12 electrons, a RAS2 space consisting of the 6*p* orbital with 1–3 electrons and 0–2 electrons in RAS3. Finally, at the highest level, CI13(B), the 5*d* orbitals were used for RAS1 and the 6*s* and 6*p* orbitals for RAS2. The occupations were 8–10 electrons in RAS1, 3–5 electrons in RAS2 and 0–2 electrons in RAS3. The different cases are summarized in Table 1. Our perturbation calculations were carried out in the basis defined by these spin-free CI calculations.

Some special considerations are necessary for the spin-orbit CI. Since the 6*p* orbitals are equivalent at the

Table 1. Notations for various CI spaces

Name	RAS1	RAS2	MINR1	MAXR3	Comment
INT	0	6*s*,6*p*	0	0	Internal CI 3 electrons correlated
CI3	0	6*s*,6*p*	0	2	SDCI for 3 electrons
CI3CV	5*d*	6*s*,6*p*	9	2	Relax *d*-shell by single excitations
CI13(A)	5*d*,6*s*	6*p*	10	2	13 electrons SDCI, 6*s* in RAS1
CI13(B)	5*d*	6*s*,6*p*	8	2	13 electrons SDCI, 6*s* in RAS2

spin-free level but not at the spin-orbit level it is crucial that the spin-orbit CI is able to describe the relaxation of the two 6*p* spinors. In order to assure this property of the spin-orbit CI we have adopted the same approach as in Ref. [14], i.e. to gradually increase the RAS2 space by moving *p*-orbitals from RAS3 to RAS2. The calculations are labelled (*r*), (1*p*), (2*p*) and (3*p*) (*f*) for no *p*-shell, one *p*-shell, two *p*-shells, three *p*-shells and all *p*-shells moved to RAS2.

Spin-orbit calculations, both at the perturbation and the CI levels, were done using the no-pair form of the spin-orbit operator and either averaging kinematic factors to estimate the SOO term (see the method section), or by neglecting it altogether. The importance of the SOO term (and consequently the reliability of the averaged kinematic factor approach) was investigated using the Breit-Pauli operator at the perturbation level with and without the SOO term.

Mean-field spin-orbit perturbation and spin-orbit CI calculations, including the SOO term, were carried out at the CI13B level (see above).

The primitive basis set used for the thallium atom was the 20*s*, 16*p*, 11*d* and 8*f* atomic basis set of Faegri [39]. Two different contractions, both of the Raffenetti type [40], were used. The smaller one consisted of 7*s*, 6*p*, 5*d* and 2*f* contracted functions, corresponding to a full contraction of all the core orbitals, doubly split 6*s* and 6*p* orbitals, a triply split 5*d* orbital and one correlating *f*-function (basis set A), while the larger basis set consisted of 8*s*, 7*p*, 5*d* and 2*f* contracted functions (basis set B). The larger basis set was obtained from the smaller one by decontracting the outermost functions in the valence orbitals.

4 Results and discussion

4.1 Perturbation theory results

Perturbation theory results are shown in Tables 2 and 3. Table 2 contains results obtained with the Breit-Pauli operator and with the no-pair spin-orbit operator with and without the SOO term (but using the averaged kinematic factor approximation in the former case). These calculations were done at the CI3 level using the [7*s*,6*p*,5*d*,2*f*] contracted basis set (basis set A). Table 3 shows results obtained with the no-pair and mean-field spin-orbit operators using the larger [8*s*,7*p*,5*d*,2*f*] contracted basis set (basis set B) and a 13-electron CI (CI13B) together with results from [14].

The spin-orbit splitting obtained with the Breit-Pauli operator is larger than the no-pair splitting by more than 3000 cm^{-1} in all cases. At the same time the Breit-Pauli SSO contribution (316 cm^{-1}) is larger than the no-pair SSO contribution (237 cm^{-1}). The effect of the SOO interaction is 70 cm^{-1} for the Breit-Pauli Hamiltonian and 47 cm^{-1} for the no-pair operator (with averaged kinematic factors) in the CI3 calculations. Assuming the effect of the SOO term to scale like the SSO term, we get an estimate of the no-pair SOO term from the BP SOO result as (70*237/316) = 53 cm^{-1}, a result which supports the averaged kinematic factor approximation. The validity of the approximation is further substantiated when we compare it with the mean-field result. The fine-structure splitting obtained at the CI13 level (i.e. when *d*-correlation is included in the calculation) is 6654 cm^{-1} with our no-pair spin-orbit Hamilton and 6651 cm^{-1} with the mean-field operator (Table 3). Differences of a few cm^{-1} are reported in [16] between splittings obtained using no-pair and mean-field spin-orbit Hamiltonians for some Pt and Pd compounds. The total effect of the SOO term in the mean-field approximation is 50 cm^{-1}, which is in excellent agreement with our no-pair result.

Table 2. Analysis of various contributions to the splitting. Perturbation theory results, energies in cm^{-1}

Operator	Basis set	CI type	$\Delta E(\text{cm}^{-1})$
$\mathscr{H}^{\text{one}}_{\text{NP}}$	A	CI3	6621
$\mathscr{H}^{\text{sso}}_{\text{NP}}$	A	CI3	6384
$\mathscr{H}^{\text{soo}}_{\text{NP}}$	A	CI3	6337
$\mathscr{H}^{\text{soo}}_{\text{NP}}$	B	CI3	6305
$\mathscr{H}^{\text{one}}_{\text{BP}}$	A	CI3	10124
$\mathscr{H}^{\text{sso}}_{\text{BP}}$	A	CI3	9808
$\mathscr{H}^{\text{soo}}_{\text{BP}}$	A	CI3	9738

Table 3. Perturbation theory results, energies in cm^{-1}

Operator	Basis set	CI type	$\Delta E(\text{cm}^{-1})$
$\mathscr{H}^{\text{sso}}_{mf}$	B	CI13(B)	6701
$\mathscr{H}^{\text{soo}}_{mf}$	B	CI13(B)	6654
$\mathscr{H}^{\text{soo}}_{\text{NP}}$	B	CI13(B)	6651
MR[a]		CI3	6221–6224
MR[a]		CI13	6255–6397

[a] Results from Refs. [13, 14]

Compared with the results presented by Rakowitz and Marian, we obtain a larger splitting both at the CI3 and the CI13 levels by more than 100 cm^{-1} and 250 cm^{-1}, respectively. We have used the same basis set and essentially the same orbital set as Rakowitz and Marian, the only difference being that they averaged their orbital basis over the cartesian components prior to the spin-orbit calculations, but this should be of minor importance. There are some differences in the active spaces used, however. Our active space is slightly larger than that used by Rakowitz and Marian at the CI3 level (our reference space, but not that used by Rakowitz and Marian, contains s^1p^2 configurations). This difference becomes even more pronounced in the CI13 calculations where we have, in contrast to Rakowitz, configurations with open *d*-shells in the reference. At least a part of the difference must be due to the different MRCIs used by us and by Rakowitz and Marian.

4.2 Spin-orbit CI results

Our spin-orbit CI results are presented in Tables 4 and 5.

An internal CI in the space spanned by only the 6*s* and the 6*p* orbitals gives the rather reasonable splitting

Table 4. Spin-orbit CI results, basis set *B*. No spin-other-orbit (SOO) term. Energies in cm^{-1}. The calculations are labelled (*r*), (1*p*), (2*p*) and (3*p*) (*f*) for no *p*-shell, one *p*-shell, two *p*-shells, three *p*-shells and all *p*-shells moved to RAS2

Operator	RAS2 type	INT	CI3	CI3CV	CI13(A)	CI13(B)
$\mathscr{H}^{\text{sso}}_{\text{NP}}$	(*r*)	7321	7603	7852	7820	7720
$\mathscr{H}^{\text{sso}}_{\text{NP}}$	(1*p*)	6676	7603	7819	7831	
$\mathscr{H}^{\text{sso}}_{\text{NP}}$	(2*p*)	7108	7604	7824	7909	
$\mathscr{H}^{\text{sso}}_{\text{NP}}$	(3*p*)	7470	7604	7825	7926	
$\mathscr{H}^{\text{sso}}_{\text{NP}}$	(*f*)	7604	7604	7826	7933	
MR[a]	(*r*)[b]		7506		7227	
MR[a]	(*f*)[b]		7519		7672	

[a] Ref. [14], including the spin-other-orbit term

[b] The references used by Rakowitz and Marian are not strictly comparable to ours

Table 5. Spin-orbit CI results, basis set *B*. SOO term included. Energies in cm^{-1}. The calculations are labelled (*r*), (1*p*), (2*p*) and (3*p*) (*f*) for no *p*-shell, one *p*-shell, two *p*-shells, three *p*-shells and all *p*-shells moved to RAS2

Operator	RAS2 type	INT	CI3CV	CI13(B)	CI19
$\mathscr{H}^{\text{soo}}_{\text{NP}}$	(*r*)	7369	7784	7656	
$\mathscr{H}^{\text{soo}}_{\text{NP}}$	(1*p*)	6625	7751		
$\mathscr{H}^{\text{soo}}_{\text{NP}}$	(*f*)	7537	7757		
$\mathscr{H}^{\text{soo}}_{mf}$	(*r*)			7660	
MR[a]	(*r*)[b]			7227	
MR[a]	(*f*)[b]			7672	7796

[a] Ref. [14], including the SOO term

[b] The references used by Rakowitz and Marian are not strictly comparable to ours

of 7321 cm^{-1}. Increasing the RAS2 space by one *p*-shell lowers the splitting by 645 cm^{-1} to 6676 cm^{-1}, making the agreement with experimental data much worse. When we expand the RAS2 space with more *p*-functions the result is gradually improved, reaching the reasonable value of 7604 cm^{-1} when all *p*-orbitals are included in the RAS2 space (it should be recalled that a full CI is performed in the RAS2 space).

At the CI3 level there is virtually no effect from increasing the RAS2 space, and the calculated splitting is the same as that obtained in the INT calculations with the largest reference space. These results can be interpreted as showing that the relaxation of the *p*-orbitals (spinors) is adequately described as soon as single excitations from a reasonable reference state are included in the CI.

Next, we consider the CI3CV results, where the CI3 has been expanded to include single excitations from the *d*-shell. The main difference between the CI3 and CI3CV calculations is that the latter also describe *d*-shell polarization effects. The effect of the *d*-shell polarization is 200–300 cm^{-1} and, not surprisingly, the trend obtained when more *p*-shells are included in RAS2 is the same as for CI3.

In the final step, CI13(B), double excitations from the *d*-shell are included in the CI expansion. The effect is a lowering of the splitting by 130 cm^{-1} relative to the corresponding CI3CV result to 7720 cm^{-1}, which is close to the experimental value of 7796 cm^{-1}.

Separate calculations are represented by CI13(A), where double excitations from the *d*-shell have been included in the CI, but where the 6*s* shell has been moved from RAS2 to RAS1. The CI13(A) results are similar to the CI3CV results, although the effect of increasing the RAS2 space is somewhat larger for CI13(A) than for CI3CV. However, it is a bit surprising that on comparing the results of CI13(B) and CI13(A), the effect of moving the 6*s* shell from RAS2 to RAS1 is as large as 100 cm^{-1}.

Rakowitz and Marian obtain results which are about 100 cm^{-1} lower than our SSO results at the CI3 level. Considering that the effect of the SOO term, which is not included in the results in Table 4, is 50–100 cm^{-1}, our CI3 results are in good agreement with the results of Rakowitz and Marian.

Finally, Table 5 shows results obtained with the full spin-orbit Hamiltonian. Compared with the results in Table 4 we see a constant SOO contribution of about 70–80 cm^{-1}, consistent with our perturbation calculation results. The agreement between the mean-field result (7660 cm^{-1}) and the no-pair result (7656 cm^{-1}) is excellent. At this point we are 137 cm^{-1} below the experimental result of 7793 cm^{-1}.

Rakowitz and Marian obtain a smaller splitting than ours for the smallest reference space, by 429 cm^{-1} (Table 5), but comparable results when they use a larger reference space (7672 vs 7656 cm^{-1}). The effect of enlarging the reference space is large in Rakowitz and Marian and calculations (445 cm^{-1}) while our corresponding effect (at the CI13(A) level) is 113 cm^{-1}. However, their reference spaces are in all cases smaller than ours (they include neither s^1p^2 configurations or open *d*-shell configurations). We conclude that the main reason for the differences between our results and the results of Rakowitz and Marian is that their smallest reference spaces are inadequate for spin-orbit calculations.

Rakowitz and Marian also report results obtained from a 19-electron CI where the 5*p* shell has also been correlated. Their CI19 result is indeed in excellent agreement with experimental data, and it shows that core correlation is reasonably important in thallium.

5 Conclusions

The results from the present study can be summarized as follows:

1. The mean-field method is an excellent approximation to the full microscopic no-pair spin-orbit Hamiltonian for Tl.

2. The SOO term, which is difficult to calculate correctly, contributes 50–100 cm^{-1} to the splitting between the Tl $^2P_{\frac{3}{2}}$ and the $^2P_{\frac{1}{2}}$ states.

3. The error induced by the averaged kinematic factor approximation is very small. The computational gain from this approximation is large [32].

4. Spin-orbit CI calculations using the no-pair form of the microscopic spin-orbit Hamiltonian, neglecting

contributions from the SOO term, gives splittings in satisfactory agreement with experimental values.

5. It is important to choose the reference states with great care in spin-orbit calculations.

6. The Breit-Pauli form of the microscopic spin-orbit Hamiltonian gives results which are too large by 2000 cm^{-1}, in agreement with results previously reported by Rakowitz and Marian [14].

7. We find that perturbation theory gives splittings which are 1000–1500 cm^{-1} too low compared to experimental values in agreement with results previously reported by Rakowitz and Marian [14]. This failure of perturbation theory is due to the difference in spatial extent of the $P_{\frac{3}{2}}$ and the $P_{\frac{1}{2}}$ atomic spinors in Tl.

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