GRECP/MRD-CI calculations of the spin-orbit splitting in the ground state of Tl and of the spectroscopic properties of TlH.

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(March 31, 2022)

Abstract

The generalized relativistic effective core potential (GRECP) approach is employed in the framework of multireference single- and double-excitation configuration interaction (MRD-CI) method to calculate the spin-orbit (SO) splitting in the $^2P^o$ ground state of the Tl atom and spectroscopic constants for the $0^+$ ground state of TlH. The 21-electron GRECP for Tl is used and the outer core 5s and 5p pseudospinors are frozen with the help of the level shift technique. The spin-orbit selection scheme with respect to relativistic multireference states and the corresponding code are developed and applied in the calculations. In this procedure both correlation and spin-orbit interactions are taken into account. A [4,4,4,3,2] basis set is optimized for the Tl atom and employed in the TlH calculations. Very good agreement is found for the equilibrium distance, vibrational frequency, and dissociation energy of the TlH ground state ($R_e = 1.870$ Å, $\omega_e = 1420$ cm$^{-1}$, $D_e = 2.049$ eV) as compared with the experimental data ($R_e = 1.868$ Å, $\omega_e = 1391$ cm$^{-1}$, $D_e = 2.06$ eV).

SHORT NAME: GRECP/MRD-CI calculations on Tl and TlH
KEYWORDS FOR INDEXING: Relativistic Effective Core Potential Configuration Interaction, Molecule with heavy atoms, Electronic structure calculation.

31.15.+q, 31.20.Di, 71.10.+x
I. INTRODUCTION

During the last few years a large number of publications have dealt with calculations of the $2P^o_{1/2} - 2P^o_{3/2}$ splitting in the ground state of the Tl atom and spectroscopic constants for the $0^+$ ground state of TlH. Such interest to these systems arises because of their relatively simple electronic structure in the valence region. This makes them very convenient objects for testing methods for the description of relativistic and correlation effects. We can mention some recent papers \[1–7\] in which the electronic structure of thallium was studied and papers \[8–11\] in which the calculation of spectroscopic constants for TlH was carried out. With the exception of the atomic RCC calculation by Eliav et al. \[6,7\] and the atomic CI/MBPT2 calculation by Dzuba et al. \[2\], the published results cannot be considered to be very accurate and reliable, however, primarily because of the rather small basis sets and the small numbers of correlated electrons.

In calculations of Tl and TlH with the use of the relativistic effective core potential (RECP) approximation \[12\], in which only 13 thallium electrons are treated explicitly (13e-RECPs), one more problem appears. The correlation of the outer core (OC) and valence (V) electrons, occupying the 5$d$ and ns, np, nd ($n = 6, 7, \ldots$) orbitals, respectively, cannot be satisfactorily described, mainly because the smoothed V-pseudoorbitals (pseudospinors) have the wrong behaviour in the OC region. One-electron functions $\phi^{\text{corr}}_{x,k}(r)$, being some linear combinations of virtual orbitals, correlate to occupied orbitals $\phi^{\text{occ}}_x$ (where $x = c, v$ stands for the OC and V orbital indices) and are usually localized in the same space region as $\phi^{\text{occ}}_x$. Therefore, the original “direct” Coulomb two-electron integrals describing the OC-V correlation of $\phi^{\text{occ}}_c$ and $\phi^{\text{occ}}_v$ can be well reproduced by those with the pseudoorbitals, despite their localization in different space regions. However, a two-electron integral describing the “exchange” part of the OC-V correlation,

$$\int d\mathbf{r} \phi^{\text{corr+}}_{c,k}(\mathbf{r})\phi^{\text{occ}}_c(\mathbf{r}) \int d\mathbf{r}' \phi^{\text{corr+}}_{c,k}(\mathbf{r}')\phi^{\text{occ}}_v(\mathbf{r}') \frac{1}{\mathbf{r} - \mathbf{r}'}$$

(1)

cannot be well reproduced because the V-pseudoorbitals are smoothed in the OC region where the OC-pseudoorbitals are localized (for more theoretical details, see Ref. \[13\]).

The first RECPs for Tl with the 5$s$, 5$p$ shells treated explicitly (21e-RECPs) for which this disadvantage of the earlier “semicore” RECPs was overcome were generated and tested in single-configurational calculations by Mosyagin et al. \[14,15\]. Some other inherent problems of the “nodeless” RECPs were also solved with the 21-electron Generalized RECP (21e-GRECP) version presented in Ref. \[14,15\]. In Ref. \[15\], for the case of the 21e-GRECP it was also shown that the 5$s$, 5$p$ pseudospinors could be frozen while still providing significantly higher accuracy than 13e-RECPs because the valence and virtual ns and np ($n = 6, 7, \ldots$) pseudoorbitals in the former case already have the proper nodal structure in the OC region.

II. THE GRECP OPERATOR IN THE SPIN-ORBIT REPRESENTATION

In most existing quantum-chemical codes for molecular calculations with RECPs (as well as in the MRD-CI code used in the present work) spin-orbit basis sets are used. In these versions the number of the two-electron integrals is substantially smaller than in the case
of spinor basis sets providing the same level of correlation treatment. Spin-orbit basis sets are preferable in the calculations in which correlation effects give a higher contribution to the properties of interest than those of a relativistic nature. This is usually the case for valence and outermost core electrons, which mainly determine chemical and spectroscopic properties of molecules.

Together with the spin-orbit basis set, the GRECP for Tl should also be employed in the spin-orbit representation. Following Ref. [16,17], the components of the spin-averaged part of the GRECP operator called the averaged relativistic effective potentials (AREP) are written in the form [13,14]:

\[
U_{nvl}^{\text{AREP}}(r) = \frac{l + 1}{2l + 1} U_{nvl+}(r) + \frac{l}{2l + 1} U_{nvl-}(r),
\]

(2)

\[
U_{nvl}^{\text{AREP}}(r) = \frac{l + 1}{2l + 1} V_{nvnvl+}(r) + \frac{l}{2l + 1} V_{nvnvl-}(r),
\]

(3)

\[
V_{nvnvl\pm}(r) = \left[ U_{nvl\pm}(r) - U_{nvl\pm}(r) \right] P_{nvl\pm}(r) + \left[ U_{nvl\pm}(r) - U_{nvl\pm}(r) \right] - \sum_{n_c'} \left[ U_{nvl\pm}(r) - U_{nvl\pm}(r) \right] P_{nvl\pm}(r),
\]

(4)

where \( U_{nvl}(r) \) are the potentials generated for the \( \tilde{\varphi}_{nvl}(r) \) pseudospinors by means of the Goddard scheme [18]; \( n_x \) is the principal quantum number of an outercore (\( n_c \)), valence (\( n_v \)) or virtual (\( n_a \)) pseudospinor; \( l \) and \( j \) are angular and total electron momenta; \( \pm \) stands for \( j = l \pm 1/2 \); \( P_{nvl\pm}(r) \) is the radial projector on the OC pseudospinors:

\[
P_{nvl\pm}(r) = \sum_m |n_c, l, \pm, m \rangle \langle n_c, l, \pm, m|.
\]

Clearly, the AREP component of the GRECP may be used in calculations with nonrelativistic quantum-chemical codes in order to take account of spin-independent relativistic effects.

The operator of the effective spin-orbit interaction can be derived following the expression for the spin-angular projector \( P_{l\pm} \) from Ref. [17]:

\[
P_{l\pm}(\Omega, \sigma) = \frac{1}{2l + 1} \left[ (l + \frac{1}{2} \pm \frac{1}{2}) P_{l}(\Omega) \pm 2P_{l}(\Omega) \mathbf{i}s P_{l}(\Omega) \right].
\]

(6)

Its components, called the effective spin-orbit potentials (ESOP), can be written as [13,14]

\[
\Delta U_{nvl}(r) = U_{nvl+}(r) - U_{nvl-}(r),
\]

(7)

\[
\Delta V_{nvnvl}(r) = V_{nvnvl+}(r) - V_{nvnvl-}(r),
\]

(8)

\[
U_{nl}^{\text{ESOP}} = \frac{2\Delta U_{nl}(r)}{2l + 1} P_{l} \mathbf{i}s,
\]

(9)
\[ P_l = \sum_{m=-l}^{l} |lm\rangle\langle lm|, \]  

(10)

where \( |lm\rangle\langle lm| \) is the projector on the spherical function \( Y_{lm} \).

Neglecting the difference between \( U_{n_v L}^{AREP} \) and \( U_{n_v L}^{ESOP} \) for virtual pseudospinors with \( l > L \) (for theoretical details see Ref. [13]), one can write the GRECP operator \( U \) as

\[
U = U_{n_v L}^{AREP}(r) + \sum_{l=0}^{L-1} \left[ U_{n_v l}^{AREP}(r) - U_{n_v L}^{AREP}(r) \right] P_l \\
+ \sum_{n_c} \sum_{l=0}^{L} U_{n_v l}^{AREP}(r) P_l + \sum_{l=1}^{L} \left[ U_{n_v l}^{ESOP} + \sum_{n_c} U_{n_v l}^{ESOP} \right] P_l.
\]

(11)

Note that the nonlocal terms with the projectors on the most important correlation functions \( \tilde{\phi}_{n_v l, x}^{corr}(r) \) (where \( x = c, v \)) localized mainly in the OC and V regions and with the corresponding potentials \( U_{n_v l, x}^{corr}(r) \) can be taken into account in the considered expressions for the GRECP operator additionally to those with the OC projectors. Obviously, the non-local GRECP terms for the frozen OC pseudospinors can be omitted in the sum over \((n_c l)\) in Eq. (11).

We should emphasize that in spite of the rather complicated form of the above GRECP operator, the main computational effort in calculating matrix elements with the GRECP is caused by the standard radially-local operator, which is also a part of conventional RECP operators, and not by the non-local GRECP terms. Thus, the additional complications in calculations with GRECPs are negligible in comparison with treatments employing conventional semi-local RECPs if comparable gaussian expansions are used for the partial potentials. The more critical point is that the effort in the calculation and transformation of two-electron integrals is always substantially higher than that in the computation of RECP integrals for all known RECP versions (including GRECPs) when appropriately large basis sets are employed in the precise calculations.

III. FROZEN-CORE APPROXIMATION FOR THE OUTER-CORE SHELLS

To perform precise calculations of chemical and spectroscopic properties, correlations should be taken into account not only within the valence regions of heavy atoms and heavy-atom molecules but in the core regions and between the valence and core electrons as well. In practice, the goal is to achieve a given level of accuracy by correlating as small a number of electrons as possible, thus reducing the computational effort. However, as discussed in the Introduction, the accuracy of the RECPs generated for a given number of explicitly treated electrons cannot always satisfy the accuracy requirements expected from correlating all these electrons in the corresponding all-electron calculation. This is true, in particular, for calculations of Tl, having a \( 5d^{10}6s^26p^1 \) leading configuration in the ground state, and its compounds.

To attain an accuracy level of 400 cm\(^{-1}\) for the \( ^2P_{1/2}^0 - ^2P_{3/2}^0 \) splitting in the ground state and for excitation energies to low-lying states of Tl and to take account of the core polarization, one should correlate at least 13 electrons, i.e. include the \( 5d \) shell. This
is achieved in the present MRD–CI calculations with \(f\) and \(g\) basis functions describing mainly polarization of the 5\(d\) shell (for other recent results see, e.g., [1,3,4]). Some data from our 13e-CI calculations of the SO-splitting in the ground state of Tl are collected in Table I in comparison with the 3e-CI results, which in our DF/CI (Dirac–Fock calculations followed by CI) and the GRECP/CI calculations have errors of about 600 cm\(^{-1}\).

We also should mention the recent relativistic coupled-cluster (RCC) results of Landau et al. [7], in which 35 electrons are correlated and a decrease of close to 90 cm\(^{-1}\) in the above mentioned SO splitting is due to the Breit interaction. Note that this interaction is not yet taken into account in the RECPs considered in the present work.

Obviously, the 5\(d\) shell should also be explicitly treated in calculations of molecules containing Tl to take into account core relaxation and polarization effects with satisfactory accuracy. For these calculations it would be optimal to use the RECPs with 13 electrons of Tl treated explicitly (13e-RECPs) such as the RECP of Ross et al. [19] or our valence RECP version [15]. None of the known nodeless 13e-RECPs can provide the aforementioned accuracy, however. Although single-configurational tests [4,13] give errors of 100 cm\(^{-1}\) or somewhat more for excitation energies to low-lying states, they are dramatically increased for 13e-RECPs if all 13 electrons are correlated. The reasons are discussed in the Introduction (one can also see the results of the 13e-RECP/MRD-CI calculations in Ref. [5] and of the 13e-PP/MRCI calculations in Ref. [4]).

To overcome this disadvantage, one should use RECPs with at least 21 electrons, e.g. 21e-GRECP [14,15] and 21e-PP [4] for Tl. The 5\(s\) and 5\(p\) pseudospinors can be treated as frozen, however, while still providing the aforementioned accuracy. The 5\(p\) orbitals have energies about four times higher and their average radii are 1.4 times shorter than those for the 5\(d\) orbitals. Moreover, their angular correlation is suppressed as compared with the 5\(d\) shell because the most important polarization functions (5\(d\) for the 5\(p\) orbitals and 5\(p\) for the 5\(s\) orbitals) are completely occupied in the lowest-lying states. Therefore, the 5\(s\), 5\(p\) orbitals are substantially less active in chemical processes.

In order to freeze the 5\(s\) and 5\(p\) pseudospinors, one can apply the energy level shift technique [13]. Following Huzinaga et al. [20], one should add the matrix elements of the SCF field operators (the Coulomb and spin-dependent exchange terms) over these OC pseudospinors to the one-electron part of the Hamiltonian together with the level terms

\[
\sum_{|c_f|,l,\pm} B_{|c_f|,l,\pm} \tilde{P}_{|c_f|,l,\pm}(r),
\]

where \(B_{|c_f|,l,\pm}\) is at least of order \(|2\varepsilon_{|c_f|,l}|\) and \(\varepsilon_{|c_f|,l}\) is the orbital energy of the OC pseudospinor \(\tilde{\phi}_{|c_f|,l}(r)\) to be frozen. Such nonlocal terms are needed in order prevent collapse of the molecular orbitals to the frozen states (the 5\(s_1/2\), 5\(p_{1/2,3/2}\) pseudospinors for Tl). All terms with the frozen core pseudospinors described here (the Coulomb and exchange interactions, and the level shift operator) can easily be presented in spin-orbit form with the help of eq. (11), as was done above for the GRECP operator.

More importantly, these OC pseudospinors can be frozen in calculations with spin-orbit basis sets and they can already be frozen at the stage of calculation of the one-electron matrix elements of the Hamiltonian, as implemented in the MOLGEP code [21]. Thus, any integrals with indices of the frozen spinors are completely excluded after the integral calculation step.
In single-configurational calculations with the numerical HFJ code [15] we have seen that the SO splitting of the 5p shell increases the resulting SO splitting of the \(^1P^o\) ground state by about 400 cm\(^{-1}\), whereas the SO splitting of the 5d shell decreases the final SO splitting by almost the same value. Therefore, it is important to freeze the 5p\(_{1/2}\) and 5p\(_{3/2}\) (pseudo)spinors and not some averaged 5p (pseudo)orbitals if the SO interaction is to be taken into account in the 5d and valence shells.

In Ref. [4], the 21e-“energy-adjusted” Pseudopotential (PP) having the features which have been emphasized [13–15,22] as inherent for GRECPs (different potentials for the 5p and 6p pseudospinors in the case of Tl) is generated and applied to the calculation of the SO splitting in Tl, with the core correlations described by the core polarization potential (CPP). Some average OC pseudoorbitals are frozen and the SO splitting of 7810 cm\(^{-1}\) obtained in their 21e-PP/MRCI calculation is quite different than our result.

After applying the projection operator of eq. (6) to the level shift (12), Coulomb and exchange terms with the frozen core pseudospinors, the AREP and ESOP parts of the GRECP operator are to be modified to include these new contributions. This technique was successfully employed in our earlier calculations of the spin-rotational Hamiltonian parameters in the BaF and YbF molecules [23].

The freezing technique discussed above can be efficiently applied to those OC shells for which the spin-orbit interaction is clearly more important than the correlation and relaxation effects. If the latter effects are neglected entirely or taken into account within “correlated” GRECP versions [13], the corresponding OC pseudospinors can be frozen and the spin-orbit basis sets can be successfully used for other explicitly treated shells. This is true for the 5p\(_{1/2,3/2}\) subshells in Tl, contrary to the case of the 5d\(_{3/2,5/2}\) subshells. Freezing the OC pseudospinors allows one to optimize an atomic basis set only for the orbitals which are varied or correlated in subsequent calculations, thus avoiding the basis set optimization for the frozen states and reducing the number of the calculated and stored two-electron integrals. Otherwise, if the 5p shell should be correlated explicitly, a spinor basis set can be more appropriate than the spin-orbit one.

IV. THE MRD-CI METHOD

In the multireference single- and double-excitation CI approach [24], the \(\Lambda S\)-basis sets of many-electron spin-adapted (and space symmetry-adapted) functions (SAFs) are employed. This method makes use of configuration selection and perturbative energy extrapolation techniques [24] and employs the Table CI algorithm [25] for efficient handling of the various open-shell cases which arise in the Hamiltonian matrix elements. Some new features of the selection scheme used in this work are considered below. The higher excitations in the CI treatment has been assessed by applying the generalized multireference analogue [27] of the Davidson correction [26] to the extrapolated \(T=0\) energies of each root.

After selecting the \(\Lambda S\)-sets of SAFs for a chosen threshold \(T_i\) (\(i = 1, 2\)), they are collected together in accord with the relativistic double-group symmetry requirements and a spin-orbit CI (SO-CI) calculation is performed with these SAFs to obtain some SO-roots (\(\Psi^{SO,T_i}_i\)) and their energies (\(E^{SO,T_i}_i\)) which are of interest in a considered double group irreducible representation (irrep). Then the linear \(T=0\) correction is evaluated in the basis of the
calculations with the $T_1$ and $T_2$ thresholds. Finally, the generalized Davidson (or full CI) correction is applied to each root of interest.

The stage of the molecular spectroscopic constants calculation begins with the fitting of the relativistic CI potential curves to polynomials which are employed to construct appropriate Born-Oppenheimer nuclear motion Schrödinger equations solved by the Dunham method with the help of the DUNHAM-SPECTR code of Mitin [28].

A. Features of the spin-orbit selection procedure

Let us define a Hamiltonian $H$ for a molecule as

$$H = H^{(0)} + V^{corr} + H^{SO},$$

(13)

where $H^{(0)}$ is an unperturbed spin-independent Hamiltonian, $V^{corr}$ is a two-electron operator describing correlations, and $H^{SO}$ is a one-electron spin-orbit operator (ESOP in our case). Let us choose an orthonormal basis set of SAFs $\{\Phi_i^{(n)AS}\}$ in the $\Lambda S$-coupling scheme (or “spin-orbit” basis set). In particular, these SAFs can be solutions of Hartree-Fock equations with a spin-averaged RECP for the molecule considered. The $H^{(0)}$ Hamiltonian is constructed to be diagonal in the given many-electron basis set:

$$H^{(0)} \Phi_i^{(n)AS} = E_i^{(n)AS} \Phi_i^{(n)AS},$$

(14)

where $n = 0, 1, \ldots$ (see below the description of the indices in more detail). Additionally define $H^{(0)}$ so that

$$< \Phi_i^{(n)AS} | H^{(0)} | \Phi_i^{(n)AS} > \equiv < \Phi_i^{(n)AS} | H | \Phi_i^{(n)AS} >$$

(15)

in order to exclude the first-order PT contributions to total energies of molecular states (this corresponds to the Epstein-Nesbet PT form).

We will ignore the two-electron spin-dependent (Breit) interactions which ordinarily can be neglected when studying chemical and spectroscopic properties. Breit and other quantum electrodynamic (QED) effects are relatively large for lanthanides and actinides, but for the V and OC shells they can be efficiently represented by the one-electron $j$-dependent RECP terms.

Let us distinguish the following types of many-electron functions which are considered in a double-group symmetry:

- $\{\Phi_i^{(0)AS}, E_i^{(0)AS}\}_{j=0}^{N^{(0)AS}}$ are reference SAFs (“Mains”) and their energies

$$E_i^{(n)AS} = < \Phi_i^{(n)AS} | H^{(0)} | \Phi_i^{(n)AS} >$$

(16)

at $n = 0$ for those $\Lambda S$-irreps which are of interest for the final spin-orbit CI (SO-CI) calculation;

- $\{\Psi_i^{(0)AS}, \mathcal{E}_i^{(0)AS}\}_{j=0}^{N^{(0)AS}}$ are some of the CI solutions (“$\Lambda S$-roots”) and their energies

$$\mathcal{E}_i^{(0)AS} = < \Psi_i^{(0)AS} | H^{(0)} + V^{corr} | \Psi_i^{(0)AS} >$$

(17)

in the $\Lambda S$-irrep which diagonalize the $(H^{(0)} + V^{corr})$ in the subspace of Mains only;
• \{ \Psi_{I}^{(0)SO}, \mathcal{E}_{I}^{(0)SO} \} \big|_{I=0}^{\infty} \) are some of the SO-CI solutions (“SO-roots” which are of interest) and their energies

\[ \mathcal{E}_{I}^{(0)SO} = \langle \Psi_{I}^{(0)SO} | H^{(0)} + V^{\text{corr}} + H^{SO} | \Psi_{I}^{(0)SO} \rangle \]  

which diagonalize the complete \( H \) Hamiltonian in the subspace of all Mains collected from all the \( \Lambda \)-irreps considered;

• \{ \Phi_{I}^{(1)AS}, E_{I}^{(1)AS} \} \big|_{I=0}^{\infty} \) are the singly-excited SAFs (SE-SAFs) and their energies at \( n = 1 \), i.e.

\[ \Phi_{I}^{(1)AS} \in \{ P^{\Lambda S} a_{p}^{+} a_{q} \Phi_{J}^{(0)AS'} \} \setminus \{ \Phi_{K}^{(0)AS} \} \quad \forall \quad (p, q; J, K) \],

where \( P^{\Lambda S} = |\Lambda S> <\Lambda S| \) is a projector on the subspace of the \( \Lambda S \)-states, \( a_{p}^{+} (a_{q}) \) are the creation (annihilation) operators of one-electron states (spin-orbitals) \( \phi_{p}(\phi_{q}) \). The SE-SAFs can be automatically selected because of their relatively small number;

• \{ \Phi_{I}^{(2)AS}, E_{I}^{(2)AS} \} \big|_{I=0}^{\infty} \) are the doubly-excited SAFs (DE-SAFs)

\[ \Phi_{I}^{(2)AS} \in \{ P^{\Lambda S} a_{p}^{+} a_{q}^{+} a_{r} a_{s} \Phi_{J}^{(0)AS'} \} \setminus \{ \Phi_{K}^{(1)AS} \} \cup \{ \Phi_{L}^{(0)AS} \} \quad \forall \quad (p, q, r, s; J, K, L) \]

and their energies at \( n = 2 \); a SAF \( \Phi_{I}^{(2)AS} \) should be selected in accordance with some selection criteria to be used in the final SO-CI calculation. In principle, triple and higher excited sets of SAFs can be similarly defined.

The correlation operator, \( V^{\text{corr}} \), has the symmetry of the molecule and, therefore, can be rewritten as

\[ V^{\text{corr}} \equiv \sum_{\Lambda S} P^{\Lambda S} V^{\text{corr}} P^{\Lambda S} . \]

It normally gives the most important contribution through the second-order Brillouin-Wigner PT energy correction in the basis set of \( \Phi_{J}^{(n)AS} \) (after appropriate redefinition of \( H^{(0)} \) in the subspace of Mains, see Ref. [23,30]):

\[ \sum_{n=1,2} \sum_{J} \frac{| \langle \Phi_{J}^{(n)AS} \big| V^{\text{corr}} \big| \Psi_{j}^{(0)AS} \rangle |^{2}}{\mathcal{E}_{0}^{\Lambda S} - E_{J}^{(n)AS}} \]

for the non-degenerate ground state \( \Psi_{0}^{\Lambda S} \) with the exact energy \( \mathcal{E}_{0}^{\Lambda S} \) in the \( \Lambda S \)-irrep (obviously, terms with \( n \geq 3 \) are automatically equal to zero because \( V^{\text{corr}} \) is a two-electron operator). A similar expression with the replacements \( \Psi_{0}^{(0)AS} \rightarrow \Psi_{I}^{(0)AS} \) and \( \mathcal{E}_{0}^{\Lambda S} \rightarrow \mathcal{E}_{I}^{\Lambda S} \) can be applied for excited states \( \Psi_{I}^{\Lambda S} \) (some precautions should be taken concerning the degenerate states and the orthogonality constraints with respect to the lower-lying states with \( J < I \)). As a result, the first rows, columns and energies on the diagonal of the Hamiltonian matrix

\[ \langle \Phi_{J}^{(n)AS} \big| V^{\text{corr}} \big| \Phi_{I}^{(0)AS} \rangle , \quad \langle \Phi_{J}^{(n)AS} \big| H \big| \Phi_{I}^{(n)AS} \rangle \]

\[ 8 \]
for \( n = 1, 2 \) are usually employed in the selection procedures for SAFs \( \{ \Phi_{I}^{(1,2)AS} \} \) based on the nonrelativistic \( A_k \) and \( B_k \) approximations (when \( H^{SO} \) is not taken into account) \cite{29,30} or on the multi-diagonalization scheme \cite{24} for subsequent calculations of \( \Psi_{I}^{AS} \). In spite of some differences between these selection schemes, they are not very essential for the final CI results if a high quality reference set (set of Mains) and a suitably small threshold are chosen.

For molecules with heavy and very heavy atoms, the \( H^{SO} \) operator can give large contributions to the energy both in second and in higher PT orders if a non-optimal set of Mains, \( \{ \Phi_{I}^{(0)AS} \} \), is chosen after an SCF calculation with the SO-averaged potentials (AREPs). The latter is the usual practice and the set of Mains generated in such a manner can be smaller than optimal for the case of large SO interaction. Therefore, not only second but third and maybe even higher PT order(s) can be important in the selection procedure because \( H^{SO} \) is a substantially off-diagonal operator contrary to \( V_{corr} \):

\[
< \Phi_{I}^{(n)AS} | H^{SO} | \Phi_{J}^{(n')AS} > \text{ (AS) and (A'S') can be different, } n' \in \{ n, |n \pm 1| \}.
\] (24)

In particular, \( H^{SO} \) gives zero matrix elements between SAFs belonging to the same \( \Lambda S \)-irrep in the \( D_{2h} \) or \( C_{2v} \) symmetry groups.

For simplicity, let us consider the selection scheme based on the \( A_k \) approximation \cite{22}.

In the nonrelativistic-type selection scheme, a SAF \( \Phi_{J}^{(1,2)AS} \) is selected in a \( \Lambda S \)-irrep if

\[
\frac{| < \Phi_{J}^{(1,2)AS} | V_{corr} | \Psi_{I}^{(0)AS} > |}{E_{J}^{(1,2)AS} - E_{I}^{(0)AS}} \geq \delta E_{T}^{AS},
\] (25)

where \( I \leq N^{SO} \) and \( \delta E_{T}^{AS} \) is a threshold criterion for the energy selection scheme in the \( \Lambda S \)-irrep. In (25) we have replaced the exact \( E_{I}^{AS} \) energies by the approximate \( E_{I}^{(0)AS} \) values \cite{7} that corresponds to the Rayleigh-Schrödinger PT case. Such a simplification is justified for small \( \delta E_{T}^{AS} \) and good reference states.

In a SO-CI calculation within some relativistic double-group irrep, substitutions for the reference state \( (\Psi_{I}^{(0)AS} \rightarrow \Psi_{I}^{(0)SO}) \) and the perturbation \( (V_{corr} \rightarrow V_{corr} + H^{SO}) \) should be used in the previous expression, so that

\[
\frac{| < \Phi_{J}^{(1,2)AS} | V_{corr}^{SO} | \Psi_{I}^{(0)SO} > |}{E_{J}^{(1,2)AS} - E_{I}^{(0)SO}} \geq \delta E_{T}^{SO},
\] (26)

where \( \delta E_{T}^{SO} \) is a selection threshold for \( \Phi_{J}^{(1,2)AS} \) to be used in the subsequent SO-CI calculation.

In more detail, the matrix element in the PT numerator of the above formula can be rewritten as

\[
| < \Phi_{J}^{(1,2)AS} | V_{corr}^{SO} | \Psi_{I}^{(0)SO} > |^2 \quad (27)
\]

\[
+ | < \Phi_{J}^{(1)AS} | H^{SO} | \Psi_{I}^{(0)SO} > |^2 \quad (28)
\]

\[
+ 2 \Re( < \Psi_{I}^{(0)SO} | V_{corr} | \Phi_{J}^{(1)AS} > < \Phi_{J}^{(1)AS} | H^{SO} | \Psi_{I}^{(0)SO} > ) \quad (29)
\]
by taking into account eq. (24) in the calculation of the matrix elements for \( V_{\text{corr}} \), contrary to those for \( H_{\text{SO}} \). In spite of mixing different \( \Lambda S \)-states due to \( H_{\text{SO}} \), the number of non-zero matrix elements with \( H_{\text{SO}} \) in eq. (24) is usually relatively small because the \( \text{SO} \) interaction is a one-electron operator (see eq. (24)) which is very localized compared with the long-range Coulomb interaction. Thus, one can see that the nonrelativistic-type selection due to \( V_{\text{corr}} \) with respect to \( \{ \Psi^0_{I} \Phi^{(0)\Lambda S} \} \) in each considered \( \Lambda S \)-irrep and automatic selection of all \( \text{SE-SAFs} \) \( \{ \Phi^{(1)\Lambda S}_{J} \} \) can be efficiently applied instead of eq. (24). It must be emphasized that contrary to the selection schemes in the nonrelativistic case, \( \text{SE-SAFs} \) should be generated with respect to the \( \text{Mains} \) from all the used \( \Lambda S' \)-irreps. In a more simplified treatment, the automatic selection of \( \text{SE-SAFs} \) can be done with respect to a subset of the most important \( \text{Mains} \), e.g. having largest CI-coefficients in the \( \Psi^{(0)\Lambda S}_{I} \) roots.

Next let us consider the terms from the third-order PT energy (PT-3) for \( \text{SAFs} \) \( \{ \Phi^{(1,2)\Lambda S}_{J} \} \) which can be essential for the \( \text{SO} \) selection procedure. Below we shall discuss only matrix elements in the PT numerators of the corresponding PT-3 terms because specific expressions for the energy denominators are not essential for our analysis and conclusions. For simplicity, we shall omit the terms conjugate to those considered.

The first two types of the PT-3 matrix elements are:

\[
< \Psi^{(0)\Lambda S}_{I} | H_{\text{SO}} | \Phi^{(1)\Lambda S}_{J} > < \Phi^{(1)\Lambda S}_{J} | H_{\text{SO}} | \Phi^{(1)\Lambda S'}_{K} > < \Phi^{(1)\Lambda S'}_{K} | H_{\text{SO}} | \Psi^{(0)\Lambda S}_{I} > , \tag{30}
\]

\[
< \Psi^{(0)\Lambda S}_{I} | H_{\text{SO}} | \Phi^{(1)\Lambda S}_{J} > < \Phi^{(1)\Lambda S}_{J} | V_{\text{corr}} | \Phi^{(1)\Lambda S}_{L} > < \Phi^{(1)\Lambda S}_{L} | H_{\text{SO}} | \Psi^{(0)\Lambda S}_{I} > . \tag{31}
\]

The first intermediate state, \( \Phi^{(1)\Lambda S}_{J} \), is a test \( \text{SE-SAF} \) and the indices for other intermediate \( \text{SAFs} \) run over all the allowed ones. The PT-3 terms summed over the indices of the second intermediate state give contributions (together with the conjugate terms) for the selection of the test \( \text{SE-SAF} \). However, the \( \text{SE-SAFs} \) can be selected automatically and these terms are out of our particular interest.

The following matrix element type

\[
< \Psi^{(0)\Lambda S}_{I} | V_{\text{corr}} | \Phi^{(1,2)\Lambda S}_{J} > < \Phi^{(1,2)\Lambda S}_{J} | H_{\text{SO}} | \Phi^{(1)\Lambda S'}_{K} > < \Phi^{(1)\Lambda S'}_{K} | H_{\text{SO}} | \Psi^{(0)\Lambda S}_{I} > . \tag{32}
\]

can be used for the selection of \( \Phi^{(1,2)\Lambda S}_{J} \) and \( \Phi^{(1)\Lambda S'}_{K} \) when summing over another set of intermediate states in the PT-3 expression. As one can see, this term can be used for the selection of both \( \text{SE-SAFs} \) and \( \text{DE-SAFs} \). The above expression is quadratic in the (large) \( H_{\text{SO}} \) interaction contrary to the remaining terms considered below. The contribution of the terms with matrix elements (33) can be essential and their use for the selection of \( \text{DE-SAFs} \) \( \Phi^{(2)\Lambda S}_{J} \) can be important for a subsequent \( \text{SO-CI} \) calculation.

The following matrix element types contain a second order perturbation in \( V_{\text{corr}} \) and, therefore, we can suggest that in general they are less important for our consideration than the above terms:

\[
< \Psi^{(0)\Lambda S}_{I} | V_{\text{corr}} | \Phi^{(1,2)\Lambda S}_{J} > < \Phi^{(1,2)\Lambda S}_{J} | V_{\text{corr}} | \Phi^{(1)\Lambda S}_{L} > < \Phi^{(1)\Lambda S}_{L} | H_{\text{SO}} | \Psi^{(0)\Lambda S}_{I} > , \tag{33}
\]

\[
< \Psi^{(0)\Lambda S}_{I} | V_{\text{corr}} | \Phi^{(1,2)\Lambda S}_{J} > < \Phi^{(1,2)\Lambda S}_{J} | H_{\text{SO}} | \Phi^{(1)\Lambda S'}_{K} > < \Phi^{(1)\Lambda S'}_{K} | V_{\text{corr}} | \Psi^{(0)\Lambda S}_{I} > . \tag{34}
\]

These terms, together with the conjugate ones, can be used for the selection of \( \Phi^{(1,2)\Lambda S}_{J} \) and \( \Phi^{(1)\Lambda S}_{L} \). The term
\begin{equation}
< \Psi_I^{(0)SO} | V_{\text{corr}} | \Phi_j^{(2)AS} > < \Phi_j^{(2)AS} | \mathbf{H}^{SO} | \Phi_K^{(2)A'S'} > < \Phi_K^{(2)A'S'} | V_{\text{corr}} | \Psi_I^{(0)SO} > \tag{35}
\end{equation}
can be analyzed separately because it contains both the intermediate states as DE-SAFs. In general, it is more difficult to take such terms into account in the selection procedure, because of the large number of tested DE-SAFs. We should note, however, that when a tested \( \Phi_j^{(2)AS} \) DE-SAF is fixed, the other intermediate states, \{ \Phi_K^{(2)A'S'} \}, are those DE-SAFs which are only singly excited with respect to the tested one. Therefore, the number of them will not be very high.

For completeness, the matrix element type which is cubic in the \( V_{\text{corr}} \) perturbation should be listed:
\begin{equation}
< \Psi_I^{(0)SO} | V_{\text{corr}} | \Phi_j^{(1,2)AS} > < \Phi_j^{(1,2)AS} | V_{\text{corr}} | \Phi_K^{(1,2)AS} > < \Phi_K^{(1,2)AS} | V_{\text{corr}} | \Psi_I^{(0)SO} > . \tag{36}
\end{equation}
This term is of nonrelativistic type and it is out of our particular interest because it does not contain the \( \mathbf{H}^{SO} \) perturbation. Again, we can separate the term
\begin{equation}
< \Psi_I^{(0)SO} | V_{\text{corr}} | \Phi_j^{(2)AS} > < \Phi_j^{(2)AS} | V_{\text{corr}} | \Phi_K^{(2)AS} > < \Phi_K^{(2)AS} | V_{\text{corr}} | \Psi_I^{(0)SO} > . \tag{37}
\end{equation}
from the previous one only because the latter contains both the DE-SAF intermediate states.

We should emphasize that the terms containing SE- or DE-SAFs in the intermediate states of the PT-3 expressions are not taken into account in the \( B_k \) and multi-diagonalization selection procedures, although these schemes include, in fact, contributions of higher than the second-order PT terms.

When analyzing the above PT-3 terms, it can be concluded that if one replaces the reference SO roots, \( \Psi_I^{(0)SO} \), by new reference states, \( \Psi_I^{(0+1)SO} \), which diagonalize the complete Hamiltonian \( \mathbf{H} \) for the sets of both Mains and SE-SAFs taken together, and applies the selection criterion based on the second-order PT (26), then the main part of the above PT-3 terms will be taken into account in such a selection. An exception occurs for terms (35) and (37), but in general they are thought to be less important than the other third-order PT terms.

In a more sophisticated treatment, the reference \( \Psi_I^{(0+1)SO} \) SO states can be generated when diagonalizing \( \mathbf{H} \) for the sets of Mains and those SE-SAFs (\{ \Phi_j^{(0)AS} \}), which are automatically generated with respect to the most important subset of Mains (\{ \Phi_I^{(0)AS} \}). The latter subset can be selected from a preliminary CI calculation for the set of Mains, e.g. in a basis of configurations with the highest CI coefficients in \( \Psi_I^{(0)SO} \), and so on. This is worthwhile in order to reduce the number of SAFs in the resulting reference states \( \Psi_I^{(0+1)SO} \) rather than in \( \Psi_I^{(0+1)SO} \), thus reducing the selection time which can otherwise be very large.

We should also note that the trial SE- and DE-SAFs, which are tested in the above selection procedure, are generated only for the set of Mains and not for the \{ \Phi_j^{(0+1)AS} \} set. Therefore, the number of the tested configurations and the selection time are reasonably limited. If the number of configurations used in \{ \Phi_j^{(0+1)AS} \} is not high, one can extend the set of Mains by including the above subset of SE-SAFs, thus obviously enlarging the set of the consequently generated and tested SE- and DE-SAFs.

Again we should emphasize that it is not necessary to use the third-order PT or the suggested automatic selection of SE-SAFs in a selection procedure if a fairly good set of
the reference roots $\Psi^{(0)SO}_I$ is used, i.e., if they provide good approximations to the required solutions $\Psi^{SO}_I$. In particular, if the $\{\Psi^{(0)SO}_I\}$ set is obtained from a preliminary series of SO-CI calculations of the studied states, this can be superfluous.

As an alternative to the above selection schemes with respect to the PT energy, the PT expressions for the CI coefficient of a trial SE- or DE-SAF can also be explored. Applying the above PT analysis to the case of the $\Psi^{(0+1)SO}_I >$ reference state, a $\Phi^{(1''\Lambda)}_S$ SAF is selected if its CI coefficient $C^{(1''\Lambda)}$ satisfies the inequality

$$|C^{(1''\Lambda)}| \geq C_{\text{min}}$$

where $C_{\text{min}}$ is the selection threshold for the CI coefficients and

$$C^{(1''\Lambda)} = \frac{\langle \Phi^{(1''\Lambda)}_S | H | \Psi^{(0+1)SO}_I \rangle}{\mathcal{E}^{(0+1)SO}_I - E^{(1''\Lambda)}_I}, \quad (38)$$

is the first-order PT value for the CI coefficient of a tested SAF which is not included in the subset of the $\Phi^{(1')}_S$ reference SE-SAFs.

Such a means of selection can be preferable if those properties of primary interest cannot be calculated from potential energy curves or surfaces. Moreover, the PT selection with respect to both the energy and the CI coefficients can be applied simultaneously if the properties are of different nature.

V. CALCULATIONS

In the CI calculations of Tl and TlH we used the MRD-CI package [24] combined with the SO selection codes based on the scheme described above. Our test calculations have shown that spin-orbit selection is very helpful for preparation of appropriate sets of Mains and for reducing effort in the final CI calculations with an optimal set of selected SAFs.

A. Spin-orbit splitting in the ground state of Tl

Calculations for the Tl atom were performed to optimize the basis set and the level shift GRECP parameters for the 21e/8fs-GRECP, i.e. the 21 electron GRECP with 8 electrons occupying the frozen OC pseudospinors, $5s_{1/2}$ and $5p_{1/2,3/2}$. The quality of the generated basis set is analyzed by calculating the $2^P_1 - 2^P_3$ splitting for the ground state.

Before discussing the present results, it is worthwhile to to make some brief comments concerning numerous values for the Tl($2^P_0$) spin-orbit splitting calculated and published in the last years. It is well known that this quantity calculated at the one-configuration Dirac-Fock level agrees very well, within 100 cm$^{-1}$, with the experimental value of 7793 cm$^{-1}$ [31]. However, such a good agreement results from the fortuitous cancellation of a number of large errors caused by the DF approximation. The situation changes dramatically when even the three outermost $6s^26p^1$ electrons are correlated. Some Tl($2^P_0$) splitting values from our 3e-CI calculations employing different codes and basis sets are given in Table I and lie between 7130 and 7210 cm$^{-1}$. The corresponding 3e-CI results obtained by other
groups after 1996 range from 6800 to 7800 cm\(^{-1}\) and such a large divergency can not be considered as satisfactory, because the ground state of Tl has a very simple configuration structure as compared to other heavy elements. We consider our calculated values of about 7200 cm\(^{-1}\) for this splitting as reliable for an approach in which the 5\(d\) spinors are frozen after the DF calculation of the nonrelativistically averaged 6s\(^2\)6p\(^4\) configuration. Taking into account that a contribution of approximately -100 cm\(^{-1}\) arises from the Breit terms, the deviation from the experimental value for the splitting is around 600-700 cm\(^{-1}\) (this size of an error can be justified theoretically). As will be shown below, the compututed value for the Tl(\(2\)\(P^o\)) splitting can be significantly improved if 5\(d\) electrons are explicitly included in the calculations and the corresponding basis set contains functions with sufficiently high angular momenta.

The optimal basis set was selected in a series of MRD-CI calculations for Tl (with different sets of primitives and numbers of contracted \(s, p, d, f\) and \(g\) functions) to minimize the sum of energies for the ground \(2\)\(P_{1/2}\) and \(2\)\(P_{3/2}\) states. In these calculations, the SAFs were selected in the \(2B_{1u}, 2B_{2u},\) and \(2B_{3u}\) irreps of the \(D_{2h}\) group (nonrelativistic-type degenerate \(2\)\(P\) ground states belong to these irreps) because these doublets are strongly mixed by the SO interaction, resulting in the splitting of the ground \(2\)\(P\) state. We have found that two \(g\) functions should be added to the basis set, giving a contribution of about 9000 cm\(^{-1}\) to the \(2\)\(P^o\) ground state total energies. The resulting \([4,4,4,3,2]\) basis set and GRECP parameters for Tl can be found on [http://www.qchem.pnpi.spb.ru](http://www.qchem.pnpi.spb.ru).

For the \([4,4,4,3,2]\) basis set we have also performed MRD-CI calculations including SAFs from the \(2A_u\) irrep and SAFs with quartet multiplicity (\(4B_{1u}, 4B_{2u}, 4B_{3u},\) and \(4A_u\)). In our calculations with different basis sets, their contributions have decreased the SO splitting by about 170 cm\(^{-1}\) and the total energy by about 2000 cm\(^{-1}\). One can see from Table I that this decrease is mainly caused by the \(p\)- and \(d\)-components which arise from reexpansion of the leading spinor configuration in terms of the spin-orbit configurations. For good accuracy we can recommend the inclusion of \(\Lambda'\asha|S \pm 1\)-irreps for the calculation of states having leading configurations in \(\Lambda S\)-irreps.

In Table I some of our final MRD-CI results are collected together with the atomic relativistic coupled-cluster (RCC) results [6] obtained with a very large basis set. In these MRD-CI calculations altogether 627 Mains in three basic irreps and about 100 Mains in five additional irreps were involved and SE-SAFs were automatically generated for three Mains to prepare the reference \(\{\Psi_j^{(0+1')SO}\}_{j=1}^{3}\) states. Relatively small thresholds, \(T_1=0.03\) and \(T_2=0.01\ \mu E_h\), are used in the final runs with the \([4,4,4,3,2]\) basis set (for the \(T=0\) threshold and full-CI extrapolations), thus selecting respectively about 190000 and 450000 SAFs altogether.

One can see that the best SO splitting calculated in the present work underestimates the experimental result [21] by about 400 cm\(^{-1}\) (recall that additionally about 90 cm\(^{-1}\) is due to the Breit interaction [7]). Analyzing our previous GRECP/RCC calculations of Hg [37] it can be concluded that this occurs due to the neglect of the OC-V correlations with the OC 5\(p\) and 4\(f\) shells, and to a lesser extent with 5\(s\) rather than due to the atomic basis set incompleteness, the GRECP errors or the restricted CI approximation. The OC-V correlation (contribution to the total energy) in Tl and Hg will have the same order of magnitude for respective pairs of correlated electrons (spinors).
We also studied the reliability of the linear $T \to 0$ extrapolation procedure currently used in the MRD-CI code. In the final results of our MRD-CI calculations the corresponding correction gives the highest contribution to the cumulative error. So this is a bottleneck of the present Tl and TlH calculations with the large number of Mains.

**B. Spectroscopic constants of the ground state in TlH**

The explicit treatment of $5d$ electrons in precise TlH (TIX) calculations is necessary not only due to the strong correlation between these and the valence electrons of Tl, but also because of the substantial influence of relaxation-polarization effects in this shell on the bond formation. This cannot be very accurately taken into account by employing a polarization potential [32,33] in combination with, e.g., 3e-RECPs [14,15]. The influence of other atoms (X) in a TlX molecule on the $5p$, $5s$ and $4f$ shells of Tl is significantly smaller and can be neglected if an accuracy of a few hundreds of wavenumbers for the excitation energies of low-lying states is sufficient. We neglected their contributions in calculation of the TlH spectroscopic constants.

In calculating spectroscopic properties for the TlH ground state (Table II) we used the contracted [4,4,4,3,2] basis set for thallium discussed above and the [4,3,1] set for hydrogen (see [http://www.qchem.pnpi.spb.ru](http://www.qchem.pnpi.spb.ru)) contracted from the primitive (6,3,1) gaussian basis set of Dunning [38]. The SAFs were selected in the $^1A_1$, $^3B_1$, $^3B_2$ and $^3A_2$ $\Lambda S$-irreps of the $C_{2v}$ group because the triplet states are most strongly admixed by the SO interaction to the nonrelativistic $^1A_1$ (or $^1\Sigma^+$ in $C_{\infty v}$) ground state producing the relativistic $0^+$ ground state in the double $C_{\infty v}$ group.

We have performed three series of TlH calculations for 16 interatomic distances. In these runs, the $\Psi^{(0+1')SO}_0$ reference SO states are generated with the MRD-CI code by diagonalizing $H$ for the set of Mains and the SE-SAFs which are automatically selected with respect to the single configuration SCF ground state (calculated with the SO-averaged GRECP), giving a contribution of more than 90 % to the final wave function.

The first run is used for preparing an optimal set of Mains for the second series of SO-CI calculations. Only one SCF configuration which has the lowest energy in each $\Lambda S$ irrep is included into the subspace of $\Lambda S$ Mains and, consequently, the SO reference state consists of these SCF configurations and the automatically selected SE-SAFs with respect to the SCF configuration from the $^1A_1$ irrep.

Those SAFs were selected as Mains for the second run which had the highest CI coefficients in the first run. As a result, 37 Mains in all irreps together are employed in the second run. Relatively small thresholds, $T_1=1.0$ and $T_2=0.1 \, \mu E_h$, are used in the second run (for the $T \to 0$ extrapolation [24]), thus causing about 20000 and 85000 SAFs to be selected in the $\Lambda S$-irreps altogether.

In the most computationally consuming third run (with the set of Mains consisting of the SAFs having the largest CI coefficients in the wave function from the second run), about 320 Mains are used altogether and the thresholds are set at $T_1=0.1$ and $T_2=0.05 \, \mu E_h$. About 70000 and 130000 SAFs, respectively, were used in the $\Lambda S$-irreps altogether in the final SO-CI calculations.
One can see from Table II that the basis set superposition error (BSSE) (see [39] and references) must be taken into account for an accurate computation of spectroscopic constants. The BSSE was studied in the Tl$^+$ ion calculations for the same interatomic distances as in TlH and estimated also in the Tl$^-$ calculations for three distances, i.e. with the ghost H atom. The same molecular basis set as in TlH was used for both the Tl and H atoms. The contribution from BSSE to the total energy is decisive for the 5d$^{10}$ and 6s$^2$ shells considered in the case of Tl$^+$, while its changing due to addition of the 6p electrons (which are bonding in TlH) can be considered as relatively small, because the difference in BSSE for Tl$^+$ and Tl$^-$ is not significant in comparison with other errors. In the calculations of the spectroscopic properties with the counterpoise corrections (CPC), the calculated TlH points on the potential curve were corrected with the calculated BSSE for Tl$^+$, i.e. for the 5d, 6s shells taken into account.

One can see that after applying the T=0, FCI, and counterpoise corrections, the calculated properties are in very good agreement with the experimental data both in the second and third runs. The accuracy obtained is notably better than for other existing results for TlH (and not only for those presented in Table II). We suggest, however, that the very good agreement of the calculated $D_e$ with the experimental value can be fortuitous and the “real” (full CI) value can be notably different from the listed one because of the approximations made.

VI. RESUME

The SO splitting in the ground $^2P$ state of Tl is calculated by the MRD-CI method with the 21e-GRECP when 5d$^{10}$, 6s$^2$ and 6p$^1$ electrons are correlated and the 5s$^2$ and 5p$^6$ pseudospinors are frozen in the framework of the level shift technique. A [4,4,4,3,2] basis set is optimized for Tl and an underestimation of about 400 cm$^{-1}$ is found for the SO splitting as compared with the experimental data.

Further improvement of the accuracy can be attained when correlations with the outer core 4f, 5p and 5s shells of Tl and Breit effects are taken into account. We expect that this can be efficiently done in the framework of the “correlated” 21e/8fs-GRECP version in which 13 electrons are treated explicitly as in the present calculation. The inclusion of $h$-type functions is also desirable, as has been demonstrated for Hg in Ref. [37].

Fourteen electrons are correlated in the calculation of spectroscopic constants for the 0$^+$ ground state of TlH and very good agreement with the experimental data is found.

The developed spin-orbit selection scheme and code are demonstrated to be efficient when large sets of basis functions and reference configurations are required in high-precision electronic-structure calculations.

ACKNOWLEDGMENTS

This work was supported by the DFG/RFBR grant N 96–03–00069 and the RFBR grant N 99–03–33249. AVT is grateful to REHE program of the European Science Foundation for fellowship grants (NN 14–95 and 22–95) to visit the laboratory of one of us (RJB), where
part of the work was done. We are thankful to K. Shulgina and T. Isaev (PNPI) for writing some codes used for automatic generation of Mains.

We are grateful to Dipl.-Ing. H.-P. Liebermann for the help in combining the MOLGEP and MRD-CI codes. We are also grateful to Dr. G. Hirsch (deceased) for his kind hospitality and invaluable help during visits to Wuppertal by AVT and NSM.

The main part of the present calculations was carried out at the computer center of the Bergische Universität GH Wuppertal. JECS codes developed by PNPI quantum chemistry group were used for remote control of the calculations.
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TABLE I. Calculations of the spin-orbit splitting of the $^2P^o$ ground state in Tl (the $[\ldots]$, 5$d$ spinors are frozen from the SCF calculation of the nonrelativistically averaged $[\ldots]6s^26p^1$ configuration).

| Method | Spin-orbit basis sets: | SO splitting in $cm^{-1}$ |
|--------|------------------------|----------------------------|
| Spinor basis sets: | [7,7,5] | [7,7,5,3] | [7,7,5,3,1] |
| 81e-DF/3e-CI \[13\] | 7129 | 7182 | 7206 |
| 21e/18fs-GRECP/3e-CI \[13\] | 7133 | 7187 | 7211 |
| Spin-orbit basis sets: | [4,4,4] | [4,4,4,3] | [4,4,4,3,2] |
| 21e/18fs-GRECP/3e-MRD-CI (Full CI) ($^2B_{1u}$, $^2B_{2u}$, $^2B_{3u}$ irreps of $D_{2h}$) | 7305 | 7373 | 7398 |
| ($\ldots + ^2A_u$, $^4B_{1u}$, $^4B_{2u}$, $^4B_{3u}$, $^4A_u$) | 7133 | 7205 | 7230 |
| 21e/8fs-GRECP/13e-MRD-CI + T=0 + FCI ($^2B_{1u}$, $^2B_{2u}$, $^2B_{3u}$ irreps of $D_{2h}$) | 7332 | 7222 | 7517 |
| ($\ldots + ^2A_u$, $^4B_{1u}$, $^4B_{2u}$, $^4B_{3u}$, $^4A_u$) | 7146 | 7044 | 7380 |
| Spinor basis set: | [35,27,21,15,9,6,4] |
| 81e-DF/35e-RCC \[1\] | | | 7710 |
| Experiment \[31\] | | | 7793 |
### TABLE II. GRECP/MRDCI calculations of the spectroscopic constants for the ground state of TlH.

| Method | $R_e$ (Å) | $\omega_e$ (cm$^{-1}$) | $D_e$ (eV) |
|--------|-----------|----------------|------------|
| SOCIEX: Tl [8,8,5,2] + H [4,3,1] (Rakowitz & Marian, 1997) | 1.86 | 1386 | 2.13 |
| 13e-RECP/SOCI: Tl [4,4,4,1] + H [4,2] (DiLabio & Christiansen, 1998) | 1.912 | 1341 | 1.908 |
| 13e-REP/KRCCSD(T): Tl [4,5,5,1] + H [3,2] (Lee et al., 1998) | 1.910 | 1360 | 2.02 |
| 21e-REP/KRCCSD(T): Tl [4,5,5,1] + H [3,2] (Han et al., 2000) | 1.877 | | 2.00 |
| 21e/8fs-GRECP/14e-MRD-CI Tl [4,4,4,3,2] + H [4,3,1] (Present calculations) | | | |
| 37 Mains, T=0.1 | 1.858 | 1481 | 2.03 |
| ——— “——— + CPC | 1.872 | 1446 | 1.984 |
| ——— “——— + T=0 + FCI | 1.858 | 1453 | 2.10 |
| ——— “——— + T=0 + FCI + CPC | 1.872 | 1410 | 2.026 |
| 320 Mains, T=0.05 | 1.866 | 1408 | 2.23 |
| ——— “——— + T=0 + FCI | 1.858 | 1449 | 2.124 |
| ——— “——— + T=0 + FCI + CPC | 1.870 | 1420 | 2.049 |
| Experiment (Grundström & Valberg, 1938) | 1.866$^a$ | 1390.7 | 2.06 |
| Experiment (Urban et al., 1989) | 1.872$^b$ | 1391.3 | |

$^a$Huber & Herzberg (1979) have published value 1.87 Å which can be obtained from the rotational constant $B_e$.

$^b$This value is calculated by us from $B_e$.  

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