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A small-core multiconfiguration Dirac–Hartree–Fock-adjusted pseudopotential for Tl – application to TlX (X = F, Cl, Br, I)

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Abstract. A relativistic pseudopotential of the energy-consistent variety simulating the Tl^{21+} ($1s - 4f$) core has been generated by adjustment to multiconfiguration Dirac–Hartree–Fock data based on the Dirac–Coulomb–Breit Hamiltonian. Valence ab initio calculations using this pseudopotential have been performed for atomic excitation energies and for spectroscopic constants of the $X0^+$ and $A0^+$ states of TlX (X = F, Cl, Br, I). Comparison is made to experiment and to four-component density functional results.

Key words: Pseudopotential – Spin–orbit potential – Thallium halides

Introduction

Pseudopotentials are routinely used nowadays in calculations for heavy-atom compounds [1, 2]. In spite of the indisputable success of such calculations, approximations are involved in this approach, and a continuous effort is needed to meet demands for increasingly higher accuracy. This does not necessarily mean to modify the basic idea of transferring information from atoms to molecules. However, very often additional approximations are involved, such as extracting the atomic information from a single state only, at an independent-particle level, working in pure *LS* or *jj* coupling, etc. Over the past decade, we have developed an energy-consistent pseudopotential (PP) approach which is, in principle, free from these limitations: only information on valence-energy spectra of near-neutral atoms/ions is needed for modelling the potentials [3]. The reference spectra can be determined at every desired theoretical level (or even taken from experiment). As a reasonable compromise between accuracy requirements and current computational feasibility, we have suggested in previous work [4] using the multiconfiguration Dirac–Hartree–Fock (MCDHF) method, in intermediate coupling, to generate the reference data. We are now developing this into a routine method for setting up PPs.

In the present report, Tl is used as an example of a heavy post-*d* main-group element. Relativistic effects are large, and the atomic ground-state spin–orbit (SO) splitting of 7793 cm^{-1} has important implications for chemical bonding. Thus, most of the theoretical methods dealing with relativistic effects have used Tl as a benchmark case. Nevertheless, there are still unresolved questions. It is clear that relaxation of the $6p$ orbital is important for a quantitative description of atomic SO splitting, but there are conflicting points of view on the amount of electron correlation needed [5, 6]. There is increasing evidence that contributions from the outer-core *d* shell are essential in compounds of post-*d* group 13 elements [7–9], but PPs simulating a frozen Tl^{3+} core seem to yield excellent results for spectroscopic constants of Tl halides [10]. We address these questions here.

While PPs take care of the most important relativistic effects, they do not usually implicitly incorporate electron correlation. On the other hand, density functional theory (DFT) has proven to be able to reliably cover (exchange–)correlation effects, formally at an independent-particle level. Relativistic four-component DFT calculations using the Dirac–Coulomb Hamiltonian have recently been found to be remarkably successful even for *f* elements [11–13]. We now wish to check, by comparison to explicitly correlated valence ab initio PP results, whether this is also the case for heavy main-group compounds.

2 Computational methods

2.1 Pseudopotentials

A relativistic energy-consistent PP for Tl has been derived, using the following atomic valence Hamiltonian:

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$$\mathscr{H} = -\frac{1}{2}\sum_i \Delta_i + \sum_i V_{\mathrm{PP}}(\boldsymbol{r}_i) + \sum_{i<j}\frac{1}{r_{ij}} \tag{1}$$

$$V_{\mathrm{PP}}(\boldsymbol{r}) = -\frac{Z_c}{r} + \sum_{ljk} B^k_{lj}\exp(-\beta^k_{lj}r^2)\mathscr{P}_{lj} \ . \tag{2}$$

The kinetic-energy and electron–electron interaction terms of $\mathscr{H}$ are nonrelativistic, all relativistic effects being implicitly included in the PP, V_{PP}. The long-range behaviour of V_{PP} is governed by the core charge, Z_{c}, i.e., the first term of V_{PP}; we chose a $1s-4f$ core ($Z_{\mathrm{c}}=21$) for Tl, since an explicit treatment of the semicore d shell ($5d$ for Tl) was found to be decisive in our previous calculations for ionic group 13 compounds [7, 8] – additionally promoting the $5s$, $5p$ shells to the valence space is necessitated by the strong interactions between subshells belonging to the same principal quantum number. The short-range part of V_{PP} is described by a semilocal ansatz, with the projection operators $\mathscr{P}_{lj}$ inducing different radial potentials for different angular-momentum quantum numbers l and $j = l \pm 1/2$. The ansatz for the radial potentials, in turn, is a linear combination of Gaussian functions, with the pre-factors and exponents in this expansion chosen in such a way that the atomic valence spectrum derived from Eqs. (1) and (2) is in optimum (in a least-squares sense) agreement with the "reference" valence spectrum determined in all-electron MCDHF calculations.

For Tl, specifically, the reference states were generated from the following nonrelativistic orbital configurations:

Tl^0	$6s^26p^1, 6s^16p^2, 6p^3, 6s^27s^1, 6s^28s^1, 5d^96s^26p^2$
Tl^+	$6s^2, 6s^16p^1, 6p^2, 5d^96s^26p^1$
Tl^{2+}	$6s^1, 6p^1, 6d^1, 7d^1$
Tl^{3+}	$5d^{10}$
Tl^{20+}	$5f^1-8f^1, 5g^1-8g^1$

All relativistic states belonging to these configurations were determined in the intermediate coupling scheme, by MCDHF average-level (AL) calculations using the finite-difference atomic GRASP code [14], and the corresponding valence energies [$E_i - E(\mathrm{Tl}^{21+}, {}^1\mathrm{S}_0)$] constituted the reference data set. The calculations were based on the Dirac–Coulomb–Breit Hamiltonian, where the Breit contribution was treated perturbatively to first order. The PP adjustment was done with a modified version of GRASP, formally putting $c \rightarrow \infty$ and enhancing the stability of the solutions by using routines originally developed for the MCHF code [15] – still, the intermediate coupling induced by the (lj)-dependent PP (Eq. 2) was fully accounted for in the AL calculations. Optimization of the PP parameters (B, β) was done for $l = 0-2$, $l = 3$ and $l = 4$ separately, with weight factors in the least-squares sum of valence-energy deviations proportional to the degeneracy, $2J+1$, of individual relativistic states but renormalized in such a way that each nonrelativistic orbital configuration acquires the same total weight.

The final parameters are given in Table 1. With two terms, $k \leq 2$, in the expansion (Eq. 2) of the radial potentials, we reached typical accuracies of a few hundredths of an electron volt for average valence energies of (nonrelativistic) orbital configurations (Table 2). The PP errors are comparable in magnitude to the contributions of the Breit interaction. The deviations for energy differences between relativistic states within orbital configurations are also of the order of 10^{-2} eV (or smaller) (Table 3). The accuracy achieved at the finite-difference level could easily be improved by more than 1 order of magnitude, simply by increasing the number of adjustable parameters; however, since correlated atomic or molecular calculations are usually performed with finite one- and many-particle basis sets, such accuracy is of little practical value.

As usual, the (lj)-dependent PP of Table 1 can be transcribed to a sum of a one-component scalar-relativistic PP and a SO potential as follows:

$$V_{\mathrm{PP}} = V^{\mathrm{av}}_{\mathrm{PP}} + V^{\mathrm{SO}}_{\mathrm{PP}} \tag{3}$$

$$\begin{aligned} V^{\mathrm{av}}_{\mathrm{PP}} = -\frac{Z_{\mathrm{c}}}{r} + \sum_{lk}\Bigg[&\frac{l}{2l+1}B^k_{l,l-1/2}\exp(-\beta^k_{l,l-1/2}r^2) \\ &+\frac{l+1}{2l+1}B^k_{l,l+1/2}\exp(-\beta^k_{l,l+1/2}r^2)\Bigg]\mathscr{P}_l \end{aligned} \tag{4}$$

$$\begin{aligned} V^{\mathrm{SO}}_{\mathrm{PP}} = \sum_{lk}\frac{2}{2l+1}\Big[&B^k_{l,l+1/2}\exp(-\beta^k_{l,l+1/2}r^2) \\ &-B^k_{l,l-1/2}\exp(-\beta^k_{l,l-1/2}r^2)\Big]\mathscr{P}_l\boldsymbol{ls}\mathscr{P}_l \ . \end{aligned} \tag{5}$$

While the parameter adjustment for the PP was done in numerical atomic calculations excluding basis-set artifacts, a valence basis set has been prepared a posteriori for molecular calculations with standard quantum-chemical program packages. Specifically, we optimized a $(12s12p9d3f2g)/[6s6p4d3f2g]$ atomic natural orbital (ANO) basis set which is available on the Web (http://www.theochem.uni-stuttgart.de).

2.2 Density functionals

A four-component Dirac–Kohn–Sham scheme has been adopted for our density functional calculations,

$$\left[c\sum_i \boldsymbol{\alpha}_i p_i + (\boldsymbol{\beta} - \mathbf{1})c^2 + V_{\mathrm{ext}} + V_{\mathrm{H}} + V_{\mathrm{xc}}\right]\varphi_j = \epsilon_j\varphi_j \ , \tag{6}$$

where the φ_j are four-component spinors; $\boldsymbol{\alpha}_i$, $\boldsymbol{\beta}$ are the usual Dirac matrices, and V_{ext}, V_{H}, V_{xc} denote the electron–nucleus, Hartree, and exchange–correlation potentials, respectively. The exchange–correlation functionals used in the present work are the local density approximation (LDA) [16] one and the Becke–Perdew (BP) gradient-corrected one [17, 18]. In the atomic calculations reported here the functionals were supplemented by a self-interaction correction [19].

We use the implementation of these methods in the Beijing density functional program package [20]. Here, numerical atomic spinors are used for describing atomic cores, while the basis sets for valence spinors are combinations of numerical atomic spinors and kinetically balanced Slater-type functions (STF). Specifically, we used the following cores: $1s^2-4d^{10}$ for Tl and I, $1s^2$ for F, $1s^2-2p^6$ for Cl, and $1s^2-3d^{10}$ for Br, and added double-zeta (s, p, d) and single-zeta (f) STFs for each valence spinor of all the elements. For TlF, we checked that addition of further diffuse Tl $6p$ and $6d$, $5f$ polarization functions does not change the spectroscopic constants discernibly.

3 Atomic results

The first application of our newly generated MCDHF-adjusted pseudopotential for Tl concerns the atomic

Table 1. Parameters of the multiconfiguration Dirac–Hartree–Fock (*MCDHF*)-adjusted energy-consistent small-core pseudopotential (*PP*) for Tl, in atomic units. For explanation, see text

l	j	B^1_{lj}	β^1_{lj}	B^2_{lj}	β^2_{lj}
s	1/2	281.28466295	12.16780538	62.43425079	8.29490948
p	1/2	216.89775826	9.89107213	13.90022492	7.15149226
p	3/2	216.83705577	9.00339077	14.01263338	5.17286483
d	3/2	89.85759781	7.13021776	25.95484818	5.41756997
d	5/2	89.84932188	6.92690605	25.97303670	5.13868111
f	5/2	36.92613983	5.62639933	6.80196239	2.87494625
f	7/2	36.93203589	5.54895176	6.81957975	2.82145078
g	7/2	−16.86270229	6.67905747	−17.54548297	7.20928381
g	9/2	−17.17303509	6.70683463	−16.66714250	7.07096378

Table 2. Relative energies for the average of a nonrelativistic configuration, from finite-difference MC all-electron (*AE*) DHF, and PP quasirelativistic HF (*QHF*) calculations. In the AE work the Dirac–Coulomb (*DC*) Hamiltonian was treated variationally, and the Breit term (*B*) was treated to first-order perturbation theory. All energies are in electron volts

Configuration		AE DHF		PP
		DC	DC + B	QHF
Tl^{1-}	$d^{10}s^2p^2$	0.216	0.216	0.215[a]
Tl	$d^{10}s^2p^1$	0.000	0.000	0.000
	$d^{10}s^1p^2$	6.335	6.325	6.312
	$d^{10}p^3$	14.553	14.533	14.511
Tl^{1+}	$d^{10}s^2$	4.972	4.968	4.988
	$d^{10}s^1p^1$	11.577	11.563	11.563
	$d^{10}p^2$	20.075	20.049	20.037
	$d^9s^2p^1$	20.008	20.036	20.111
Tl^{2+}	$d^{10}s^1$	23.394	23.368	23.396
	$d^{10}p^1$	32.118	32.080	32.089
Tl^{3+}	d^{10}	51.572	51.516	51.555
	d^9s^1	62.146	62.131	62.248[a]
Tl^{4+}	d^9	101.766	101.713	101.840[a]

[a] Configuration not considered in the PP adjustment

Table 3. Selected fine structure splittings from AE and PP finite-difference calculations. For details see Table 2. All values are in reciprocal centimetres

	Level		AE DHF		PP
			DC	DC + B	QHF
Tl	$d^{10}s^2p^1$	$^2P_{1/2}$	0	0	0
		$^2P_{3/2}$	7640	7505	7446
	$d^{10}s^1p^2$	$^4P_{1/2}$	0	0	0
		$^4P_{3/2}$	3816	3733	3704
		$^4P_{5/2}$	8631	8532	8455
		$^2D_{3/2}$	22522	22418	22515
		$^2D_{1/2}$	26344	26186	26191
		$^2S_{1/2}$	32538	32484	32628
		$^2P_{1/2}$	41041	40874	40999
		$^2P_{3/2}$	43624	43442	43607
Tl^{1+}	$d^{10}s^1p^1$	$^3P_0$	0	0	0
		$^3P_1$	3486	3450	3408
		$^3P_2$	12115	11945	11793
		$^1P_1$	35607	35473	35551
Tl^{2+}	$d^{10}p^1$	$^2P_{1/2}$	0	0	0
		$^2P_{3/2}$	13536	13338	13183

Table 4. Influence of correlation level and outer-core treatment on the $^2P_{1/2} - {}^2P_{3/2}$ spin–orbit (*SO*) splitting of the Tl $6s^26p$ ground state, from PP calculation using (*A*) the *spdf* atomic natural orbital basis (see text) and (B) the same set with p, d functions uncontracted. All values are in reciprocal centimetres

	A	B
Self-consistent field[a]	6580	–
CIS[b], 5*s*5*p*5*d* frozen	7938	8280
CIS[b], 5*s*5*p* frozen	7576	7901
CIS[b], 5*s* frozen	7041	7268
CISD[c], 5*s*5*p*5*d* frozen, valence doubles only[d]	7613	–
CISD[c], 5s frozen, valence doubles only[d]	6791	–
CISD[c,e], 5*s* frozen	7530	–
Exp.	7793	

[a] Spin–orbit configuration interaction in the reference space of the degenerate ^2P states

[b] Spin–orbit configuration interaction with all single excitations from the reference space

[c] Spin–orbit configuration interaction with all single and double excitations from reference space, restrictions are explicitly mentioned above

[d] Double excitations involving the 5*p*, 5*d* shells are excluded

[e] Core–core excitations involving simultaneous excitations from two orbitals of the 5*p*, 5*d* shells are excluded

ground-state $^2P_{1/2} - {}^2P_{3/2}$ SO splitting. The calculations were done using Pitzer's SO configuration-interaction (CI) code [22] and employing the (partially decontracted, see later) $(12s12p9d3f)/[6s6p4d3f]$ ANO basis set of Sect. 2. The results are collected in Table 4.

The CI starts from a one-component self-consistent-field (SCF) calculation (without SO potential); thus, orbital relaxation due to SO effects only comes in with single excitations at the CI level (CIS). In fact, degenerate SO perturbation theory within the reference space of the three ^2P states yields a SO splitting smaller than experiment by 1200 cm^{-1}. Including single excitations from the valence shell and outer-core 5*p*5*d* orbitals reduces this deviation to 750 cm^{-1}, or even 520 cm^{-1}, when a more flexible contraction of the ANO basis (p, d sets fully uncontracted) is used. It turns out, however, that relaxation of the 6*p* orbital alone ($6p \rightarrow 6p_{1/2}, 6p_{3/2}$) highly exaggerates the effect – it overshoots by 1000 cm^{-1} with respect to the calculation mentioned before! Thus, calculations which do not account for SO relaxation effects of the outer-core shells ($5p \rightarrow 5p_{1/2}$, $5p_{3/2}$; $5d \rightarrow 5d_{3/2}, 5d_{5/2}$) should be considered with some reservation. Genuine correlation effects come in with double excitations. In line with other authors [5, 23], we find that valence correlation involving the 6*s*6*p* shell leads to a moderate reduction in SO splitting, by about 250 cm^{-1}, while core-valence correlation, i.e. simultaneous excitations from the valence shell and the outer-core 5*p*5*d* shells, overcompensates this reduction and leads to a net increase in SO splitting, due to electron correlation, by about 500 cm^{-1}. Our final result is still too low, compared to experiment, by 260 cm^{-1}, but most of this deficiency (230 cm^{-1}) can be attributed to the lack of flexibility of the ANO basis, as monitored by the effect of decontraction at the CIS level.

Comparing our results with other theoretical calculations from the literature, we find reasonable agreement with the PP and all-electron data of Refs. [5, 6, 22–24]. Rakowitz and Marian [5] reported first-order perturbation theory (FOPT) and valence (6*s*6*p*)-correlated results of about 6400 and about 7500 cm^{-1}, which agree with our values within 200 cm^{-1}. Large-core (three valence-electron, 5*s*5*p*5*d* in core) PPs [22, 23, 25] lead to FOPT values around 7000 cm^{-1} and, eventually, to quite good agreement with experiment (to about 100–500 cm^{-1}). This is consistent with our small-core PP results – freezing the 5*s*5*p*5*d* core, we obtain a SO splitting of 7613 cm^{-1}, i.e. only 200 cm^{-1} below the experimental value; however, the good agreement is to some extent fortuitous, since it relies on the mutual cancellation of outer-core relaxation and outer-core–valence correlation effects. Medium-core (13-valence-electron, 5*s*5*p* in core)

PPs [23, 25, 26], on the other hand, seem to be less successful: the ground-state SO splitting is underestimated by 500–1300 cm^{-1}, depending on the adjustment procedure. In order to gain more detailed insight, we performed calculations with the most recent of these potentials [26], using an optimized basis set of the same size as used for our own PP of this work. We found considerable differences to the results with our small-core PP at nearly every stage considered: the FOPT value differs by around 800 cm^{-1}, valence and core relaxation effects are only half as large, and the relative importance of valence and core–valence correlation is reversed. This is not unexpected, since $6p-5d$ interactions should be strongly affected by the elimination of (all) the radial nodes of the $6p$ orbital, including that in the region where the $5d$ orbital has its maximum.

Let us now turn, more generally, to PP and all-electron density functional results for a variety of atomic energy differences of neutral Tl and its ions (Table 5). Since relativistic effects at the level of the Dirac–Coulomb Hamiltonian are fully recovered in the four-component DFT treatment, and a small-core definition is used for the frozen core, the DFT results essentially directly monitor the accuracy of the density functionals for valence exchange and correlation effects. It is seen that deviations from experiment are small (less than 0.3 eV for ionization potentials, around 400 cm^{-1} for the ground-state SO splitting), as far as energy differences involving only $6s, 6p$ orbitals are concerned. Much larger, but quite systematic, errors arise for excitations involving the $5d$ shell, however; they are underestimated by 0.8–0.9 eV. The errors are connected to the well-known deficiency of the LDA to describe accurately intershell exchange interactions for orbitals with different numbers of nodes [27]. Deviations between the two density functionals used (LDA, BP), on the other hand, are relatively insignificant (around 0.1 eV), with the BP functional providing a slightly better description. The PP calculations were performed at the CI level with single and double excitations including a Davidson correction, and at the averaged coupled-pair functional (ACPF) level, using the program RELMOL. The starting point was a set of Kramers-restricted spinors, represented in a generalized contracted $(13s13p9d1f)/\ [7s9p4d1f]$ basis set. Different contractions were used for the occupied spinors of $j=l-1/2$ and $j=l+1/2$ symmetry. The electron affinity and the ionization potentials are systematically underestimated by 0.2–0.3 eV. The errors are mainly due to deficiencies in the one-particle basis set and the lack of triple excitations: on adding SO corrections extracted from the ACPF calculations to coupled-cluster singles and doubles results including a perturbative estimate of triples [CCSD(T)], which were obtained with an uncontracted $(14s14p10d8f6g)$ basis set, the agreement with the experimental ionization potentials is improved significantly, whereas the electron affinity increases only slightly. Excitation energies are accurate within 0.1 eV as far as the Tl^{3+} d^{10} core remains untouched, whereas those for Tl^{3+} $d^{10} \rightarrow d^9s^1$ are too high by 0.2–0.3 eV.

4 Molecular results

The next application of our small-core Tl PP concerns Tl*X* (*X* = F, Cl, Br, I), i.e., ionic compounds of the type where outer-core contributions should be large, according to our previous studies on group 13 compounds.

Table 5. Electron affinity (*EA*), ionization potentials (*IP*) and excitation energies (*EE*), as evaluated in two-component PP and four-component density functional (*DFT*) calculations. *PPa* and *PPb* denote two-component configuration interaction and averaged coupled-pair functional results, respectively, using a $(13s13p9d1f)/[7s9p4d1f]$ generalized contracted basis set. *PPc* corresponds to one-component coupled-cluster singles and doubles with perturbative estimate of triples [*CCSD(T)*] results obtained with an extended $(14s14p10d8f6g)$ basis set and corrected for SO coupling according to approach b. *DFTa*, *DFTb* stand for the local density approximation (*LDA*) and Becke–Perdew (*BP*) exchange–correlation functionals, respectively. All energies are in electron volts

		PPa	PPb	PPc	DFTa	DFTb	Exp.[a]
Tl $^2P_{1/2}$	EA	0.08	0.16	0.20	0.28	0.34	0.40[b]
	EE($^2P_{3/2}$)	0.97[c]	0.91[c]		1.03	1.01	0.97
	IP	5.78	5.83	6.02	5.85	5.93	6.11
Tl$^+$ $^1S_0$	IP	20.11	20.12	20.36	20.41	20.41	20.42
Tl^{2+} $^2S_{1/2}$	EE($^2P_{1/2}$)	8.05	8.02	7.96	7.95	7.94	7.95
	EE($^2P_{3/2}$)	9.81	9.76		10.01	9.96	9.79
	EE($^2D_{5/2}$)[d]	8.09	8.09	8.11	7.27	7.37	
	EE($^2D_{3/2}$)[d]	10.33	10.33		9.64	9.73	
	IP	29.54	29.54	29.78	30.16	30.19	29.8
Tl^{3+} $^1S_0$	EE($^3D_3$)	9.60	9.59	9.60	8.38	8.40	9.31
	EE($^3D_2$)	10.07	10.06		8.81	8.87	9.75
	EE($^3D_1$)	11.82	11.82		10.71	10.74	11.61
	EE($^1D_2$)	12.25	12.27		11.14	11.21	11.99
	IP	50.37	50.36	50.55	50.03	50.12	50.7

[a] Experimental values from Ref. [33]
[b] Calculated value from Ref. [34]
[c] $5s5p$ frozen due to program limitations
[d] $5d^96s^2$ configuration

In a preliminary series of calculations, we applied various PPs at different theoretical levels for the TlCl ground state (Table 6); in these calculations, PPs were used for Tl only, but not for Cl, in order to concentrate on possible deficiencies in the simulation of the heavy core. At the SCF level, using large basis sets and applying our previously published one-component small-core (21-valence-electron) [23] and large-core (three-valence-electron) [22] PPs, we indeed find discrepancies. In the large-core case, the bond length, R_e, is smaller by 0.02 Å than in the small-core reference calculations, while the frozen-core approximation (implicitly involved in the large-core PP!) leads to an increase in R_e by 0.02 Å when explicitly introduced in the reference calculations. This is in line with our previous experience for group 13 compounds [7, 8] and can be explained by a too weak closed-shell repulsion when the valence electrons of a partner atom come into direct contact with a core simulated by a PP.

Compared to experiment, the SCF bond length is still far too long (by 0.06 Å with the most reliable of the PPs, the 21-valence-electron PP). Electron correlation, treated in our calculations at the CCSD(T) level, helps to reduce this deviation. However, it turns out that practically all the correlation effects on R_e involve the outer-core Tl 5*d* shell, and extended basis sets including g functions on Tl and Cl are necessary to get a sizable reduction of the gap to the experimental value. It is to be noted that the simple semiempirical device of adding a core-polarization potential (CPP) [23] to a calculation with a frozen Tl^{3+} (5*s*5*p*5*d*) core – which requires much less basis-set effort – also leads to quite reliable results, mimicking the R_e value of our best calculation to about 0.01 Å. The latter agrees with experiment to 0.02 Å in R_e, around 5 cm^{-1} in ω_e, and D_e is practically exact (when the atomic SO splitting is corrected for, using experimental atomic data).

Table 6. PP results for bond lengths, R_e (Å), vibrational constants ω_e (cm^{-1}), and binding energies, D_e (kJ/mol) of the TlCl ground state, from one-component calculations using different basis sets/valence ab initio methods

	R_e	ω_e	D_e^a
Self-consistent field			
21-valence-electron-PP[b]	2.545	264	265
3-valence-electron-PP[c]	2.525	243	263
21-valence-electron-PP[b] Tl 5*s*5*p*5*d* frozen[d]	2.567	269	261
CCSD(T)			
21-valence-electron-PP[b,e]	2.530	272	357
21-valence-electron-PP[b] extended basis[f]	2.506	279	370
21-valence-electron-PP[b] core-polarization potential for frozen Tl 5*s*5*p*5*d* core[d,g]	2.519	277	360
Exp.	2.485	284	370

[a] Calculated values corrected by experimental atomic SO splitting [33]

[b] Ref. [23], basis set (11*s*11*p*8*d*3*f*)/[6*s*6*p*4*d*3*f*] for Tl; all electrons explicitly treated, augmented valence triple-zeta [35] basis set for Cl

[c] Ref. [22], basis set (8*s*8*p*8*d*) for Tl; Cl basis set as in footnote b

[d] Tl^{3+} core frozen with orbitals from atomic ground-state calculation

[e] Cl(1*s* − 2*p*) shells and Tl(5*s*, 5*p*) shells not correlated

[f] Additional 2 g functions on Tl, augmented quadruple-zeta [35] basis set for Cl; Tl (5*s*, 5*p*) shells included in correlation treatment

[g] Static/dynamic polarization of Tl^{3+} core described by means of a core-polarization potential [23]

Comparing our results to previously published theoretical data by other authors [10, 28], we note considerable differences. Schwerdtfeger and Ischtwan [10] found excellent agreement with experiment, in quadratic CI (QCI) calculations using a three-valence-electron PP for Tl; their R_e are accurate to 0.01 or 0.001 Å at the SCF and QCI levels, respectively. It is clear that this is due to a fortuitous error compensation: the three-valence-electron PP underestimates the Tl^+–Cl^- Pauli repulsion (even more than our own one [22]), and this error is compensated by the neglect of core (Tl5*d*)–valence correlation. Li et al. [28], on the other hand, using the 13-valence-electron PP of Ross et al. [25], found a TlCl ground-state R_e longer than experiment by 0.07 Å. Again, the diagnosis is clear: the Pauli repulsion is essentially correct now (leading to an elongation of R_e), while the reduction due to core–valence correlation could not be realistically described with the rather small [4*s*4*p*3*d*] Tl basis set used in Ref. [28].

In a second series of calculations, we evaluated spectroscopic constants for the four Tl*X* compounds ($X = F$, Cl, Br, I) (Table 7). In each case, four theoretical levels were considered. Firstly, valence CCSD(T) calculations were performed using two different scalar-relativistic small-core PPs for Tl, that of Ref. [23], and our newly generated MCDHF-adjusted one of Table 1; additional PPs for the halogen atoms [29, 30] were used in these calculations, and all valence electrons (including Tl5*s*5*p*) were correlated; in the case of Br and I, we supplemented the PPs by CPPs, in order to account for core–valence correlation effects originating from the halogen X^{7+} core. Secondly, four-component relativistic DFT calculations were performed using two different exchange–correlation functionals, LDA and BP. Let us now compare calculated bond lengths with experimental values. It turns out that the ab initio PP treatment leads to R_e values for the heavier halogens which are systematically too large by 0.01–0.02 Å. Among themselves, the PP results are virtually identical (to less than 0.004 Å), showing that in the one-component case adjustment to scalar-relativistic reference data in Ref. [23] and the fully relativistic MCDHF adjustment presented here (with subsequent one-component averaging) are of comparable accuracy. We claim that the remaining deviations from experiment are mainly due to the influence of SO coupling: on adding SO contributions from Kramers-restricted HF calculations to the CCSD(T) potential curves, the largest deviation from experiment is 0.006 Å. SO effects are included in the DFT calculations, but there is a systematic underestimation of the experimental R_e by around 0.02–0.03 Å in the LDA case, while bond lengths become too long by 0.04–0.05 Å with the BP functional – thus, the errors due to the approximate nature of the density functionals used are not negligible and, in fact, are considerably larger than those of the PPs. The dissociation energies, D_e, agree with experiment to better than 10 kJ/mol with the two scalar-relativistic PPs, deviations among them being very small again (less than 3 kJ/mol). As is well known, the LDA

Table 7. Bond lengths, R_e (Å), vibrational constants, ω_e (cm^{-1}), and binding energies, D_e (kJ/mol), from PP and DFT calculations of TlX (X = F, Cl, Br, I); PPa and PPb denote one-component valence CCSD(T) results with the 21-valence-electron PPs of Ref. [23] and this work, respectively; PPc denotes PPb including SO corrections; DFTa and DFTb stand for four-component density functional results with the LDA and BP exchange–correlation functionals, respectively

		PPa[a]	PPb[b]	PPc[c]	DFTa	DFTb	Exp.[d]
TlF	R_e	2.086	2.085	2.078	2.084	2.130	2.084
	ω_e	477	478	481	481	447	477
	D_e	517	514	450	540	487	444
TlCl	R_e	2.500	2.497	2.486	2.465	2.525	2.485
	ω_e	280	282	283	293	270	284
	D_e	435	433	367	418	370	370
TlBr	R_e	2.635	2.631	2.618	2.596	2.661	2.618
	ω_e	191	191	194	200	184	192
	D_e	399	398	321	369	319	331
TlI	R_e	2.834	2.830	2.813	2.789	2.863	2.814
	ω_e	150	150	152	154	142	(150)
	D_e	356	354	262	312	263	267

[a] Basis sets: $(11s11p8d3f2g)/[6s6p4d3f2g]$ for Tl, $(7s7p4d3f2g)/[6s6p4d3f2g]$ for halogens

[b] Basis sets: $(12s12p9d3f2g)/[6s6p4d3f2g]$ for Tl, $(7s7p4d3f2g)/[6s6p4d3f2g]$ for halogens

[c] Calculated D_e values have been corrected by experimental atomic ground-state SO splittings [33]; SO contributions extracted from two-component Kramers-restricted HF calculations have been added to the CCSD(T) PPb potential curves

[d] From Ref. [36]

overestimates dissociation energies considerably (by 40–100 kJ/mol in the present application); with gradient corrections (BP), the results are much better ($\Delta D_e \leq 10$ kJ/mol for TlCl to TlI), but are still off by 40 kJ/mol in the case of TlF. It should be mentioned that the atomic calculations were performed for moment-polarized spherical densities. This was found to yield good results for heavy elements, such as lanthanides [11, 20] and actinides [13]. Allowing for symmetry-breaking would reduce the BP binding energy for TlF from 487 kJ/mol (Table 7) to 457 kJ/mol, the latter value being close to the SO-ZORA result [31] (and only 13 kJ/mol off the experimental one). This effect is quite small for F at the LDA level and is also small for the heavier halogen homologues at both the LDA and BP levels.

Table 8. PP (MCDHF-adjusted T1 21-valence-electron PP of this work, PPs of Refs. [29, 30] for the halogens; for basis sets, see Table 7) results (including SO coupling) for bond lengths, R_e (Å), vibrational constants, ω_e (cm^{-1}), and term energies, T_e (cm^{-1}), of the excited A0$^+$ state of TlX (X = F, Cl, Br, I), determined at the CCSD(T)/complete-active-space self-consisted-field levels (see text), experimental values [36] in parentheses

	R_e	ω_e	T_e^a
TlF	2.038 (2.049)	467 (436)	35470 (35186)
TlCl	2.464 (2.473)	232 (223)	31442 (31049)
TlBr	2.650 –	123 (108)	29356 (29192)
TlI	2.985 –	61 (30)	25812 (26250)

[a] Adiabatic A0$^+$ ← X0$^+$ separation

Excited states, including SO effects, are at the focus of our last set of calculations. In contrast to the nondegenerate X0$^+$ ground state of the Tl monohalides ($^1\Sigma^+$ in ΛS coupling), the first excited A0$^+$ state is predominantly derived from the degenerate $^3\Pi(5\sigma \rightarrow \pi^*)$ state and consequently undergoes significant SO splitting. The π^* orbital occupied in the $^3\Pi$ state is essentially the Tl $6p\pi$ orbital, so supplementing the scalar-relativistic PP at Tl by SO terms is imperative – we used our new MCDHF-adjusted 21-valence-electron PP here which naturally comprises both parts; however, in order to make the treatment consistent, we also included SO potentials at the halogen atoms [30]. The basis sets employed were the same as for the ground-state calculations (Table 7). We first calculated the $^1\Sigma^+ - {}^3\Pi$ separation at the (restricted open-shell) CCSD(T) level, with orbitals taken from a state-averaged complete-active-space SCF (CASSCF) calculation; the active space in the latter was $(5\sigma, \pi^*)$ and all orbitals except Tl $5s5p$ were correlated in the former. SO matrix elements between the $^3\Pi_{x,y}$ and $^1\Sigma^+$ states were determined in the next step at the CASSCF level. The $^3\Pi - {}^1\Sigma^+$ matrix elements were small (leading to a lowering of the TlCl ground state, e.g., by only about 200 cm^{-1}) and were neglected in the following. The matrix elements within the triplet space are quite large, in contrast; since we could not explicitly introduce orbital relaxation here, for technical reasons – if not mentioned otherwise, we used the program package MOLPRO [32] for all the molecular calculations of the present section – , we scaled the $^3\Pi_x - {}^3\Pi_y$ matrix element by a semiempirical factor determined by the ratio of experimental and CASSCF SO splitting for the Tl atom. (This scaling lowers the A0$^+$ state with respect to the $^3\Pi$ state by around 600 cm^{-1} for TlCl). Diagonalizing the SO matrix just described, we obtain properties of the TlX A0$^+$ state as well as A0$^+$ ← X0$^+$ excitation energies (Table 8). Compared to experiment, the results for bond lengths are of about the same accuracy as for the ground state ($\Delta R_e \sim 0.01$ Å), although the deviations are of opposite sign now; the vibrational frequencies are too large by 10–30 cm^{-1}; the errors in the excitation energies are less than 400 cm^{-1} (2%). For TlCl, comparison is also possible to the work of Li et al. [28]. Their results ($R_e = 2.476$ Å, $\omega_e = 248\ \mathrm{cm}^{-1}$, $T_e = 30890\ \mathrm{cm}^{-1}$) are quite similar to ours. Why their $R_e(\mathrm{A}0^+)$ is virtually identical to the experimental value, while $R_e(\mathrm{X}0^+)$ was off by 0.07 Å, is unclear, though.

5 Conclusions

A relativistic PP for the Tl^{21+} $(1s-4f)$ core (and a corresponding optimized valence basis set) has been generated without reference to orbital data – the reference data were total energies of ground and excited states of the neutral atom and near-neutral ions, evaluated at the MCDHF level, including SO effects in intermediate coupling. This is a logical continuation of our previous adjustment of scalar-relativistic energy-consistent PPs to valence spectra from quasirelativistic *LS*-coupled HF data. The newly derived PP has been applied, in valence ab initio correlated calculations, to the determination of the atomic excitation/ionization energies and to spectroscopic constants of the ground ($\mathrm{X}0^+$) and first excited ($\mathrm{A}0^+$) states of Tl monohalides. For the atomic SO splitting, an accuracy of around 200 cm^{-1} was achieved, while for the molecules maximum deviations from experiment were 0.01 Å for bond lengths, 30 cm^{-1} for vibrational frequencies, 10 kJ/mol for dissociation energies, and 400 cm^{-1} for excitation energies. The remaining errors are likely to be due to approximations in the valence and outer-core shells rather than to deficiencies of the PP.

The possibility to treat valence interaction in a simplified way has been explored by means of four-component DFT calculations. Satisfactory agreement with experiment is achieved in many cases; for the quantities mentioned above, for example, the maximum errors are 300 cm^{-1} (Tl) and 0.05 Å, 30 cm^{-1}, and 40 kJ/mol (TlX), with a gradient-corrected density functional; however, errors up to almost 1 eV arise when excitations from the outer-core Tl 5*d* shell are considered. The outer-core contributions in Tl compounds are not negligible in any case, and three-valence-electron PPs can yield reasonable results only due to some fortuitous error cancellation.

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