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*Letter*

# Relativistic calculations on thallium hydride

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**Abstract.** The spectroscopic parameters of the ground state of thallium hydride are obtained using the four-component relativistic Dirac–Coulomb–Gaunt–coupled-cluster wave function with single and double excitations and an estimated triples correction method. Core correlation effects make the bond weaker but have little effect on the bond length. Inclusion of the distance dependence of the Gaunt part of the two-electron Breit interaction has an opposite but smaller effect on these properties.

**Key words:** Relativistic calculations – Dirac–Hartree–Fock – Coupled-cluster wavefunction with single and double excitations and an estimated triples correction–TlH

## 1 Introduction

The thallium hydride molecule has emerged as one of the standard test systems for quantum chemical methods that attempt to include the description of relativistic effects. TlH is small enough to lend itself to even the more demanding methods, yet it still presents many of the challenges found in larger systems. Also, reliable spectroscopic data are available [1, 2] for comparison with computational results. The various computational results for this system have been reviewed by Hess and Marian [3]. In a recent article Seth et al. [4] reported results from correlated relativistic four-component calculations using a coupled-cluster wavefunction with single and double excitations and an estimated triples correction [CCSD(T) [5]]. These results must be regarded as representative of the highest obtainable accuracy available up to now.

Recent advances in program technology coupled with the increasing availability of parallel processing now offer the opportunity to proceed beyond this level of accuracy. The calculation by Seth et al. was restricted to single-node software (presently parallelized versions of the four-component programs MOLFDIR [6] and DIRAC [7] are available), allowing the use of larger basis sets and more extensive correlation. The aim of this work is therefore twofold: firstly, to establish limit values for the bond length and force constant of TlH from the independent particle model as represented by high-quality Dirac–Fock calculations; secondly, to fully exploit the presently available technology for correlated calculations using large uncontracted basis sets and including parts of the core correlation.

## 2 Computational details

### *2.1 Method*

The first set of calculations were carried out using the Hartree–Fock (HF) method based on the four-component Dirac–Coulomb (DC) Hamiltonian [6, 8] – an approach referred to by us as DC–HF. The equations were solved via basis set expansion in a large uncontracted Gaussian basis set using the integral-direct DIRAC [7] program system. In the DC–HF calculations there is a negligible contribution to the spin–orbit and spin–spin effects from two-electron integrals involving only small component functions – the $(SS|SS)$ class of integrals [9]. We have therefore discarded these integrals from our calculations. The electron repulsion potential from these terms has been incorporated as the Coulomb repulsion between the atomic small component charge densities [9]. For the DC–HF this approximation leads to a decrease in the bond length of 0.04 pm and a decrease of 0.1–0.3 N/m in the force constant.

Following the HF step we treat electron correlation at the CCSD(T) level of theory using the no-pair coupled–cluster method [10]. Here we also investigate the effect of core correlation by correlating 14, 20, or 36 electrons, respectively. Virtual orbitals with energies above 10 $E_h$ were excluded from the virtual space in all calculations. For correlated calculations basis set superposition errors (BSSE) were corrected using the counterpoise method [11].

The second set of calculations were done with the MOLFDIR [6] electronic structure code in order to study the importance of the Gaunt correction to the Coulomb two-electron interaction. We performed HF calculations using contracted basis sets for both the DC and DC–Gaunt (DCG) Hamiltonians. The difference in energy between these two types of calculations gives the magnitude of the Gaunt correction to the energy as a function of bond length. These energy corrections were then used to improve the potential-energy curves obtained from the first set of calculations.

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### *2.2 Basis sets*

For the DC–HF calculations we used several different basis sets. Two of these were dual family sets derived in DC–HF calculations on the atoms [12]. The smaller of these was a (23,21,15:8,10:10) set which was supplemented with diffuse s and p functions of exponents 0.04 and 0.02 respectively, and the d range was extended by including one more exponent from the s set.[1] The final set was then of the size (24,22,16:8,10:10). To investigate the effect of f functions at this level, we derived a second set which was similar, but containing 12f functions and with no diffuse p added. The final size was (24,21,16:8,12:10). In addition, we also used the large even-tempered set employed previously by Quiney et al. [13]: this has the size (34,34,16,9). Finally we used a nonrelativistically optimized family set of size (22,19,13:9,8:8); this set was also used for the nonrelativistic calculations (vide infra). Hydrogen was described by an (8,1) basis throughout the DC–HF calculations, where all basis sets were used uncontracted, and small component basis sets were generated by kinetic balance [12].

For the correlated calculations, the uncontracted thallium basis set was derived from the first of the relativistically optimized sets referred to earlier, but supplemented with family g functions for a (24,22,16,10,2) set for the large-component functions. To obtain a set which could be used with MOLFDIR to study the effect of the Gaunt interaction, this set was generally contracted to (9,12,5,3) large component functions, providing an approximate triple-zeta description for the valence. The deletion of the two uncontracted g functions probably gives the largest source of errors, but this should not influence the differential Gaunt effect that we study in these calculations. For the correlated calculations the hydrogen basis was (8,2,1), which was contracted to (4,2,1) for the MOLFDIR calculations.

### *2.3 Potential-energy curves*

Potential-energy curves on an evenly spaced grid of TlH bond lengths ranging from 185.5 to 190.0 pm were calculated at the DC–HF and CCSD(T) levels of theory. The minimum was found using a quartic polynomial fit, after which the harmonic frequency was obtained by a quadratic fit using three points spaced 0.5 pm around the minimum. The BSSE correction was applied prior to fitting the curve so that its effect on the force constants and bond length is taken into account. No BSSE correction was applied for uncorrelated calculations, as initial test runs showed the error to be insignificant at that level.

## 3 Results and discussion

The results of our DC–HF calculations are presented in Table 1. For comparison, results from nonrelativistic calculations and from first-order perturbation calculations (mass–velocity and Darwin terms, MVD) are included. All the basis sets tried give DC–HF bond lengths within 0.3 pm at this level, a range that also includes the result by Seth et al. [4]. The relativistically optimized sets give the shortest bond lengths and may be better able to account for the relativistic core contraction than the nonrelativistic set and the large even-tempered set. Force constants as well as frequencies similarly fall in a very narrow range, although it is interesting to note that the nonrelativistic and MVD values are also very close to the DC–HF results. We conclude that the DC–HF limit values should be found within the ranges displayed in Table 1.

**Table 1.** Results of Dirac–Coulomb (*DC*)–Hartree–Fock (*HF*) calculations

| Basis set used | $R_e$ (pm) | $k_e$ (N/m) | $\omega$ (cm$^{-1}$) |
|---|---|---|---|
| Ref. [4] | 186.9 | 124 | 1454 |
| (24,22,16:8,10:10) | 186.9 | 124.0 | 1454 |
| (24,21,16:8,12:10) | 186.9 | 122.4 | 1445 |
| (34,34,16,9) | 187.2 | 121.8 | 1441 |
| (22,19,13:9,8:8) | 187.2 | 122.8 | 1447 |
| (24,22,16,10,2) | 187.0 | 123.7 | 1447 |
| Nonrelativistic | 194.9 | 126.4 | 1468 |
| Mass–velocity and Darwin | 189.7 | 122.1 | 1442 |

**Table 2.** Results of correlated relativistic calculations

| Method | $R_e$ (pm) | $k_e$ (N/m) | $\omega$ (cm$^{-1}$) | $D_e$ (ev) |
|---|---|---|---|---|
| MP2 [4] | 186.2 | 121 | 1437 | 1.83 |
| DC–CCSD(T) [4] | 188.5 | 111 | 1376 | 2.07 |
| DC–CCSD(T) 14 | 187.6 | 113.3 | 1385 | 2.00 |
| DC–CCSD(T) 20 | 187.4 | 112.1 | 1378 | 1.98 |
| DC–CCSD(T) 36 | 187.4 | 111.1 | 1371 | 1.98 |
| DCG–CCSD(T) 36 | 187.7 | 111.9 | 1376 | 2.06 |
| Exp [1, 2] | 186.8 | 114.4 | 1391 | 2.06 |

Our DC–CCSD(T) 14electron results (14 active electrons) are in good agreement with the values published by Seth et al. [4] using the same method with contracted basis sets. This demonstrates the adequacy of their contraction scheme. The additional two g functions in our basis do not influence the result much relative to the values of Seth et al.

Core correlation effects have been less extensively studied using ab initio methods. In some of the effective-core-potential calculations [14, 15], these effects are accounted for via a core-polarization potential, but in these cases the ten *d* electrons were also included into the core. Especially, the correlation of the 5*d* and 4*f* orbitals requires an extensive basis set, a condition that we try to fulfill by using uncontracted functions and by having two g functions (exponents 1.61 and 0.663) in the basis. Still the BSSE correction is substantial (of the order of 3 pm on the bond length and 4 N/m on the force constant), indicating that we have not reached basis set completeness yet. The final core correlation effect, defined as the difference between the 14- and 46-electron calculations, hardly affects the bond length (shorter by 0.2 pm) but weakens it substantially by −2.3 N/m.

The effect of core correlation is counteracted by the Gaunt interaction, which shifts the calculated values in the opposite direction, making the bond slightly longer (0.3 pm) and weaker (1 N/m). The final DCG–CCSD(T) values obtained with 36 active electrons and corrected for both BSSE and the distance dependence of the Gaunt interaction are in quite good agreement with experiment.

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[1] For a dual family basis, the notation (23,21,15:8,10:10) denotes that there are 23s, 21p, 15d and 10f functions. The exponents of the d functions are taken from the s set, such that the highest d exponent coincides with s exponent number 8, and the f exponents are from the p set, with the highest f exponent equal to p exponent 10.

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## References

1. Grundström B, Valberg P (1937) Z Phys 108: 326
2. Urban RD, Bahnmaier AH, Magg U, Jones H (1989) Chem Phys Lett 158: 443
3. Hess BA, Marian CM (1999) In: Jensen P, Bunker PR (eds) Computational molecular spectroscopy. Wiley, Chicester, p 169
4. Seth M, Schwerdtfeger P, Faegri K Jr (1999) J Chem Phys 111: 6422
5. Scuseria GE, Lee TJ (1990) J Chem Phys 93: 5851
6. Visscher L, Visser O, Aerts PJC, Merenga H, Nieuwpoort WC (1994) Comput Phys Commun 81: 120
7. Saue T, Fægri K Jr, Helgaker T, Gropen O (1997) Mol Phys 91: 937
8. Dyall KG, Taylor PR, Fægri K Jr, Partridge H (1991) J Chem Phys 95: 2583
9. Visscher L (1997) Theor Chem Acc 98: 68
10. Visscher L, Lee TJ, Dyall KG (1996) J Chem Phys 105: 8769
11. Boys SF, Bernardi F (1970) Mol Phys 19: 553
12. Dyall KG, Fægri K Jr (1996) Theor Chim Acta 94: 39
13. Quiney HM, Laerdahl JK, Fægri K Jr, Saue T (1998) Phys Rev A 57: 920
14. Wadt WR (1984) J Chem Phys 82: 284
15. Schwerdtfeger P, Heath GA, Dolg M, Bennett MA (1992) J Am Chem Soc 114: 7518