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# TlF ( $^1\Sigma^+$ ): Some preliminary electronic structure calculations\*

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## Abstract

Some preliminary calculations, using the matrix Hartree-Fock model, for the ground ( $X^1\Sigma^+$ ) state of the thallium fluoride molecule are presented. The convergence of the calculations, carried out within the algebraic approximation, is monitored by employing systematically constructed basis sets of increasing size. The importance of bond centred functions is emphasized. For diatomic molecules containing light atoms the finite difference method has proved useful in calibrating calculations carried out with finite basis sets. The prospects for finite difference calculations for diatomic systems containing heavy atoms is assessed.

## 1 Introduction

Mårtensson-Pendrill [1] has recently surveyed the calculation of parity(P)- and time(T)-violating effects in atoms and molecules. An electron dipole moment on an elementary particle constitutes a violation of both parity and time reversal invariance [2]. Several reasons have been advanced for the choice of  $^{205}\text{Tl } ^{19}\text{F}$  as a promising system to work with in the search for P- and T-violating effects[3] [4]. The most important advantage is the  $Z^2$  of higher enhancement of the various P- and T- violating interactions for the Tl nucleus. The large mass number for  $^{205}\text{Tl}$  implies a large nuclear radius maximizing any possible 'volume effect'. It is estimated that the polarization in the TlF molecule will lead to effects which are  $10^5$  larger than for the free  $^{205}\text{Tl}$  atom [5]. Tl and F nuclei have spin  $I=\frac{1}{2}$  and no additional complexity due to non-spherical nuclei is introduced.  $^{205}\text{Tl } (^{19}\text{F})$  has a single unpaired proton (hole) hence for volume and magnetic effects, the measure electric dipole moment is, to a first approximation, that of a proton. Finally, the  $^{205}\text{Tl } ^{19}\text{F}$  is particularly suitable for molecular beam experiments [6].

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The theoretical determination of proton electric dipole moment essentially requires the calculation of the electric field gradient at the  $Tl$  nucleus. Coveney and Sandars [4] conclude that

*The electronic part of this problem poses the greatest theoretical difficulties. The molecular orbital calculations have been performed well away from the Hartree-Fock limit; this accounts for the strong dependence of our results both on the basis set employed and the internuclear distance used.*

Pseudo potential methods which are widely used in the study of molecules containing such heavy atoms are not useful for our present purposes because they are not capable of providing an accurate description of the electron density in the region of the nuclei. The use of an *ab initio* approach which describes all electrons in the system is an essential ingredient of any serious study of P- and T- violating interactions in the  $TlF$  molecule. However, even with today's high performance computing machines the accurate determination of the properties of the  $TlF$  molecule constitute a considerable challenge.

The independent electron model provides a first approximation for the description of the electronic structure of such systems. The non-relativistic Hartree-Fock model, formulated within the algebraic approximation, is ubiquitous in molecular electronic structure studies. The single particle functions (orbitals) are parameterized by expansion in some finite basis set and the resulting algebraic equations solved for the expansion coefficients according to some self-consistent field procedure. This matrix Hartree-Fock method yields a representation of the single particle spectrum, occupied and unoccupied, which can be used to develop a description of electron correlation effects. In recent years, fundamental problems, which arise when formulating the relativistic Dirac-Hartree-Fock method within the algebraic approximation, have been overcome permitting an accurate description of systems containing heavy atoms for which the single particle functions associated with the atomic cores require a relativistic description. Beyond the independent electron model, electron correlation effects can be systematically described by using the many-body perturbation theory within the algebraic approximation. The relativistic many-body perturbation theory can also be formulated within the algebraic approximation, within the no-virtual-pair approximation in which excitation from the negative energy sea are not considered, and beyond.

Although an accurate energy does not necessarily imply accurate electric field gradient at the nucleus, it is suggested that the determination of an accurate energy must be considered a necessary first requirement, since any calculation which results in the accurate determination of a property such as the electric field gradient without obtaining an accurate energy value must result from a fortuitous cancellation of errors. However, the determination of an accurate energy value is a necessary but not sufficient condition for the determination of reliable electric field gradients at nuclei. Indeed, Sundholm *et al* [7] have emphasized that

*The electric field gradient,  $q$ , at a nucleus can be a notoriously difficult property to calculate reliably using the LCAO approach. For a simple system, like  $H_2^+$ , the errors range from 2.1 percent [8] to 0.5 percent [9]. Already for  $q_{Li}$  in  $LiH$ , the typical basis set truncation errors for the largest basis sets are of the order of 10 percent [9].*

For molecules the use of basis set expansion techniques is ubiquitous. For diatomic molecules containing light atoms finite difference and finite element methods can afford very accurate Hartree-Fock energies. The finite basis set method also involves an error attributable to truncation of the basis set. Comparisons of finite basis set studies with the results of finite difference and finite element calculations can afford a useful calibration of the former. This work describes our preliminary attempts to obtain an accurate non-relativistic Hartree-Fock description of the  $TlF$  ( $^1\Sigma^+$ ) system

and is merely the first step to a high precision description of this system incorporating a description of both relativistic and electron correlation effects.

The ground state electronic configuration for the  $Tl$  atom is

$$Tl(^2P) : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p$$

The Hartree-Fock energy (determined by finite difference calculation) for this atom has been quoted as  $-18,961.825$  hartree [10]. The ground state electronic configuration for the  $F$  atom is

$$F(^2P) : 1s^2 2s^2 2p^5$$

and the Hartree-Fock energy for this has been quoted as  $-99.409349$  hartree [10]. The ground state electronic configuration for the  $TlF(^1\Sigma^+)$  molecule

$$\begin{aligned} TlF(^1\Sigma^+) : & 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 8\sigma^2 9\sigma^2 10\sigma^2 11\sigma^2 12\sigma^2 13\sigma^2 \\ & 14\sigma^2 15\sigma^2 1\pi^4 2\pi^4 3\pi^4 4\pi^4 5\pi^4 6\pi^4 7\pi^4 8\pi^4 9\pi^4 10\pi^4 \\ & 1\delta^4 2\delta^4 3\delta^4 4\delta^4 1\varphi^4 \end{aligned}$$

It has recently been demonstrated that finite basis set Hartree-Fock calculations can yield energies which are of an accuracy approaching that achieved in finite difference and finite element calculations[11] [12] [13] [14]. The ground state of the  $N_2$  molecule at its equilibrium nuclear separation was used as a prototype[12]. The potential energy curve for the ground state of the  $CO$  molecule determined by the matrix Hartree-Fock method for those nuclear separations close to equilibrium for which the Hartree-Fock model provides a useful approximation have been shown to be in close agreement with the curve resulting from finite difference calculations[13]. Very recent work has examined the ground state of the  $CS$  molecule using finite basis set and finite difference approaches[14]. Two-dimensional finite difference Hartree-Fock calculations for diatomic molecules are computationally feasible and give very accurate total energies and occupied orbital energies [15] [16] [17]. The finite difference approach has been refined over recent years both in terms of the accuracy achieved and in terms of efficiency of the computational implementation [17] and has been shown to be competitive with the alternative fully numerical approach, the finite element technique[18]. Algorithms have been designed to take advantage of the vector processing capabilities of modern high performance computers [19]. It has been stressed [17] that, whilst finite difference and finite element techniques are often described as basis set independent methods, *they are in fact grid dependent and ... inadequate grid size can easily spoil the results, ensuring that the Hartree-Fock limit values are never reached.*

## 2 The accuracy of finite basis set Hartree-Fock calculations for diatomic molecules

Almost ten years ago, it was established [20] that an accuracy approaching that achieved in finite difference Hartree-Fock calculations for diatomic molecules containing light atoms could be reproduced in finite basis set calculations by using basis functions adapted to the special coordinate system available for such systems, namely, elliptical basis functions

$$(2\pi R^3)^{-\frac{1}{2}} \exp(-\alpha\xi) \exp(-\beta\eta) \xi^p \eta^q \left[ (\xi^2 - 1) (1 - \eta^2) \right]^{|p|/2} \exp(i\nu\varphi) \quad (1)$$

in which  $\alpha$  and  $\beta$  are screening constants and the prolate spheroidal coordinates

$$\xi = (r_1 + r_2)/R, \quad (1 \leq \xi \leq \infty), \quad (2)$$

$$\eta = (r_1 - r_2)/R, \quad (-1 \leq \eta \leq 1) \quad (3)$$

and

$$\varphi, \quad (0 \leq \varphi \leq 2\pi), \quad (4)$$

the azimuthal angle.  $R$  is the internuclear separation and  $r_1$  and  $r_2$  are the distances of a given point from nucleus 1 and 2, respectively. In addition to not being readily applicable to polyatomic molecular systems, basis sets of elliptical function exhibit more pronounced near linear dependent than the more common basis sets of exponential- or Gaussian-type basis function. Furthermore, evaluation of integrals over the electron-electron repulsion for basis sets of elliptical functions involve numerical integration which can affect the accuracy with which they are determined.

Over the past year, it has been demonstrated that Hartree-Fock calculations for diatomic molecules containing first-row atoms carried out with finite basis sets expansions of Gaussian-type functions [11] [12] [13] [14] can lead to total energies approaching a sub- $\mu$ hartree level of accuracy which had previously only been realized in fully numerical calculations using finite difference [15] [17] or finite element [18] techniques.

The finite basis sets employed in the present study comprise spherical harmonic Gaussian-type functions

$$\chi_{k\ell m}^N = R_{k\ell}(r) r^\ell Y_\ell^m(\theta, \varphi) \quad (5)$$

where the  $Y_\ell^m(\theta, \varphi)$  are normalized spherical harmonics and the radial functions,  $R_{k\ell}(r)$ , have the form

$$R_{k\ell}(r) = \{(\zeta_{k\ell}^N)^{2\ell+3} 2^{4\ell+7} / \pi(2\ell+1)!!^2\}^{\frac{1}{4}} \exp(-\zeta_{k\ell}^N r^2) \quad (6)$$

with the exponents,  $\zeta_{k\ell}^N$ , forming a geometric progression

$$\ln \zeta_{k\ell}^N = \ln \alpha_\ell^N + k \ln \beta_\ell^N, \quad \beta_\ell^N > 1, \quad k = 1, 2, \dots, N \quad (7)$$

As the number of basis functions,  $N$ , is increased we require that the basis set approach a complete set. The generalized Müntz-Szász theorem [21] [22] [23] can be used to show that this is the case if

$$\lim_{N \rightarrow \infty} \alpha_\ell^N = 0 \quad (8)$$

$$\lim_{N \rightarrow \infty} \beta_\ell^N = 1 \quad (9)$$

and

$$\lim_{N \rightarrow \infty} (\beta_\ell^N)^N = \infty. \quad (10)$$

The limits can be guaranteed by generating successive basis sets according to the following empirical recursions [24]

$$\alpha_\ell^N = \left[ \frac{\beta_\ell^{N-1} - 1}{\beta_\ell^{N-1} - 1} \right]^{a_\ell} \alpha_\ell^{N-1}, \quad a_\ell > 0 \quad (11)$$

$$\ln \beta_\ell^N = \left[ \frac{N}{N-1} \right]^{b_\ell} \ln \beta_\ell^{N-1}, \quad -1 < b_\ell < 0 \quad (12)$$

In the present work the parameters employed in generating the basis sets are those used in our previous study of the ground state of the  $N_2$  molecule [11] [12] and the  $CO$  molecule [13], and which has also recently been employed as a universal basis set in a study of a series of isoelectronic diatomic molecules [25].

For diatomic molecules, the use of prolate spheroidal coordinates leads to two-dimensional, finite difference Hartree-Fock equations [15] which exhibit both stability and high precision [17] [19].

Table I: Values of the parameters  $\alpha$  and  $\beta$  defining a sequence of even-tempered basis sets

N	$\alpha$	$\beta$
5	0.0938	4.9427
6	0.0857	4.2906
7	0.0797	3.8444
8	0.0750	3.5192
9	0.0712	3.2710
10	0.0681	3.0749
11	0.0654	2.9157
12	0.0632	2.7838
13	0.0612	2.6724
14	0.0594	2.5770
15	0.05782	2.4942

A detailed description of the finite difference approach to the Hartree-Fock problem for diatomic molecules may be found elsewhere [15] [17] [19]. The solution of the Hartree-Fock equations involves the solution of Poisson-like, two-dimensional partial differential equations for the molecular orbitals and potentials, which are written in prolate spheroidal coordinates. The equations are defined on a rectangular region

$$[1, \xi_\infty] \times [-1, 1] \quad (13)$$

with  $\xi_\infty$  sufficiently large. The coordinate system actually employed in the present finite difference calculations is defined through the transformation

$$\mu = \cosh^{-1} \xi, (0 \leq \mu \leq \infty) \quad (14)$$

and

$$\nu = \cos^{-1} \eta, (0 \leq \nu \leq \pi) \quad (15)$$

In these coordinates the grid points were distributed uniformly according to

$$\mu_i = \mu_{i-1} + \delta_\mu, i = 1, 2, \dots, n_\mu, \mu_0 = 0 \quad (16)$$

with a step given by

$$\delta_\mu = R_\infty/n_\mu \quad (17)$$

where  $R_\infty$  is an approximation to infinity and  $n_\mu$  is the number of points, and

$$\nu_j = \nu_{j-1} + \delta_\nu, j = 1, 2, \dots, n_\nu, \nu_0 = 0 \quad (18)$$

with a step given by  $\delta_\nu = 2\pi/n_\nu$  where  $n_\nu$  is the number of points.

In Table II, the accuracy that can be achieved in matrix Hartree-Fock calculations of the total electronic energy using basis sets of atom-centred Gaussian-type functions is compared with the corresponding finite difference result for the ground state of the nitrogen molecule at its equilibrium nuclear geometry. The improved accuracy obtained in the finite basis set calculations upon adding

Table II: Matrix Hartree-Fock energies for the nitrogen molecule ground state from a sequence of atom-centred Gaussian-type functions<sup>†</sup>

Basis set	$-E/\text{hartree}$
30s15p	108.91072760
30s15p15d	108.99063433
30s15p15d15f	108.99361015
finite difference <sup>‡</sup>	108.993808

<sup>†</sup> D.Moncrieff & S.Wilson, J. Phys. B: At. Mol. & Opt. Phys. **26**, 1605 (1993)

<sup>‡</sup> D.Sundholm, P.Pyykkö & L.Laaksonen, Molec. Phys. **56**, 1411 (1985)

Table III: Comparison of finite basis set, finite difference and finite element Hartree-Fock calculations for the nitrogen molecule ground state

Method	$-E/\text{hartree}$
finite basis set <sup>†</sup>	108.9938234
finite difference <sup>‡</sup>	108.9938257
finite element*	108.993826

<sup>†</sup> D.Moncrieff & S.Wilson, Chem. Phys. Lett. **209**, 423 (1993)

<sup>‡</sup> J.Kobus, Chem. Phys. Lett. **202**, 7 (1993)

\* D.Heinemann, A.Rosen & B.Fricke, Physica Scripta **42**, 692 (1990);  
D.Heinemann, B.Fricke & D.Kolb, Phys. Rev. A **38**, 4994 (1988)

Table IV: Calculated Hartree-Fock energies for the ground state of the CO molecule as a function of internuclear distance<sup>†</sup>

$r$	$E_{\text{finite difference}}$	$E_{\text{finite basis}}$	$\delta$
1.970	-112.781 702 3	-112.781 699 7	2.6
2.000	-112.787 019 0	-112.787 016 4	2.6
2.030	-112.790 497 7	-112.790 495 2	2.5
2.080	-112.792 699 7	-112.792 697 1	2.6
2.132	-112.790 907 2	-112.790 904 5	2.7
2.180	-112.786 171 2	-112.786 168 6	2.6
2.200	-112.783 446 6	-112.783 443 9	2.7
2.230	-112.778 628 4	-112.778 625 8	2.6
2.280	-112.768 885 1	-112.768 882 4	2.7
2.330	-112.757 342 7	-112.757 340 0	2.7

Energies are in hartree; energy differences,  $\delta = E_{\text{finite difference}} - E_{\text{finite basis}}$ , are in  $\mu\text{hartree}$ ; internuclear distance,  $r$ , is in bohr.

<sup>†</sup> J. Kobus, D. Moncrieff and S. Wilson, submitted for publication



bond centred functions is illustrated in Table III where a difference of 2.3  $\mu$ hartree between the matrix Hartree-Fock and the numerical Hartree-Fock energy values is recorded. Table IV shows some recently obtained results for the ground state of the carbon monoxide molecule for that portion of the ground state potential energy curve which is adequately described by the Hartree-Fock model. Finally, in Table V, the results of some recently completed calculations for the ground state of the carbon monosulphide molecules are presented. They demonstrate little degradation of the accuracy achieved for a molecule containing a second row atom.

Table V: A comparison of the recent Hartree-Fock calculations for CS with previous work<sup>†</sup>

Method	$R$	$E_{(M)HF}$	Reference
Finite difference	2.9006	-435.362 73	Pyykkö <i>et al</i> [26]
	2.89964	-435.362 419	Kobus <i>et al</i> [13]
	2.89964	-435.362 419 81	Kobus <i>et al</i> [13]
Finite basis set		-435.329 69	Richards [27]
	2.8	-435.329	Robbe and Schamps [28]
	2.9	-435.309 4	Bruna <i>et al</i> [29]
	2.89964	-435.331 7	Green [30]
	2.89964	-435.346 27	Wilson [31]
	2.89964	-435.362 417 7	Kobus <i>et al</i> [13]

Energies are in hartree; internuclear distance,  $r$ , is in bohr.

<sup>†</sup> J.Kobus, D.Moncrieff and S.Wilson, J. Phys B: At. Mol. Opt. Phys. (in press)

### 3 The accuracy of finite basis set Dirac-Hartree-Fock calculations

The basis set requirement for relativistic electronic structure calculations are similar to those in the corresponding non-relativistic calculations. Table VI demonstrates the convergence of a Dirac-Hartree-Fock calculation for the ground state of the argon atom using a systematically constructed sequence of even-tempered basis sets. The total relativistic electronic energy converges to an accuracy which is comparable with that achieved in finite difference calculations. However, unlike the finite difference calculations, the calculations carried out within the algebraic approximation also yield a representation of the entire Dirac spectrum, both positive and negative energy branches, which can be employed in a many-body perturbation expansion for correlation effects. Some relativistic many-body perturbation theory calculations for the ground state of the argon atom are displayed in Table VII.

Once the algebraic approximation has been invoked there is no difference in principle between atomic and molecular calculations. The molecular calculations are more demanding from a computational point of view and it is, therefore, often necessary to use a restricted basis set in order to maintain tractability. In Table VIII, the results of some previously reported Dirac-Hartree-Fock calculations for the ground state of the hydrogen chloride molecule are shown. They demonstrate the magnitude of the basis set truncation error in such calculations. However, by introducing basis sets of the type described in the preceding section for the non-relativistic case, it is to be ex-

Table VI: Relativistic matrix Dirac-Hartree-Fock calculations for the ground state of the argon atom from a sequence of even-tempered basis sets<sup>†</sup>

$N$	$\alpha$	$\beta$	$-E/\text{hartree}$
9	0.500	1.500	528.64394819
10	0.484	1.516	528.68336415
11	0.470	1.486	528.68431173
12	0.458	1.462	528.68428973
13	0.447	1.440	528.68443068
14	0.437	1.421	528.68443246
15	0.429	1.404	528.68444856
16	0.421	1.389	528.68444990
17	0.413	1.376	528.68445050
finite difference			528.68445077

<sup>†</sup> H.M.Quiney, I.P.Grant & S.Wilson, in *Many-Body Methods in Quantum Chemistry*, edited by U.Kaldor, Lecture Notes in Chemistry 52, 307 (1989)

Table VII: Relativistic finite basis set calculations for the argon ground state taking account of the effects of electron correlation

	$E/\text{hartree}$
Hartree-Fock (HF) energy <sup>†</sup>	-526.817 48
(Finite difference HF energy) <sup>†</sup>	-526.817 51
Dirac-Hartree-Fock-Coulomb (DHFC) energy*	-528.684 45
(Finite difference DHFC energy)*	-528.684 45
Dirac-Hartree-Fock-Breit (DHFB) energy*	-528.552 12
First order Breit energy*	+0.132 37
Dirac-Hartree-Fock-Breit energy plus first order Breit energy*	-528.552 09
Non-relativistic correlation energy (HF/MBPT-2)*	-0.638 68
Total non-relativistic energy (HF+MBPT-2)*	-527.456 16
Relativistic correlation energy (DHFC/MBPT-2)*	-0.639 42
Total relativistic energy (DHFC+MBPT-2)*	-529.323 87
Relativistic correlation energy (DHFB/MBPT-2)*	-0.646 20
Total relativistic energy (DHFB+MBPT-2)*	-529.198 32

<sup>†</sup> B.H. Wells & S. Wilson, J. Phys. B: At. Mol. Phys. 19, 2411 (1986)

<sup>†</sup> C. Froese Fischer, *The Hartree-Fock Method for Atoms. A numerical approach* (New York, Interscience, 1977)

\* H.M. Quiney, I.P. Grant & S. Wilson, J. Phys. B: At. Mol. Phys. 23, L271 (1990)

Table VIII: Some calculated energies for the ground state of the HCl molecule with an internuclear separation of 2.40 bohr<sup>†</sup>

	E/hartree
E(MHF)	-460.060 54
E(NHF)	-460.113 05
E(MDHFC)	-461.525 38
$\epsilon_{\text{BSTE}}$	0.054 52
$\epsilon_{\text{Rel.}}$	-1.464 56
$\epsilon_{\text{Non-Rel. MBPT-2}}$	-0.304 06

MHF: Matrix Hartree-Fock; NHF: Numerical Hartree-Fock;

MDHFC: Matrix Dirac-Hartree-Fock-Coulomb; BSTE: Basis Set Truncation Error

<sup>†</sup> L. Laaksonen, I.P. Grant & S. Wilson, J. Phys. B: At. Mol. Opt. Phys. 21, 1969 (1988)

pected that a sub- $\mu$ hartree level of accuracy can also be achieved in relativistic Dirac-Hartree-Fock calculations.

## 4 Preliminary calculations for the TlF molecule

A series of non-relativistic calculations for the ground state of the thallium fluoride molecule have been commenced using the approach which has been described above and previously been employed in our study of the nitrogen, carbon monoxide and carbon monosulphide molecules. The calculations were performed with the program of Frisch *et al* [32].

A basis set for the *Tl* and *F* atoms was developed using the parameters which have previously been employed for the ground state of the nitrogen molecule and in a study of universal basis set for high precision studies. Following Bardo and Ruedenberg [33] and Clementi [10] the exponents for each symmetry type were taken to be identical although only certain functions were taken to be "active" in each case. Starting from the 27*s* basis set for the nitrogen atom extra diffuse and contracted functions were added until the range of values taken by the exponents included the range covered by the exponents given by Clementi in his extra-large geometric basis set [10]. Explicitly, the exponents were generated using the formula

$$\zeta_p = \alpha\beta^p, \quad p = i_l, i_l + 1, \dots, f_l - 1, f_l$$

The specific values of the exponents employed are presented in Table IX. This table defines a basis set of 379 primitive, atom-centred, Gaussian-type functions which is designated [*Tl* : 31*s*25*p*19*d*14; *F* : 26*s*18*p*]. The energy calculated with this basis set was found to lie  $\sim 21$  hartree below the value reported by Coveney and Sandars [4]

The basis set was further extended by keeping the parameters  $\alpha$  and  $\beta$  fixed and varying the indices  $i_l$  and  $f_l$ . The details of this refinement of the basis set are presented in Table XI. The corresponding energies are given in Table X. Linear dependence in the basis sets was monitored by recording the number of eigenvalues of the overlap matrix lying below  $10^{-5}$  together with the smallest eigenvalue. This is done in Table XII. In Table XIII, the variation of the energy associated with the *Tl* core orbital is given for each of the basis sets studied. Finally, in Table X, the improvement obtained on adding a set of bond centred functions is recorded.

Table IX: Even-tempered basis sets for thallium and fluorine

$\zeta_P$	$TI$	$F$
0.0120	P	
0.0237	SP	
0.0466	SP	SP
0.0918	SPD	SP
0.1808	SPD	SP
0.3562	SPD	SP
0.7015	SPDF	SP
1.3818	SPDF	SP
2.7216	SPDF	SP
5.3606	SPDF	SP
10.558	SPDF	SP
20.796	SPDF	SP
40.961	SPDF	SP
80.677	SPDF	SP
158.90	SPDF	SP
312.98	SPDF	SP
616.46	SPDF	SP
1214.21	SPDF	SP
2391.55	SPDF	SP
4710.5	SPDF	SP
9277.9	SPD	S
18274.1	SPD	S
35993.2	SP	S
70893.4	SP	S
139634.0	SP	S
275027.9	S	S
541704.1	S	S
1066958.5	S	S
2101517.1	S	
4139218.2	S	
8152742.4	S	
16057913.7	S	

Table X: Some calculated total Hartree-Fock energies for the ground state of the TlF molecule

Basis set	N <sub>basis</sub>	Reference	E/hartree
Minimum set of exponential functions	33	<i>a</i>	-19019.27264
Double zeta set of exponential functions	51	<i>a</i>	-19040.30775
[ <i>Tl</i> : 31 <i>s</i> 25 <i>p</i> 19 <i>d</i> 14; <i>F</i> : 26 <i>s</i> 18 <i>p</i> ]	379	<i>b</i>	-19061.36279
[ <i>Tl</i> : 37 <i>s</i> 28 <i>p</i> 21 <i>d</i> 15; <i>F</i> : 30 <i>s</i> 20 <i>p</i> ]	421	<i>b</i>	-19061.36789
[ <i>Tl</i> : 43 <i>s</i> 31 <i>p</i> 23 <i>d</i> 165 <i>f</i> ; <i>F</i> : 34 <i>s</i> 22 <i>p</i> ]	463	<i>b</i>	-19061.36855
[ <i>Tl</i> : 44 <i>s</i> 33 <i>p</i> 26 <i>d</i> 18 <i>f</i> ; <i>F</i> : 34 <i>s</i> 22 <i>p</i> ]	499	<i>b</i>	-19061.36856
[ <i>Tl</i> : 44 <i>s</i> 33 <i>p</i> 26 <i>d</i> 18 <i>f</i> ; <i>F</i> : 34 <i>s</i> 22 <i>p</i> ; 27 <i>s bc</i> ]	526	<i>b</i>	-19061.37001

<sup>a</sup> Coveney & Sandars (1983)

<sup>b</sup> Present work

Table XI: Even-tempered basis sets of Gaussian-type functions employed in preliminary calculations for the TlF ground state

Basis set	<i>i<sub>s</sub></i>	<i>f<sub>s</sub></i>	<i>i<sub>p</sub></i>	<i>f<sub>p</sub></i>	<i>i<sub>d</sub></i>	<i>f<sub>d</sub></i>	<i>i<sub>f</sub></i>	<i>f<sub>f</sub></i>
<i>Tl</i> : 31 <i>s</i> 25 <i>p</i> 19 <i>d</i> 14	-1	29	-2	22	1	19	4	17
<i>F</i> : 26 <i>s</i> 18 <i>p</i>	0	25	0	17	—	—	—	—
<i>Tl</i> : 37 <i>s</i> 28 <i>p</i> 21 <i>d</i> 15	-5	31	-4	23	0	20	3	17
<i>F</i> : 30 <i>s</i> 20 <i>p</i>	-1	28	-1	18	—	—	—	—
<i>Tl</i> : 43 <i>s</i> 31 <i>p</i> 23 <i>d</i> 165 <i>f</i>	-7	35	-5	25	-1	21	3	18
<i>F</i> : 34 <i>s</i> 22 <i>p</i>	-2	31	-2	19				
<i>Tl</i> : 44 <i>s</i> 33 <i>p</i> 26 <i>d</i> 18 <i>f</i>	-7	36	-5	27	-1	24	3	20

Table XII: Near linear dependence in the basis sets *m* is the number of eigenvalues of the overlap matrix which are less than  $10^{-5}$ ,  $\epsilon$  is the smallest eigenvalue of the overlap matrix

Basis set	N <sub>basis</sub>	<i>m</i>	$\epsilon$
[ <i>Tl</i> : 31 <i>s</i> 25 <i>p</i> 19 <i>d</i> 14; <i>F</i> : 26 <i>s</i> 18 <i>p</i> ]	379	0	$6.7 \times 10^{-5}$
[ <i>Tl</i> : 37 <i>s</i> 28 <i>p</i> 21 <i>d</i> 15; <i>F</i> : 30 <i>s</i> 20 <i>p</i> ]	421	0	$4.1 \times 10^{-5}$
[ <i>Tl</i> : 43 <i>s</i> 31 <i>p</i> 23 <i>d</i> 165 <i>f</i> ; <i>F</i> : 34 <i>s</i> 22 <i>p</i> ]	463	3	$1.5 \times 10^{-6}$
[ <i>Tl</i> : 44 <i>s</i> 33 <i>p</i> 26 <i>d</i> 18 <i>f</i> ; <i>F</i> : 34 <i>s</i> 22 <i>p</i> ]	499	5	$3.6 \times 10^{-7}$

Table XIII: Orbital energy for the thallium core

Basis set	$\epsilon_{1\sigma}$
[ <i>Tl</i> : 31 <i>s</i> 25 <i>p</i> 19 <i>d</i> 14; <i>F</i> : 26 <i>s</i> 18 <i>p</i> ]	−2851.560 147 62
[ <i>Tl</i> : 37 <i>s</i> 28 <i>p</i> 21 <i>d</i> 15; <i>F</i> : 30 <i>s</i> 20 <i>p</i> ]	−2851.559 019 11
[ <i>Tl</i> : 43 <i>s</i> 31 <i>p</i> 23 <i>d</i> 165 <i>f</i> ; <i>F</i> : 34 <i>s</i> 22 <i>p</i> ]	−2851.558 829 13
[ <i>Tl</i> : 44 <i>s</i> 33 <i>p</i> 26 <i>d</i> 18 <i>f</i> ; <i>F</i> : 34 <i>s</i> 22 <i>p</i> ]	−2851.558 821 02

The convergence of finite basis set calculations can be monitored by comparison with the results of finite difference (or finite element) Hartree-Fock calculations when available. Finite difference programs for diatomic molecules available at present employ an equidistant grid [19]. Now for the ground state of the *Tl* atom a finite difference calculation using the GRASP2 package has shown that the 1*s* orbital assumes a maximum at  $\sim 0.01$  bohr whilst the 6*s* orbital has nodes at  $\sim 0.019$ ,  $\sim 0.076$ ,  $\sim 0.19$ ,  $\sim 0.46$ ,  $\sim 1.0$  bohr and an outermost maximum at  $\sim 2.3$  bohr. To be able to reproduce the orbitals and their nodal structure in the *TlF* molecule to a reasonable level of accuracy one might expect to adopt an equidistant grid with a step size of  $\sim 0.002$  bohr. Setting the practical approximation to infinity,  $R_\infty$ , at 10 bohr, which is probably not adequate, leads to a requirement of 5000 points in  $\mu$ , which together with an estimated 1000 points in  $\nu$ , gives a total of  $5 \times 10^6$  points. Calculations of this magnitude will only be rendered tractable by exploiting sparsity and/or by using multiple grids.

## 5 Prospect

Some preliminary matrix Hartree-Fock studies of the ground state of the *TlF* molecule using systematically constructed basis sets of even-tempered basis sets of Gaussian-type functions have been presented. The results suggest that it will be possible to achieve the level of accuracy which has been realized in previous studies of diatomic molecules containing lighter atoms. It is proposed that, by studying the sequence *BF*, *AlF*, *GaF*, *InF*, *TlF*, the accuracy that can be obtained for the *TlF* molecule within the Hartree-Fock approximation can be reliably assessed. Fully numerical Hartree-Fock calculations for the first two members of this sequence have been reported by Pyykkö *et al* [26]. The prospects for fully numerical Hartree-Fock calculations for the remaining member of this sequence have been briefly discussed. The matrix Hartree-Fock study will yield a basis set that can be employed in high precision Dirac-Hartree-Fock-Breit calculations and representation of the virtual spectrum which can be employed in describing developing accurate descriptions of electron correlation effects.

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### Note added in proof.

Ishikawa [34] has pointed out that it is possible to calculate accurate electric field gradients at nuclei with Gaussian-type basis sets provided that the point nucleus model is abandoned in favour of a more realistic finite nucleus model.

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