Calculation of P, T-Odd Effects in ^{205}TlF Including Electron Correlation

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A method and codes for two-step correlation calculations of heavy-atom molecules have been developed, employing the generalized relativistic effective core potential (GRECP) and relativistic coupled cluster (RCC) methods at the first step, followed by nonvariational one-center restoration of proper four-component spinors in the heavy cores. Electron correlation is included for the first time in an *ab initio* calculation of the interaction of the permanent P, T-odd proton electric dipole moments with the internal electromagnetic field in a molecule. Inclusion of electron correlation by GRECP/RCC has a major effect on the P, T-odd parameters of ^{205}TlF, decreasing M by 17% and X by 22%.

The measurement of permanent electric dipole moments (EDM) of elementary particles is highly important for the theory of P, T-odd interactions. Experiments performed so far have given only upper bounds for the EDMs. The extraction of EDMs from measurements on molecules containing heavy atoms requires knowledge of nuclear and electronic properties of the molecule. High quality calculations of the relevant electronic properties are therefore essential for accurate determination of the EDMs [1,2].

Here we consider the interaction of the proton EDM with the internal electromagnetic field of the ^{205}TlF molecule. This molecule is one of the best candidates for proton EDM measurements. Following Hinds and Sandars [3], the effective interaction with the proton EDM in TlF is written in the form

$$H_{\text{eff}} = (d^V + d^M)\vec{\sigma}_N \cdot \vec{\lambda}, \tag{1}$$

where $\vec{\sigma}_N$ is the Tl nuclear spin operator, $\vec{\lambda}$ is the unit vector along the internuclear axis z from Tl to F, and d^V and d^M are constants corresponding, respectively, to the volume and magnetic effects according to Schiff's theory [4]. Hinds and Sandars showed [3] that the volume effect in a coordinate system centered on the Tl nucleus is given by

$$d^V = -d_p X R, \tag{2}$$

where d_p is the proton EDM, R is a factor determined by the nuclear structure of ^{205}Tl, and

$$X = \frac{2\pi}{3}\left[\frac{\partial}{\partial z}\rho_\psi(\vec{r})\right]_{x,y,z=0} \tag{3}$$

$[\rho_\psi(\vec{r})$ is the electronic density calculated from the wave function ψ]. Keeping only the dominant diagonal terms of the two-electron operator for the magnetic effect (see [2]) they have

$$d^M = 2\sqrt{2}\, d_p\left(\frac{\mu}{Z} + \frac{1}{2mc}\right)M, \tag{4}$$

where μ, m, and Z are the magnetic moment, mass, and

charge of the Tl nucleus, c is the velocity of light,

$$M = \frac{1}{\sqrt{2}}\langle\psi|\sum_i\left(\frac{\vec{\alpha}_i \times \vec{\mathbf{l}}_i}{r_i^3}\right)_z|\psi\rangle, \tag{5}$$

$\vec{\mathbf{l}}_i$ is the orbital momentum operator of electron i, and $\vec{\alpha}_i$ are its Dirac matrices. H_{eff} leads to different hyperfine splitting of TlF in parallel and antiparallel electric and magnetic fields. The level shift $h\nu = 4(d^V + d^M)\langle\vec{\sigma}_N \cdot \vec{\lambda}\rangle$ is measured experimentally (for the latest data, see [5]; another experiment is now in preparation at the Petersburg Nuclear Physics Institute).

The parameters X of Eq. (3) and M of Eq. (5) are determined by the electronic structure of the molecule. They were calculated recently for the $X0^+$ ground state of TlF by Parpia [6] and by Quiney *et al.* [7] using the Dirac-Hartree-Fock (DHF) method with large Gaussian basis sets (see Table I). No calculation which includes correlation effects is available. The main goal of the present work is to calculate the X and M parameters for the molecule with correlation included to high order.

Methods.—The generalized relativistic effective core potential (GRECP) method [8] is applied to the TlF molecule. A two-component electronic (pseudo)wave function is first obtained with the 21-electron GRECP [9,10] for Tl, providing proper electronic density in the valence and outer core regions, followed by restoration of the proper shape of the four-component molecular spinors in the inner core region of Tl. Details of the method may be found elsewhere [8,11–13].

The correlation spin-orbital basis set used consisted of $26s$, $25p$, $18d$, $12f$, and $10g$ Gaussian-type orbitals on Tl, contracted to $6s6p4d2f1g$. The basis was optimized in a series of atomic two-component GRECP calculations, with correlation included by the all-order relativistic coupled cluster (RCC) method [14] with single and double excitations; the average energy of the two lowest states of the atom was minimized. The basis set generation procedure is described in Refs. [15,16]. The basis set was designed

TABLE I. Calculated X and M parameters [Eqs. (3) and (5)] for the ^{205}TlF ground state, compared with DHF values with different basis sets [6,7]. Individual shell contributions are calculated from spin-averaged GRECP/SCF orbitals. GRECP/RCC-S results include spin-orbit interaction, and GRECP/RCC-SD values also account for electron correlation. All values in a.u.

| Expansion / Shell:main contribution | $R_e = 2.0844$ Å | | | | $R = 2.1$ Å | | |
| | s, p | s, p, d | s, p, d, f | s, p | s, p | s, p, d, f | s, p |
			M	X		M	X
$1\sigma^2$:$1s^2$(F)	0.01	0.02	0.02	3	0.00	0.02	1
$2\sigma^2$:$5s^2$(Tl)	−2.49	−2.49	−2.49	−1114	−2.44	−2.44	−1089
$3\sigma^2$:$5p_z^2$(Tl)	4.21	3.91	3.91	1897	4.10	3.82	1851
$4\sigma^2$:$2s^2$(F)	−0.79	−0.64	−0.64	−358	−0.74	−0.60	−335
$5\sigma^2$:$5d_{z^2}^2$(Tl)	−0.01	−0.04	−0.05	−2	−0.01	−0.05	−2
$6\sigma^2$:$[6s(\text{Tl}) + 2p_z(\text{F})]^2$	−9.38	−10.05	−10.06	−4414	−9.38	−10.02	−4422
$7\sigma^2$:$[6s(\text{Tl}) - 2p_z(\text{F})]^2$	28.13	27.19	27.19	12954	27.98	27.07	12893
$1\pi^4$:$5p_x^2 5p_y^2$(Tl)	0.00	−0.26	−0.26	0	0.00	−0.25	0
$2\pi^4$:$5d_{xz}^2 5d_{yz}^2$(Tl)	0.00	0.31	0.30	0	0.00	0.27	0
$3\pi^4$:$2p_x^2 2p_y^2$(F)	0.00	−0.39	−0.40	0	0.00	−0.38	0
$1\delta^4$:$5d_{x^2-y^2}^2 5d_{xy}^2$(Tl)	0.00	0.00	−0.02	0	0.00	−0.02	0
Total SCF (spin-averaged)	19.67	17.56	17.51	8967	19.52	17.43	8897
GRECP/RCC-S	16.12		13.84	9813	16.02	13.82	9726
DHF [6] Tl:$(28s28p12d8f)$	15.61			7743			
DHF [7] Tl:$(25s25p12d8f)$						13.64[a]	8098
Tl:$(28s28p14d8f)$						13.62[a]	8089
Tl:$(31s31p15d8f)$						13.66[a]	8492
Tl:$(34s34p16d9f)$						13.63[a]	8747
GRECP/RCC-SD			11.50	7635			

[a]M is calculated in Ref. [7] using two-center molecular spinors, corresponding to infinite $L_{\max}$ in Eq. (7).

to describe correlation in the outer core $5s$ and $5p$ shells of Tl, in addition to the $5d$ and valence shells. While $5s$ and $5p$ correlation may not be important for many of the chemical and physical properties of the atom, it is essential for describing properties coming from inner regions, including P, T-odd effects. The $(14s9p4d3f)/[4s3p2d1f]$ basis set from the ANO-L (Atomic Natural Orbitals-Large) library [17] is used for fluorine.

A one-component self-consistent-field (SCF) calculation of the $(1\sigma \cdots 7\sigma)^{14}(1\pi 2\pi 3\pi)^{12}(1\delta)^4$ ground state of TlF is performed first, using the GRECP for Tl which simulates the interactions of the valence and outer core $(5s5p5d)$ electrons with the inner core $[\text{Kr}]4d_{3/2}^4 4d_{5/2}^6 4f_{5/2}^6 4f_{7/2}^8$. This is followed by two-component RCC calculations, with only single (RCC-S) or with single and double (RCC-SD) cluster amplitudes. The RCC-S calculations with the spin-dependent GRECP operator take into account effects of spin-orbit interaction at the level of the one-configurational SCF-type method. The RCC-SD calculations include, in addition, the most important electron correlation effects.

The electron density obtained from the two-component GRECP/RCC (pseudo)wave function in the valence and outer core regions is very close to that of the corresponding all-electron four-component function. The pseudospinors are smoothed in the inner core region [8], so that the electronic density in this region is not correct. The opera-

tors in Eqs. (3) and (5) are heavily concentrated near the nucleus and are therefore strongly affected by the wave function in the inner region. The four-component molecular spinors must therefore be restored in the inner region of Tl. All molecular spinors ϕ_i are restored as one-center expansions on the Tl nucleus, using the nonvariational restoration scheme (see [8,11–13] and references therein).

The restoration is started by generating equivalent basis sets of atomic (one-center) four-component spinors

$$\left\{ \begin{pmatrix} f_{nlj}(r)\chi_{ljm} \\ g_{nlj}(r)\chi_{l'jm} \end{pmatrix} \right\}$$

and two-component pseudospinors $\{\tilde{f}_{nlj}(r)\chi_{ljm}\}$ by atomic finite-difference all-electron DHF and two-component GRECP/SCF calculations of the same valence configurations of Tl and its ions. Here n is the principal quantum number, j and m are the total electronic momentum and its projection on the internuclear axis, l and l' are the orbital momenta, and $l' = 2j - l$. The nucleus is modeled as a uniform charge distribution within a sphere with radius $r_{\text{nucl}} = 7.1$ fm $\equiv 1.34 \times 10^{-4}$ a.u., whereas previous calculations employed a spherical Gaussian nuclear charge distribution [6,7] (the root mean square radius in all calculations is 5.5 fm, in accord with the parametrization of Johnson and Soff [18], and agrees with the experimental value 5.483 fm for the ^{205}Tl nucleus [19]). The all-electron four-component HFD [20] and

two-component GRECP/HFJ [9,10] codes were employed to generate the two equivalent $[15s12p12d8f]$ numerical basis sets for restoration. These sets, describing mainly the core region, are generated independently of the basis set for the molecular GRECP calculations discussed earlier. The molecular pseudospinorbitals are then expanded in the basis set of one-center two-component atomic pseudospinors,

$$\tilde{\phi}_i(\mathbf{r}) \approx \sum_{l=0}^{L_{\max}} \sum_{j=|l-1/2|}^{j=|l+1/2|} \sum_{n,m} c_{nljm}^i \tilde{f}_{nlj}(r) \chi_{ljm}. \quad (6)$$

Note that for linear molecules only one value of m survives in the sum for every ϕ_i. Finally, the two-component pseudospinors in the basis are replaced by the equivalent four-component spinors and the expansion coefficients from Eq. (6) are preserved [11–13]:

$$\phi_i(\mathbf{r}) \approx \sum_{l=0}^{L_{\max}} \sum_{j=|l-1/2|}^{j=|l+1/2|} \sum_{n,m} c_{nljm}^i \begin{pmatrix} f_{nlj}(r)\chi_{ljm} \\ g_{nlj}(r)\chi_{l'jm} \end{pmatrix}. \quad (7)$$

The molecular four-component spinors constructed this way are orthogonal to the inner core spinors of Tl, as the atomic basis functions used in Eq. (7) are generated with the inner core electrons treated as frozen.

The quality of the approximation for the two-center molecular spinors and, consequently, of the calculated properties increases with the value of $L_{\max}$. A series of calculations of the M parameter was performed using Eq. (7) with basis functions going up to p, d, and f harmonics. We found (see Table I) that including only s and p functions in the expansion determines M with 90% accuracy. Because the contribution of f is only about 0.3% and amplitudes of higher harmonics on the nucleus are suppressed by the leading term $\sim r^{(j-1/2)}$, the error due to the neglect of spherical harmonics beyond f is estimated to be below 0.1%. Calculation of the X parameter requires s and p harmonics (see Ref. [7]), although, strictly speaking, d harmonics also give nonzero contributions.

The restoration procedure implemented here gives a very good description of the wave function in the core region, which is important for accurate evaluation of the X and M parameters. This is done at a fraction of the cost necessary for all-electron four-component molecular calculations with Gaussian basis sets, where a large number of additional basis functions must be included for a proper description of the inner core region and small components of spinors [7]. Here we calculate (restore) the four-component electronic wave function in the core region from the (pseudo)wave function obtained in the molecular GRECP calculation, which may be considered "frozen" in the valence region at the restoration stage. Basis functions describing a large number of chemically inert core electrons may thus be excluded from the molecular GRECP calculation.

The X and M parameters were calculated by the finite field method (see, e.g., Refs. [21,22]). The operator corresponding to a desired property [see Eqs. (3) and (5)] is

multiplied by a small parameter λ and added to the Hamiltonian. The derivative of the energy with respect to λ gives the computed property. This is strictly correct only at the limit of vanishing λ, but it is usually possible to find a range of λ values where the energy is linear with λ and energy changes are large enough to allow sufficient precision. The quadratic dependence on λ is eliminated in the present calculations by averaging absolute energy changes obtained with λ of opposite signs.

Results and discussion.—Calculations were carried out at two internuclear separations, the equilibrium $R_e = 2.0844$ Å as in Ref. [6], and 2.1 Å, for comparison with Ref. [7]. The results are collected in Table I. The first point to notice is the difference between spin-averaged SCF and RCC-S values, which include spin-orbit interaction effects. These effects increase X by 9% and decrease M by 21%. The RCC-S function may be written as a single determinant, and results may therefore be compared with DHF values, even though the RCC-S function is not variational. GRECP/RCC-S values of the M parameter are indeed within 3% and 1% of corresponding DHF values [6,7] (Table I). This agreement confirms the validity of the approximations made by us. In particular, freezing the inner core shells is justified, as inner core relaxation effects have little influence on the properties calculated here, a conclusion already drawn by Quiney *et al.* [7].

Much larger differences occur for the X parameter. Here there are also large differences between the two DHF calculations, which cannot be explained by the small change in internuclear separation. The value of X may be expected to be less stable than M, because it is determined by the derivative of the electronic density at the Tl nucleus and involves large cancellations [7] between contributions of large and small components, each of which is about 20 times larger than their sum. Thus, a strong dependence of X on the basis used may be expected. The DHF values collected in Table I indeed show such dependence. Results obtained in Refs. [6] and [7] with comparable even-tempered basis sets, $(28s28p12d8f)$ and $(28s28p14d8f)$, are rather close, differing by 340 a.u. Improving the Tl basis to $(34s34p16d9f)$ [7] increases X by 650 a.u. or 8%. Further improvement of the basis may be expected to yield even higher X values. The numerical basis functions obtained in atomic DHF calculations and used for the restoration are highly accurate near the nucleus, so that our RCC-S value for X, which is higher than that of Quiney *et al.* [7], seems reasonable. The different nuclear models used in the present and DHF [6,7] calculations may also contribute to the disagreement in X, which is determined by the derivative of the electronic charge density at a single point, the Tl origin. M is affected by ψ in a broader region and is therefore far less sensitive to the nuclear model.

The main goal of this work is the evaluation of electron correlation effects on the P, T-odd parameters. These effects are calculated by the RCC-SD method at the molecular equilibrium separation R_e. A major correlation

contribution is observed, decreasing M by 17% and X by 22%.

Using the correlated values for X and M calculated here and $R = 1.036 \times 10^{-9}$ a.u. from [23], one obtains from Eqs. (2) and (4)

$$d^V = -7.909 \times 10^{-6} d_p \text{ a.u.}, \qquad (8)$$

$$d^M = 1.622 \times 10^{-6} d_p \text{ a.u.} \qquad (9)$$

The effective electric field interacting with the EDM of the valence proton of ^{205}Tl in the fully polarized TlF molecule is $E = |d^V + d^M|/d_p = 6.287 \times 10^{-6}$ a.u. = 32.33 kV/cm; the revised proton EDM limit for the experiment of Ref. [5] is $d_p = (-1.7 \pm 2.8) \times 10^{-23}$ e cm.

The hyperfine structure constants of Tl $6p^1_{1/2}$ and Tl^{2+} $6s^1$, which (like X and M) depend on operators concentrated near the Tl nucleus, were also calculated. The errors in the DF values are 10%–15%; RCC-SD results are within 1%–4% of experiment. The improvement in X and M upon inclusion of correlation is expected to be similar.

Concluding remarks.—Note that the codes developed for GRECP/RCC calculation followed by nonvariational one-center restoration in heavy cores are equally applicable to calculation of other properties described by operators singular near nuclei (hyperfine structure, quantum electrodynamic effects, etc.). Because the Fock-space RCC-SD approach [14] is used, the two-step method is applicable to both closed-shell and open-shell systems, including excited states. In particular, calculations for the ground state of YbF and for excited states of PbO are in progress now. Triple and higher cluster amplitudes in the valence region are important for chemical and spectroscopic properties, but not for the effects discussed here, as concluded from previous calculations for YbF [12]. These excitations are believed to be unimportant in the core region, too. We therefore suggest that further improvement in the correlation treatment will not seriously affect our M and X values.

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[1] I. B. Khriplovich, *Parity Non-Conservation in Atomic Phenomena* (Gordon and Breach, New York, 1991); M. G. Kozlov and L. N. Labzowsky, J. Phys. B **28**, 1933 (1995); M.-A. Bouchiat and C. Bouchiat, Rep. Prog. Phys. **60**, 1351 (1997).

[2] A.-M. Martensson-Pendrill, in *Methods in Computational Chemistry,* edited by S. Wilson (Plenum, New York, 1992), Vol. 5, p. 99.

[3] E. A. Hinds and P. G. H. Sandars, Phys. Rev. A **21**, 471 (1980).

[4] L. I. Schiff, Phys. Rev. **132**, 2194 (1963).

[5] D. Cho, K. Sangster, and E. A. Hinds, Phys. Rev. A **44**, 2783 (1991).

[6] F. A. Parpia, J. Phys. B **30**, 3983 (1997).

[7] H. M. Quiney, J. K. Laerdahl, K. Faegri, Jr., and T. Saue, Phys. Rev. A **57**, 920 (1998).

[8] A. V. Titov and N. S. Mosyagin, Int. J. Quantum Chem. **71**, 359 (1999); A. V. Titov and N. S. Mosyagin, Russ. J. Phys. Chem. **74**, Suppl. 2, S376 (2000).

[9] I. I. Tupitsyn, N. S. Mosyagin, and A. V. Titov, J. Chem. Phys. **103**, 6548 (1995).

[10] N. S. Mosyagin, A. V. Titov, and Z. Latajka, Int. J. Quantum Chem. **63**, 1107 (1997).

[11] A. V. Titov, Int. J. Quantum Chem. **57**, 453 (1996); M. G. Kozlov, A. V. Titov, N. S. Mosyagin, and P. V. Souchko, Phys. Rev. A **56**, R3326 (1997).

[12] A. V. Titov, N. S. Mosyagin, and V. F. Ezhov, Phys. Rev. Lett. **77**, 5346 (1996).

[13] N. S. Mosyagin, M. G. Kozlov, and A. V. Titov, J. Phys. B **31**, L763 (1998).

[14] U. Kaldor and E. Eliav, Adv. Quantum Chem. **31**, 313 (1998), and references therein.

[15] N. S. Mosyagin, E. Eliav, A. V. Titov, and U. Kaldor, J. Phys. B **33**, 667 (2000); T. A. Isaev, N. S. Mosyagin, M. G. Kozlov, A. V. Titov, E. Eliav, and U. Kaldor, J. Phys. B **33**, 5139 (2000).

[16] N. S. Mosyagin, A. V. Titov, E. Eliav, and U. Kaldor, J. Chem. Phys. **115**, 2007 (2001).

[17] K. Andersson, M. R. A. Blomberg, M. P. Fülscher, G. Karlström, R. Lindh, P.-A. Malmqvist, P. Neogrády, J. Olsen, B. O. Roos, A. J. Sadlej, M. Schütz, L. Seijo, L. Serrano-Andrés, P. E. M. Siegbahn, and P.-O. Widmark, MOLCAS, VERSION 4.1.

[18] W. R. Johnson and G. Soff, At. Data Nucl. Data Tables **33**, 405 (1985).

[19] G. Fricke, C. Bernhardt, K. Heilig, L. A. Schaller, L. Schellenberg, E. B. Shera, and C. W. Dejager, At. Data Nucl. Data Tables **60**, 177 (1995).

[20] V. F. Bratzev, G. B. Deyneka, and I. I. Tupitsyn, Bull. Acad. Sci. USSR, Phys. Ser. **41**, 173 (1977).

[21] D. Kunik and U. Kaldor, J. Chem. Phys. **55**, 4127 (1971).

[22] H. J. Monkhorst, Int. J. Quantum Chem. **11**, 421 (1977).

[23] P. V. Coveney and P. G. H. Sandars, J. Phys. B **16**, 3727 (1983).