Ab initio Study of *PT*-Odd Interactions in Thallium Fluoride

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Ab initio Dirac-Fock calculations of *PT*-odd interactions in TlF are reported which employ large sets of kinetically balanced Gaussian basis functions. Revised estimates are reported of bounds on the value of the electric dipole moment of the proton, d_p, the tensor-pseudotensor coupling constant, C_T, and the Schiff moment of the ^{205}Tl nucleus, Q, based on analysis of existing experimental data. [S0031-9007(97)03928-8]

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Quantum electrodynamics, which is the synthesis of relativistic quantum mechanics and electromagnetic theory, is manifestly symmetric with respect to both parity inversion and time reversal (*PT* even), and is firmly established by experiment. Purcell and Ramsey [1] were the first to suggest that violation of these mirror symmetries due to interactions between electrons and nucleons or between nucleons, which fall outside the theory of quantum electrodynamics, could not be ruled out without experimental evidence. The observation that parity is not conserved under spatial inversion of coordinates in the β decay of nuclei [2] led to an extensive search for other phenomena which are not mirror-symmetric with respect to spatial inversion (*P* odd), to time-reversal (*T* odd), or to spatial *and* time reversal (*PT* odd) [3]. Despite these efforts, however, the decay of the neutral K^0 meson remains the only known example of a *T*-odd process [4]. The origin of this effect is not understood, though several particle physics theories have been proposed to account for it [3]. Here, we are concerned solely with the molecular physics implications of *PT*-odd symmetry violations, the phenomenology of which has been surveyed extensively by Sandars [5,6].

The characteristic signature of a *PT*-odd effect in an atom or molecule is an effective interaction of the form

$$H_{\mathrm{eff}} = -d\boldsymbol{\sigma}_N \cdot \boldsymbol{\lambda}\,, \tag{1}$$

where the nuclear spin operator is denoted by $\boldsymbol{\sigma}_N$, and $\boldsymbol{\lambda}$ is a unit vector in the direction of the molecular axis. We restrict our attention to the evaluation of coupling constants, d, which arise due to the presence of a proton electric dipole moment (edm), d_p, a weak neutral current interaction, or an nuclear edm induced by *PT*-odd nuclear forces.

Sandars [7] noted that effects due to d_p would be enhanced by the internal electric field of a polar molecule, since spin-rotational states close in energy but opposite in parity are mixed by *PT*-odd interactions. As a consequence of Schiff's theorem [8], however, the first-order interaction of an edm with the internal electric field of a molecule is nonvanishing only because of the magnetic interactions and the finite size of the nucleus [8,9]. Accurate theoretical calculations of these effects can only be achieved if the electronic motion is treated relativistically. The TlF molecule was identified as the most promising candidate for the study of *PT*-odd interactions involving d_p in diatomic molecules. Since TlF is diamagnetic, the first-order interaction energy due solely to the electron edm, d_e, vanishes identically, yet the molecule is polar, highly polarizable, and chemically stable. The nuclei ^{205}Tl and ^{19}F have a single unpaired proton spin in the shell model, which facilitates analysis of the experiments and eliminates any contribution from the neutron edm, d_n. A series of theoretical and experimental investigations have been made to search for the signature of *PT*-odd interactions in TlF [10–17], whose null results have led to one of the best experimental upper bounds on d_p. The interpretation of the experimental results depends, however, on nuclear and electronic structure calculations, and it is the electronic part of the analysis of the TlF experiments which is addressed in this Letter. This study represents a considerable advance in the state of the art of relativistic molecular electronic structure calculations.

The wave function of the TlF system is denoted by $\boldsymbol{\Psi}$, and is assumed to have the approximate form

$$\boldsymbol{\Psi} = \psi_N(\mathbf{r}_N)\psi_F(\mathbf{r}_f)\psi_e(\mathbf{r}_e)\psi_R(\mathbf{r}_N, \mathbf{I})\,. \tag{2}$$

It comprises a nuclear wave function, $\psi_N(\mathbf{r}_n)$ for ^{205}Tl, a nuclear wave function, $\psi_F(\mathbf{r}_f)$ for ^{19}F, an electronic wave function $\psi_e(\mathbf{r}_e)$, and a spin-rotational wave function, $\psi_R(\mathbf{r}_N, \mathbf{I})$.

Hinds and Sandars [12] demonstrated that the coupling constant in Eq. (1) resulting from a nonzero d_p could be separated into a contribution arising from the finite volume of the nucleus, d^V, and from a magnetic contribution, d^M, which perturbs the electrostatic equilibrium of the system.

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These constants are given explicitly by

$$d^V = d_p R X, \qquad \text{where } X = \sum_j X_j\,, \tag{3a}$$

$$X_j = \frac{2\pi}{3}\,[\nabla(\psi_j^\dagger(0)\psi_j(0))]_\lambda\,, \tag{3b}$$

$$d^M = -2\sqrt{2}\,d_p\left(\frac{\mu_N}{Z} + \frac{1}{2m_N c}\right)M, \qquad \text{where } M = \sum_j M_j\,, \tag{3c}$$

$$M_j = \frac{1}{\sqrt{2}}\,\langle\psi_j|\,\frac{(\boldsymbol{\alpha}\times\boldsymbol{\ell})_{j,\lambda}}{r^3}\,|\psi_j\rangle\,. \tag{3d}$$

The sum over j includes all occupied single-particle states which are used to construct $\psi_e(\mathbf{r}_e)$. The subscript λ indicates that only the component in the direction of $\boldsymbol{\lambda}$ has a nonvanishing expectation value. The nuclear parameters occurring in d^V and d^M are derived from experiment or from calculations based on nuclear shell theory. In particular, μ_N is the nuclear magnetic moment, m_N is the mass of the nucleus, and Z is the nuclear charge. The nuclear structure parameter, R, is defined by

$$R = \langle r_N^2\rangle_{Av} - \langle r_N^2\rangle_{3s}\,, \tag{4}$$

and represents the difference between the average mean-square radius of all the protons in the nucleus, and the mean-square radius of the unpaired $3s$ nuclear proton in ^{205}Tl.

An interaction may also be defined [14], involving a weak PT-odd neutral current interaction between electrons and neutrons. The effective Hamiltonian is also of the form Eq. (1), with an interaction constant, d^T, given by

$$d^T = -\sqrt{2}\,C_T T, \qquad \text{where } T = \sum_j T_j\,, \tag{5a}$$

$$T_j = -i\langle\psi_j|\varrho_p(\mathbf{r}_j)\,(\gamma_0\boldsymbol{\alpha})_{j,\lambda}|\psi_j\rangle\,. \tag{5b}$$

The unknown coupling constant C_T is characteristic of the strength of the tensor-pseudotensor weak neutral current interaction, and $\varrho_p(\mathbf{r})$ is the normalized distribution of the unpaired proton in the shell model of ^{205}Tl.

Even if the proton and neutron possess no permanent edm, the structure of the ^{205}Tl nucleus may induce a permanent nuclear edm [14] through the action of PT-odd nuclear forces. Preserving only contributions which lead to an effective interaction of the form of Eq. (1), we define an interaction constant, d^Q, where

$$d^Q = -6QX\,, \tag{6a}$$

$$Q = \frac{1}{6}\left[\frac{3}{5}\,\langle\psi_N|\sum_n q_n r_n^3\mathbf{C}_n^1|\psi_N\rangle - 1/Z\langle\psi_N|\sum_n q_n r_n^2|\psi_N\rangle \times \langle\psi_N|\sum_n q_n r_n\mathbf{C}_n^1|\psi_N\rangle\right]_\lambda. \tag{6b}$$

The Schiff moment [18], Q, of the nucleus involves a sum over its constituent nucleons, n, whose individual charges are q_n. The spherical tensor, $\mathbf{C}^1$, has its usual definition [19].

In practice, the coefficients X_j are calculated using the relation

$$X_j = \lim_{r_n\to 0}\frac{1}{r_n^2}\left[\int_0^{2\pi} d\varphi_j\int_0^{\pi}\sin\theta_j\,d\theta_j \times\int_0^{r_n} r_j^2\,dr_j\,\psi_j^\dagger(\mathbf{r}_j)\,\frac{\cos\theta_j}{r_j^2}\,\psi_j(\mathbf{r}_j)\right], \tag{7}$$

while the contributions M_j and T_j are reduced to expansions involving single-particle integrals.

Nuclear magnetic resonance experiments have been performed on a molecular beam of TlF subjected to external electric and magnetic fields [17]. In these experiments the hyperfine structure is measured with the external fields aligned both parallel and antiparallel. The frequency shift, $\delta\nu$, in the hyperfine structure due to the reversal of one of the external fields is related to the effective molecular edm constants, $d^{V,M,T,Q}$, by

$$h\delta\nu = 4d^{V,M,T,Q}|\langle\boldsymbol{\sigma}_N\cdot\boldsymbol{\lambda}\rangle|\,. \tag{8}$$

From the experimental null results, bounds on the value of d_p may be deduced from the experiment using $d^{V,M}$, d^T places bounds on C^T, and d^Q determines bounds on the ^{205}Tl nuclear structure factor, Q.

Our numerical values of X, M, and T are obtained within the Dirac-Fock approximation [20,21], using an uncontracted kinetically balanced $34s34p16d9f$ basis set centered on the ^{205}Tl nucleus, a $9s6p2d$ basis centered on ^{19}F, and an internuclear separation of 210 pm. The Tl-centered basis set is constructed from a master list of 35 exponents, $\{\zeta_k, k = 1, 2, \ldots, 35\}$, which span the range $0.02 \le \zeta_k \le 5.0\times 10^8$. The basis sets for each l-value comprise subsets of the master list. This atomic basis set yields an average of configuration electronic energy for Tl of $-20\,274.838\,713$ a.u., which is 11.9×10^{-3} a.u. above the Dirac-Fock limit. The *ab initio* values of X, M, and T calculated in this basis set and values of d_p, C_T, and Q derived from them are presented in Table I, together with the corresponding data deduced from [14] and [17]. The quoted uncertainties are purely experimental, and the corrections to the results of [14] noted in Refs. (30) and (35) of [17] have been incorporated in our summary. The value $R = 2.9$ fm^2 [Eq. (4)] has been used in the evaluation of X to facilitate comparison with [17].

We have performed extensive numerical studies that indicate that the values of X, M, and T vary only slightly with the internuclear separation in the vicinity of the equilibrium geometry. On the basis of our investigations into the effects of vibrational averaging at different internuclear separations, basis set superposition errors and basis set incompleteness, numerical limits on the Dirac-Fock value of X are estimated to be $\pm 8\%$. In the derivation of Eq. (3a) it is required that the electrostatic forces on

TABLE I. Numerical values of X, M, and T, and the PT-odd parameters d_p, C_T, and Q deduced from the TlF molecular beam experiments reported in [17].

	X (a.u.)	M (a.u.)	T (a.u.)	d_p (e cm)	C_T	Q (e fm^3)
Refs. [14,17]	2128	4.41	−4.12	$(-3.7 \pm 6.3) \times 10^{-23}$	$(-1.5 \pm 2.6) \times 10^{-7}$	$(2.3 \pm 3.9) \times 10^{-10}$
This work	8747	13.63	−22.44	$(-1.5 \pm 2.5) \times 10^{-23}$	$(-2.8 \pm 4.8) \times 10^{-8}$	$(5.6 \pm 9.5) \times 10^{-11}$

the nuclei vanish at the equilibrium geometry. We have verified that the calculated electrostatic force on the ^{205}Tl nucleus vanishes very close to the minimum of the potential energy curve if g-type polarization functions are added to the Tl basis set. The small electrostatic fields which persist in basis set solutions of self-consistent field equations with an incomplete basis set have an insignificant effect on X, though there is some perturbation of the single particle contributions, X_j, for core orbitals, which cancel in a manner reminiscent of the behavior reported in [12]. Since the contributions to X and T are very localized, only ^{205}Tl-centered basis functions are included in their evaluation. The calculated value of M, however, includes all one- and two-center contributions, since the amplitudes which define it extend significantly beyond the dimensions of the nucleus. The values of M and T are less sensitive to details of the calculation than the value of X, and appear to have converged to within $\pm 2\%$ of the Dirac-Fock limit. These numerical studies of the electronic structure of TlF revealed several technical difficulties specific to *ab initio* calculation of molecular PT-odd effects, and will be published elsewhere [22].

We have rederived Eq. (18) and Eq. (45) of [12] and are able to reproduce their results in all details. Given the numerical values of the constants appearing in Eqs. (22), (25), (45), and (49) of [12], however, the sign of d^V/d_p [Eq. (51)] should be reversed if it is to be combined with d^M/d_p to obtain estimates of the experimental limits on d_p. This is the sign convention which has been adopted in our interpretation of the experimental data, which is summarized in Table I. Consequently, our values of X and M are both about four times larger than the corresponding results deduced from [14], but this ratio is not reflected directly in the deduced values of d_p.

Since TlF has a closed-shell electronic configuration, and the values of X, M, and T are determined almost wholly by wave function amplitudes in the vicinity of the nucleus, we do not expect electron correlation effects to change substantially the magnitudes of these quantities. Clearly, the calculations of Hinds and Sandars [12] and Coveney and Sandars [14] do provide reliable order-of-magnitude estimates of X, M, and T. Our calculations have reduced significantly the upper bounds on d_p, C_T, and Q, so that the values in Table I are now the most restrictive experimental limits available for these quantities.

These Dirac-Fock calculations indicate clearly that there has been substantial progress in relativistic molecular electronic structure theory since the recent comprehensive reviews of Mårtensson-Pendrill [23] and Kozlov and Labzowsky [24]. All-electron *ab initio* molecular orbital calculations of the structures of small molecules containing heavy elements using large basis sets may now be performed routinely within the restricted kinetic balance basis set prescription, which ensures accurate representation of four-spinor amplitudes in the neighborhood of heavy nuclei. These developments are essential, since the molecular experiments which are now underway to investigate PT-odd interactions [25] in paramagnetic diatomic molecules are sensitive probes of electron density near heavy nuclei, and require an accurate treatment of relativistic and many-body effects for their interpretation. *Ab initio* calculations of electron edm parameters for YbF, HgF, and BaF have already been performed [26] which, together with a detailed technical account of the computational techniques adopted in the present work [22], will be published in due course.

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