

# Study of P,T-Parity Violation Effects in Polar Heavy-Atom Molecules

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**Summary.** Investigation of P,T-parity nonconservation (PNC) phenomena is of fundamental importance for physics. Experiments to search for PNC effects have been performed on TlF and YbF molecules and are in progress for PbO and PbF molecules. For interpretation of molecular PNC experiments it is necessary to calculate those needed molecular properties which cannot be measured. In particular, electronic densities in heavy-atom cores are required for interpretation of the measured data in terms of the P,T-odd properties of elementary particles or P,T-odd interactions between them. Reliable calculations of the core properties (PNC effect, hyperfine structure etc., which are described by the operators heavily concentrated in atomic cores or on nuclei) usually require accurate accounting for both relativistic and correlation effects in heavy-atom systems. In this paper, some basic aspects of the experimental search for PNC effects in heavy-atom molecules and the computational methods used in their electronic structure calculations are discussed. The latter include the generalized relativistic effective core potential (GRECP) approach and the methods of nonvariational and variational one-center restoration of correct shapes of four-component spinors in atomic cores after a two-component GRECP calculation of a molecule. Their efficiency is illustrated with calculations of parameters of the effective P,T-odd spin-rotational Hamiltonians in the molecules PbF, HgF, YbF, BaF, TlF, and PbO.

**Key words:** electronic structure, heavy-atom molecules, *ab initio* method, relativistic effective core potential, hyperfine structure, parity violation.

## Introduction

It is well recognized that polar diatomics containing heavy elements are very promising objects for the experimental search for the break of inversion symmetry (P) and time-reversal invariance (T). Though the search for the P,T-parity nonconservation (PNC) effects in heavy atoms and heavy-atom molecules has produced null results up to now, there are serious reasons to search for them with the presently accessible (expected) level of experimental sensitivity. The observation of non-zero P,T-odd effects at this level would indicate the presence of so-called “new physics” [1, 2] beyond the Standard Model (SM) of electroweak and strong interactions [3–6] that is certainly of fundamental importance. Despite well known drawbacks and unresolved

problems of the Standard Model (radiative corrections to the Higgs mass are quadratically divergent; rather artificial Higgs mechanism of symmetry breaking is not yet verified in experiment; the problem of CP-violation is not well understood, where “C” is charge conjugation symmetry etc.) there are no experimental data available which would be in direct contradiction with this theory (see section 2 and papers [2, 7] for more details and references). In turn, some popular extensions of the Standard Model, which allow one to overcome its disadvantages, are not confirmed experimentally.

A crucial feature of PNC experiments in atoms, molecules, liquids or solids is that for interpretation of measured data in terms of fundamental constants of the P,T-odd interactions, one must calculate those properties of the systems, which establish a connection between the measured data and studied fundamental constants (see section 3). These properties are described by operators heavily concentrated near or on heavy nuclei; they cannot be measured and their theoretical study is not a trivial task. During the last several years the significance of (and requirement for) *ab initio* calculation of electronic structure providing a high level of reliability and accuracy in accounting for both relativistic and correlation effects has only increased (see sections 2 and 9).

The main goal of the paper is to discuss the present status of relativistic calculations of P,T-odd properties in heavy-atom molecules, the two-step methodology used in these calculations, and the accuracy of this method. The historical background of the PNC study in atoms and molecules, its current status and some general remarks on the PNC experiments are presented in sections 1, 2 and 3, correspondingly. The *ab initio* relativistic methods and the two-step techniques of calculation designed for studying PNC properties in heavy-atom molecules are discussed in sections 4 and 5. The calculations of PNC properties and hyperfine structure in molecules PbF, HgF, YbF, BaF, TlF and PbO are presented in sections 6–9. Concluding remarks are outlined in section 10.

## 1 Study of P- and T-parity nonconservation effects in heavy-atom molecules: Historical background

After discovery of the combined charge and space parity violation, or CP-violation, in  $K_L^0$ -meson decay [8], the search for the electric dipole moments (EDMs) of elementary particles has become one of the most fundamental problems in physics [1, 2, 7, 9, 10]. A permanent EDM is induced by the weak interaction that breaks both the space symmetry inversion and time-reversal invariance [11]. Considerable experimental effort has been invested in probing for atomic EDMs induced by EDMs of the proton, neutron and electron, and by P,T-odd interactions between them. The best available restriction for the electron EDM,  $d_e$ , was obtained in the atomic Tl experiment [12], which established an upper limit of  $|d_e| < 1.6 \times 10^{-27} e\text{-cm}$ , where  $e$  is the charge

of the electron. The benchmark upper limit on a nuclear EDM is obtained in atomic experiment on  $^{199}\text{Hg}$  [13],  $|d_{\text{Hg}}| < 2.1 \times 10^{-28} e\text{-cm}$ , from which the best restriction on the proton EDM,  $|d_p| < 5.4 \times 10^{-24} e\text{-cm}$ , was also recently obtained by Dzuba *et al.* [14] and Dmitriev & Sen'kov [15] (the previous upper limit on the proton EDM was obtained in  $^{129}\text{Xe}$  [14, 16] and the TIF experiment, see below).

Since 1967, when Sandars suggested the use of polar heavy-atom molecules in the experimental search for the proton EDM [17], molecules have been considered the most promising objects for such experiments. Sandars also noticed earlier [18] that the P- and P,T-parity nonconservation effects are strongly enhanced in heavy atoms due to relativistic and other effects. For example, in paramagnetic atoms the enhancement factor for an electron EDM,  $d_{\text{atom}}/d_e$ , is roughly proportional to  $\alpha^2 Z^3 \alpha_D$ , where  $\alpha \approx 1/137$  is the fine structure constant,  $Z$  is the nuclear charge and  $\alpha_D$  is the atomic polarisability (the  $\alpha^2 Z^3$  enhancement formula was first derived by Flambaum [19]). It can be of order 100 or greater for highly polarizable heavy atoms ( $Z \geq 50$ ). Furthermore, the effective intramolecular electric field acting on electrons in polar molecules can be five or more orders of magnitude higher than the maximal field accessible in a laboratory. The first molecular EDM experiment was performed on TIF by Sandars *et al.* [20] (Oxford, UK); it was interpreted as a search for the proton EDM and other nuclear P,T-odd effects. In 1991, in the last series of the  $^{205}\text{TlF}$  experiments by Hinds *et al.* [21] (Yale, USA), the restriction  $d_p = (-4 \pm 6) \times 10^{-23} e\text{-cm}$  was obtained (this was finally recalculated in 2002 by Petrov *et al.* [22] as  $d_p = (-1.7 \pm 2.8) \times 10^{-23} e\text{-cm}$ ).

The experimental search for the P-odd effects and electron EDM was further stimulated since 1978 by theoretical papers of Labzowsky [23] and Sushkov & Flambaum [24], respectively, who clarified the possibilities of additional enhancement of these effects in diatomic radicals like BiS and PbF due to the closeness of levels of opposite parity in  $\Omega$ -doublets having a  $^2\Pi_{1/2}$  ground state (see also papers [25, 26], in which similar ideas are independently proposed). Then Sushkov *et al.* [27] and Flambaum & Khriplovich [28] suggested the use of  $\Omega$ -doubling in diatomic radicals with a  $^2\Sigma_{1/2}$  ground state for such experiments and the HgF, HgH and BaF molecules were first studied semiempirically by Kozlov [29]. At the same time, the first two-step *ab initio* calculation of PNC effects in PbF initiated by Labzowsky was finished by Titov *et al.* [30, 31]. A few years later, Hinds started an experimental search for the electron EDM in the YbF molecule, on which the first result was obtained by his group in 2002 (Sussex, UK) [32],  $d_e = (-0.2 \pm 3.2) \times 10^{-26} e\text{-cm}$ . Though that restriction is worse than the best current  $d_e$  datum (from the Tl experiment, see above), nevertheless, it is limited by only counting statistics, as Hinds *et al.* pointed out in [32].

A new series of electron EDM experiments on YbF by Hinds' group (Imperial College, UK) are in progress [33] and a new generation of electron EDM experiments using a vapor cell, on the metastable  $a(1)$  state of PbO,

is being prepared by the group of DeMille (Yale, USA). The unique suitability of PbO for searching for the elusive  $d_e$  is demonstrated by the very high projected statistical sensitivity of the Yale experiment to the electron EDM. In prospect, it allows one to detect  $d_e$  of order of  $10^{-29} \div 10^{-31} e\cdot\text{cm}$  [34], two–four orders of magnitude lower than the current limit quoted above. Some other candidates for the EDM experiments, in particular, HgH, HgF, TeO\*, and HI<sup>+</sup> are being discussed and an experiment on PbF is planned (Oklahoma Univ., USA).

## 2 Present status of the electron EDM search

As is mentioned in the introduction, the observation of a non-zero EDM would point out the presence of so called “new physics” (see [2, 35] and references) beyond the Standard Model [3–6, 36] or CP violation in the QCD sector of SM,  $SU(3)_C$ . The discovery of a lepton EDM (electron EDM in our case) would have an advantage as compared to the cases of neutron or proton EDMs because the latter are not considered as elementary particles within the SM and its extensions.

In Table 1 some estimates for the electron EDM predicted by different theoretical models are given (e.g., see [7] for more details). One can see from the table that the most conservative estimate is given by the Standard Model. This is explained by severe cancellations and suppressions of the contributions producing the electron EDM within the SM. In turn, the “new physics” (extensions of the Standard Model: supersymmetry (SUSY) [2, 37, 38] multi-Higgs [39–41], left-right symmetry [38, 40, 42], lepton flavor-changing [43, 44] etc.) is very sensitive to the EDMs of elementary particles. This is especially true for the minimal (“naive”) SUSY model, which predicts an electron EDM already at the level of  $10^{-25} e\cdot\text{cm}$ . However, the best experimental estimate on the electron EDM,  $1.6 \times 10^{-27} e\cdot\text{cm}$ , obtained in the experiment on the Tl atom [12], is almost two orders of magnitude smaller. More sophisticated SUSY models (which are extremely popular among theorists because they allow one to overcome serious theoretical drawbacks of SM, explain the “gauge hierarchy problem”, solve the problem of dark matter in astrophysics etc.) still predict the electron EDM at the level of  $10^{-27} e\cdot\text{cm}$  or somewhat smaller. Since the Tl experiment is finished now, an intriguing expectation is connected with the ongoing experiment on the  $a(1)$  state of the PbO molecule, which is expected to be sensitive to the electron EDM at least two orders of magnitude smaller. Thus, the most popular extensions of SM can be severely examined by this experiment, i.e. even the result compatible with zero will dramatically influence their status.

**Table 1.** Prediction for the electron EDM,  $|d_e|$ , in popular theoretical models

Model	$ d_e $ (in $e\cdot\text{cm}$ )
Standard Model	$< 10^{-38}$
Left-right symmetric	$10^{-28} - 10^{-26}$
Lepton flavor-changing	$10^{-29} - 10^{-26}$
Multi-Higgs	$10^{-28} - 10^{-27}$
Supersymmetric	$\leq 10^{-25}$
Experimental limit [12]	$< 1.6 \times 10^{-27}$

### 3 General remarks on experimental search for EDMs in atoms and molecules

The experiments to search for EDMs in atoms and molecules are carried out using different approaches [7, 45]. The experimental technique depends on the properties of the atoms and molecules used in such an experiment. These properties influence the atomic and molecular sources, resonance region and detector. For example, for diatomic radicals like YbF or PbF the experiments on molecular beams are most reasonable, while for molecules with closed electronic shells in the ground state like PbO the EDM measurements can be carried out in optical cells.

Nevertheless, the statistical sensitivity of the experiments to the electron or proton EDM usually depends on some parameters common for all such EDM experiments. The easiest way to see this is to apply the Heisenberg uncertainty principle to evaluate the sensitivity of the EDM measurement. Suppose that the EDM of a molecule is measured in some electric field,  $\mathbf{E}$ . (Do not confuse the *EDM of a polar molecule* with the large conventional *dipole moment* of the molecule, which averages to zero in the absence of external electric field in the laboratory coordinate system. In contrast to the latter, the (vanishingly small) molecular EDM can exist only due to P,T-odd interactions; it is *permanent* and its direction depends on the sign of the projection of the total electronic momentum on the molecular axis. See [7] for more details.) Thus the energy of interaction of the molecular EDM,  $\mathbf{d} = d\boldsymbol{\sigma}$  (where  $\boldsymbol{\sigma}$  is a unit vector along the total angular momentum of the molecule), with the electric field is  $\mathbf{d} \cdot \mathbf{E}$  (linear Stark effect) and the energy difference between the levels with opposite directions of the total angular momentum (leading to the contributions of different signs) is  $2\mathbf{d} \cdot \mathbf{E}$ . If a measurement is carried out by detecting the energy shift during a time  $T$ , the uncertainty in the  $d$  determination is  $\delta d = \hbar/(2T\mathbf{E} \cdot \boldsymbol{\sigma})$ . For such measurement on  $N$  uncorrelated molecules one, obviously, has

$$\delta d = \hbar / (2T\sqrt{N}\mathbf{E} \cdot \boldsymbol{\sigma}) = \hbar / (2TE_{\sigma}\sqrt{\tau dN/dt}),$$

where  $dN/dt$  is the counting rate,  $E_{\sigma} = \mathbf{E} \cdot \boldsymbol{\sigma}$ , and  $\tau$  is the total measurement time (usually  $\tau \gg T$  and  $T$  is limited by the *coherence time* of the considered system). Up to now we deal with the molecular EDM  $\mathbf{d}$ . Let us write  $d = Gd_e$ , where  $d_e$  is the value of the *electron EDM* (the same is valid, of course, for the proton EDM) and  $G$  is the proportionality coefficient (usually called the *enhancement factor*). Thus, the final expression for  $\delta d_e$  is

$$\delta d_e = \frac{\hbar}{2TGE_{\sigma}\sqrt{\tau dN/dt}} = \frac{\hbar}{2TW\sqrt{\tau dN/dt}}, \quad (1)$$

where the value  $W = GE_{\sigma}$  is the *effective electric field* in the molecule, which can be interpreted as the field that should be applied along the EDM of a free electron to give the energy shift  $2Wd_e \equiv 2E_{\sigma}d$ .

From expression (1), the basic conditions which should be met in any prospective EDM experiment can be derived:

1. The counting rate ( $dN/dt$ ) should be made as high as possible. From this point of view the experiments on vapor cells, like that planned for PbO, have a clear advantage as compared to beam experiments because molecular vapor density can be usually made much higher than molecular beam density. Thus, in the experiment on the PbO cell the counting rate is estimated to be of order  $10^{11}$ – $10^{15}$  Hz [34], while in the experiment on the YbF molecular beam the counting rate was of order  $10^4$  Hz [32].
2. It is crucial to attain high coherence time  $T$ . In the beam experiments that time is just the time of flight through the region with the electric field. For a gas-dynamic molecular source the typical time of flight is 1 – 10 ms. On the other hand, for the PbO experiment in vapor cell  $T$  is close to the lifetime of the excited (metastable) state  $a(1)$ ,  $T \approx 0.1$  ms. So, the beam experiments have advantage in the coherence time.
3. It is also critical to have a high value of the effective electric field  $W$ , acting on the electron. The only way to know that parameter is to perform relativistic calculations. It is notable that the first semiempirical estimates of this kind were performed by Sandars in [17, 18] for Cs and TlF, correspondingly. In these papers the importance of accounting for relativistic effects and using heavy atoms and heavy-atom molecules in EDM experiments was first understood.

The expected energy difference,  $2\mathbf{d} \cdot \mathbf{E}$  is extremely small even for completely polarized heavy-atom molecules. Thus, in practice, the EDM experiment is usually carried out in parallel and antiparallel electric and magnetic ( $\mathbf{B}$ ) fields. Interaction energy of the molecular magnetic moment,  $\boldsymbol{\mu}$ , with the magnetic field is much higher than that of the EDM with the electric field and the energy differences are

$$2\boldsymbol{\mu} \cdot \mathbf{B} + 2\mathbf{d} \cdot \mathbf{E}$$

and

$$2\boldsymbol{\mu} \cdot \mathbf{B} - 2\mathbf{d} \cdot \mathbf{E}$$

for parallel and antiparallel fields, respectively (in practice, the atomic or molecular spin precession is usually studied instead of direct measurement of the energy shift, see [45]). When the electric field is reversed, the energy shift,  $4\mathbf{d} \cdot \mathbf{E} = 4d_e W$ , points to the existence of the permanent molecular EDM. The same measurement technique is applicable to studying other P,T-odd interactions in atoms and molecules.

The electronic structure parameters describing the P,T-odd interactions of electrons (sections 6, 7, and 9) and nucleons (section 8) including the interactions with their EDMs should be *reliably* calculated for interpretation of the experimental data. Moreover, *ab initio* calculations of some molecular properties are usually required even for the stage of preparation of the experimental setup. Thus, electronic structure calculations suppose a high level of accounting for both correlations and relativistic effects (see below). Modern methods of relativistic *ab initio* calculations (including very recently developed approaches) allow one to achieve the required high accuracy. These approaches will be outlined and discussed in the following sections.

#### 4 Heavy-atom molecules: Computational strategies.

The most straightforward method for electronic structure calculation of heavy-atom molecules is solution of the eigenvalue problem using the Dirac-Coulomb (DC) or Dirac-Coulomb-Breit (DCB) Hamiltonians [46–48] when some approximation for the four-component wave function is chosen.

However, even applying the four-component single configuration (SCF) approximation, Dirac-Fock (DF) or Dirac-Fock-Breit (DFB), to calculation of heavy-atom molecules (followed by transformation of two-electron integrals to the basis of molecular spinors is not always an easy task) because a very large set of primitive atomic basis functions can be required for such all-electron four-component SCF calculations (see [49]). Starting from the Pauli approximation and Foldy–Wouthuysen transformation, many different two-component approaches were developed in which only large components are treated explicitly (e.g., see [50–53] and references). In addition, the approaches with perturbative treatment of relativistic effects [54] have been developed in which a nonrelativistic wavefunction is used as reference. During the last few years, good progress was also attained in four-component techniques [46, 55–57] which allowed one to reduce efforts in calculation and transformation of two-electron matrix elements with small components of four-component molecular spinors. These developments are applied, in particular, in the DIRAC [58] and BERTHA [59, 60] molecular programs. Thus, accurate DC(B) calculations of relatively simple heavy-atom molecules can be performed on modern computers now.

The greatest computational savings are achieved when the two-component relativistic effective core potential (RECP) approximation suggested originally by Lee *et al.* [61] is used (e.g., see reviews [62–64]). There are several reasons for using RECPs (including model potentials and pseudopotentials) in calculations of complicated heavy-atom molecules, clusters and solids. The RECP approaches allow one to exclude the large number of chemically inactive electrons from molecular calculations and to treat explicitly only valence and outermost core electrons from the beginning. Then, the oscillations of the valence spinors are usually smoothed in heavy-atom cores simultaneously with excluding small components from the explicit treatment. As a result the number of primitive basis functions can be reduced dramatically; this is especially important for calculation and transformation of two-electron integrals when studying many-atomic systems and compounds of very heavy elements including actinides and superheavies. The RECP method is based on a well-developed nonrelativistic technique of calculations; however, an effective spin-orbit interaction and other scalar-relativistic effects are taken into account usually by means of radially-local [62–65], separable [66–68] or Huzinaga-type [69–71] operators.

Correlation molecular calculations with RECPs are naturally performed in the basis of spin-orbitals (and not of spinors as is in all-electron four-component calculations) even for the cases when quantum electrodynamics (two-electron Breit etc.) effects are taken into account [49,72]. Note, however, that the DCB technique with the separated spin-free and spin-dependent terms also has been developed [73], but it can be efficiently applied only in the cases when spin-dependent effects can be neglected both for valence and for core shells. In the RECP method, the interactions with the excluded inner core shells (spinors!) are described by spin-dependent potentials whereas the explicitly treated valence and outer core shells are usually described by spin-orbitals in molecular calculations. It means that some “soft” way of accounting for the core-valence orthogonality constraints is applied in the latter case [74] (note, meantime, that the strict core-valence orthogonality can be retrieved after the RECP calculation by using the restoration procedures described below). Another merit of the RECP method is in its natural ability to account for correlations with the explicitly excluded inner core electrons [75] (this direction is actively developed during last years). The use of the molecular spin-orbitals and the “correlated” RECPs allows one to reduce dramatically the expenses at the stage of correlation calculation of heavy-atom molecules. These are important advantages when a very high level of accounting for correlations is required even in studying diatomics (e.g., see calculations of PbO described in section 9). Thus, many complications of the DC(B) molecular calculations are avoided when employing RECPs.

The “shape-consistent” (or “norm-conserving”) RECP approaches are most widely employed in calculations of heavy-atom molecules though “energy-adjusted/consistent” pseudopotentials [63] by Stuttgart team are also ac-



tively used as well as the Huzinaga-type “*ab initio* model potentials” [71]. In plane wave calculations of many-atom systems and in molecular dynamics, the separable pseudopotentials [66–68] are more popular now because they provide linear scaling of computational effort with the basis set size in contrast to the radially-local RECPs. The nonrelativistic shape-consistent effective core potential was first proposed by Durand & Barthelat [76] and then a modified scheme of the pseudoorbital construction was suggested by Christiansen *et al.* [77] and by Hamann *et al.* [78].

In a series of papers (see [72, 74, 75, 79, 80] and references) a generalized RECP approach was developed that involves both radially-local, separable and Huzinaga-type potentials as its components in particular cases. It allows one to attain very high accuracy of calculation of valence properties and electronic densities in the valence region when treating outermost core shells in calculations explicitly (see section 5 for more details).

Nevertheless, calculation of such properties as spin-dependent electronic densities near nuclei, hyperfine constants, P,T-parity nonconservation effects, chemical shifts etc. with the help of the two-component pseudospinors smoothed in cores is impossible. We should notice, however, that the above core properties (and the majority of other properties of practical interest which are described by the operators heavily concentrated within inner cores or on nuclei) are mainly determined by electronic densities of the valence and outer core shells near to, or on, nuclei. The valence shells can be open or easily perturbed by external fields, chemical bonding etc., whereas outer core shells are noticeably polarized (relaxed) in contrast to the inner core shells. Therefore, accurate calculation of electronic structure in the valence and outer core region is of primary interest for such properties.

For evaluation of the matrix elements of the operators concentrated on (or close to) nuclei, proper shapes of the valence molecular four-component spinors must be restored in atomic core regions after performing the RECP calculation of that molecule. In 1959, a nonrelativistic procedure of restoration of the orbitals from smoothed Phillips–Kleinman pseudoorbitals was proposed [81] based on the orthogonalization of the latter to the original atomic core orbitals. In 1985, Pacios & Christiansen [82] suggested a modified orthogonalization scheme in the case of shape-consistent pseudospinors. At the same time, a simple procedure of “nonvariational” one-center restoration (NOCR, see below) employing the idea of generation of equivalent basis sets in four-component Dirac-Fock and two-component RECP/SCF calculations was proposed and first applied in [30] to evaluation of the P,T-odd spin-rotational Hamiltonian parameters in the PbF molecule. In 1994, a similar procedure was used by Blöchl inside the augmentation regions [83] in solids to construct the transformation operator between pseudoorbitals (“PS”) and original orbitals (“AE”) in his projector augmented-wave method.

All the above restoration schemes are called “nonvariational” as compared to the “variational” one-center restoration (VOCR, see below) proce-

ture proposed in [84, 85]. Proper behavior of the molecular orbitals (four-component spinors) in atomic cores of molecules can be restored in the scope of a variational procedure if the molecular pseudoorbitals (two-component pseudospinors) match correctly the original orbitals (large components of bispinors) in the valence region after the molecular RECP calculation. As is demonstrated in [49, 74], this condition is rather correct when the shape-consistent RECP is involved to the molecular calculation with explicitly treated outermost core orbitals and, especially, when the generalized RECP operator is used since the above matching condition is implemented at their generation.

At the restoration stage, a one-center expansion in the spherical harmonics with numerical radial parts is most appropriate both for orbitals (spinors) and for the description of “external” interactions with respect to the core regions of a considered molecule. In the scope of the discussed two-step methods for the electronic structure calculation of a molecule, finite nucleus models and quantum electrodynamic terms including, in particular, two-electron Breit interaction may be taken into account without problems [72].

One-center expansion was first applied to whole molecules by Desclaux & Pyykkö in relativistic and nonrelativistic Hartree-Fock calculations for the series  $\text{CH}_4$  to  $\text{PbH}_4$  [86] and then in the Dirac-Fock calculations of  $\text{CuH}$ ,  $\text{AgH}$  and  $\text{AuH}$  [87] and other molecules [88]. A large bond length contraction due to the relativistic effects was estimated. However, the accuracy of such calculations is limited in practice because the orbitals of the hydrogen atom are reexpanded on a heavy nucleus in the entire coordinate space. It is notable that the RECP and one-center expansion approaches were considered earlier as alternatives to each other [89, 90].

The applicability of the discussed two-step algorithms for calculation of wavefunctions of molecules with heavy atoms is a consequence of the fact that the valence and core electrons may be considered as two subsystems, interaction between which is described mainly by some integrated properties of these subsystems. The methods for consequent calculation of the valence and core parts of electronic structure of molecules give us a way to combine the relative simplicity and accessibility both of molecular RECP calculations in gaussian basis set, and of relativistic finite-difference one-center calculations inside a sphere with the atomic core radius.

The first two-step calculations of the P,T-odd spin-rotational Hamiltonian parameters were performed for the  $\text{PbF}$  radical about 20 years ago [30, 31], with a semiempirical accounting for the spin-orbit interaction. Before, only nonrelativistic SCF calculation of the  $\text{TlF}$  molecule using the relativistic scaling was carried out [91, 92]; here the P,T-odd values were underestimated by almost a factor of three as compared to the later relativistic Dirac-Fock calculations. The latter were first performed only in 1997 by Laerdahl *et al.* [93] and by Parpia [94]. The next two-step calculation, for  $\text{PbF}$  and

HgF molecules [95], was carried out with the spin-orbit RECP part taken into account using the method suggested in [96].

Later we performed correlation GRECP/NOCR calculations of the core properties in YbF [97], BaF [98], again in YbF [99] and in TlF [22]. In 1998, first all-electron Dirac-Fock calculations of the YbF molecule were also performed by Quiney *et al.* [100] and by Parpia [101]. Recently we finished extensive two-step calculations of the P,T-odd properties and hyperfine structure of the excited states of the PbO molecule [102, 103]. One more two-step calculation of the electron EDM enhancement effect was performed very recently for the molecular ion  $\text{HI}^+$  [104].

We would like to emphasize here that the all-electron Dirac-Fock calculations on TlF and YbF are, in particular, important for checking the quality of the approximations made in the two-step method. The comparison of appropriate results, Dirac-Fock vs. RECP/SCF/NOCR, is, therefore, performed in papers [22, 99] and discussed in the present paper.

In this paper, the main features of the two-step method are presented and PNC calculations are discussed, both those without accounting for correlation effects (PbF and HgF) and those in which electron correlations are taken into account by a combined method of the second-order perturbation theory (PT2) and configuration interaction (CI), or “PT2/CI” [105] (for BaF and YbF), by the relativistic coupled cluster (RCC) method [106, 107] (for TlF, PbO, and  $\text{HI}^+$ ), and by the spin-orbit direct-CI method [108–110] (for PbO). In the *ab initio* calculations discussed here, the best accuracy of any current method has been attained for the hyperfine constants and P,T-odd parameters regarding the molecules containing heavy atoms.

## 5 Two-step method of calculation of core properties

The two-step method consists of a two-component molecular RECP calculation at the first step, followed by restoration of the proper four-component wave function in atomic cores at the second step. Though the method was developed originally for studying core properties in heavy-atom molecules, it can be efficiently applied to studying the properties described by the operators heavily concentrated in cores or on nuclei of light atoms in other computationally difficult cases, e.g., in many-atom molecules and solids. The details of these steps are described below.

### *Generalized RECP*

When core electrons of a heavy-atom molecule do not play an active role, the effective Hamiltonian with RECP can be presented in the form

$$\mathbf{H}^{\text{Ef}} = \sum_{i_v} [\mathbf{h}^{\text{Schr}}(i_v) + \mathbf{U}^{\text{Ef}}(i_v)] + \sum_{i_v > j_v} \frac{1}{r_{i_v j_v}}. \quad (2)$$

This Hamiltonian is written only for a valence subspace of electrons which are treated explicitly and denoted by indices  $i_v$  and  $j_v$ . In practice, this subspace is often extended by inclusion of some outermost core shells for better accuracy but we will consider them as the valence shells below if these outermost core and valence shells are not treated using different approximations. In Eq. (2),  $\mathbf{h}^{\text{Schr}}$  is the one-electron Schrödinger Hamiltonian

$$\mathbf{h}^{\text{Schr}} = -\frac{1}{2}\nabla^2 - \frac{Z_{ic}}{r}, \quad (3)$$

where  $Z_{ic}$  is the charge of the nucleus decreased by the number of inner core electrons.  $\mathbf{U}^{\text{Ef}}$  in (2) is an RECP (relativistic pseudopotential) operator that is usually written in the radially-local (semi-local) [62] or separable (e.g., see [68] and references) approximations when the valence pseudospinors are smoothed in the heavy-atom cores. Contrary to the four-component wave function used in Dirac-Coulomb(-Breit) calculations, the pseudo-wave function in the RECP case can be both two- and one-component. The use of the effective Hamiltonian (2) instead of all-electron four-component Hamiltonians leads to the question about its accuracy. It was shown both theoretically and in many calculations (see [74, 80] and references) that the typical accuracy of the radially-local RECPs is within 1000–3000  $\text{cm}^{-1}$  for transition energies between low-lying states though otherwise is sometime stated (see [111, 112]).

In our two-step calculations the generalized RECP operator [74, 79] is used that includes the operators of radially-local shape-consistent RECP, separable pseudopotential and Huzinaga-type model potential as its components. Additionally, the GRECP operator can include terms of other types, known as “self-consistent” and two-electron “term-splitting” corrections [74, 79, 113], which are important particularly for economical (but precise!) treatment of transition metals, lanthanides and actinides. With these terms, the accuracy provided by GRECPs can be even higher than the accuracy of the frozen core approximation (employing the same number of explicitly treated electrons) because they can account for relaxation of explicitly excluded (inner core) electrons [74, 80]. The theoretical background of the GRECP concept is developed in a series of papers [49, 72, 74, 75, 79, 80]. In contrast to other RECP methods, GRECP employs the idea of separating the space around a heavy atom into three regions: inner core, outer core and valence, which are first treated employing different approximations for each. It allows one to attain practically any desired accuracy, while requiring moderate computational efforts since the overall accuracy is limited in practice by possibilities of correlation methods.

When innermost core shells must be treated explicitly, the four-component versions of the GRECP operator can be used, in principle, together with the all-electron relativistic Hamiltonians. The GRECP can describe here some quantum electrodynamics effects (self-energy, vacuum polarization etc.) thus avoiding their direct treatment. One more remark is that the two-component GRECP operator can be applied even to very light atoms when smoothing

the large components of the four-component spinors only in the vicinity of the nucleus just to account for relativistic effects (the GRECP for hydrogen provides accuracy of treatment of very small relativistic contributions within 5%).

#### *Nonvariational One-Center Restoration*

The electronic densities evaluated from the two-component pseudo-wave function very accurately reproduce the corresponding all-electron four-component densities in the valence and outer core regions not only for the state used in the GRECP generation but also for other states which differ by excitations of valence electrons. This is illustrated in figure 1 (see also tables 8 and 9 in [49]), where the radial parts of the large components of the thallium bispinor and the corresponding pseudospinor are compared for the state averaged over the relativistic  $6s^2_{1/2}6p^1_{1/2}$  configuration, whereas the 21-electron GRECP is generated for the state averaged over the nonrelativistic  $6s^16p^16d^1$  configuration. That is true also for the electronic densities obtained in the corresponding Dirac-Coulomb(-Breit) and GRECP calculations accounting for correlation.

In the inner core region, the pseudospinors are smoothed, so that the electronic density with the pseudo-wave function is not correct. When operators describing properties of interest are heavily concentrated near or on nuclei, their mean values are strongly affected by the wave function in the inner region. The four-component molecular spinors must, therefore, be restored in the heavy-atom cores.

All molecular spinors  $\phi_p$  can be restored as one-center expansions in the cores using the nonvariational one-center restoration (NOCR) scheme [22, 30, 31, 95, 97–99, 102, 103] that consists of the following steps:

- Generation of *equivalent* basis sets of one-center four-component spinors  $\begin{pmatrix} f_{nlj}(r)\chi_{ljm} \\ g_{nlj}(r)\chi_{2j-l,jm} \end{pmatrix}$  and smoothed two-component pseudospinors  $\tilde{f}_{nlj}(r)\chi_{ljm}$  in finite-difference all-electron Dirac-Fock(-Breit) and GRECP/SCF calculations of the same configurations of a considered atom and its ions. The nucleus is usually modeled by a uniform charge distribution within a sphere. The all-electron four-component HFDB [114–116] and two-component GRECP/HFJ [117, 118] codes are employed to generate two equivalent numerical basis sets used at the restoration. These sets, describing mainly the atomic core region, are generated independently of the basis set used for the molecular GRECP calculations.
- The molecular *pseudospinorbitals* are then expanded in the basis set of one-center two-component atomic *pseudospinors* (for  $r \leq R_{\text{nocr}}$ , where  $R_{\text{nocr}}$  is the radius of restoration that should be sufficiently large for calculating core properties with required accuracy),

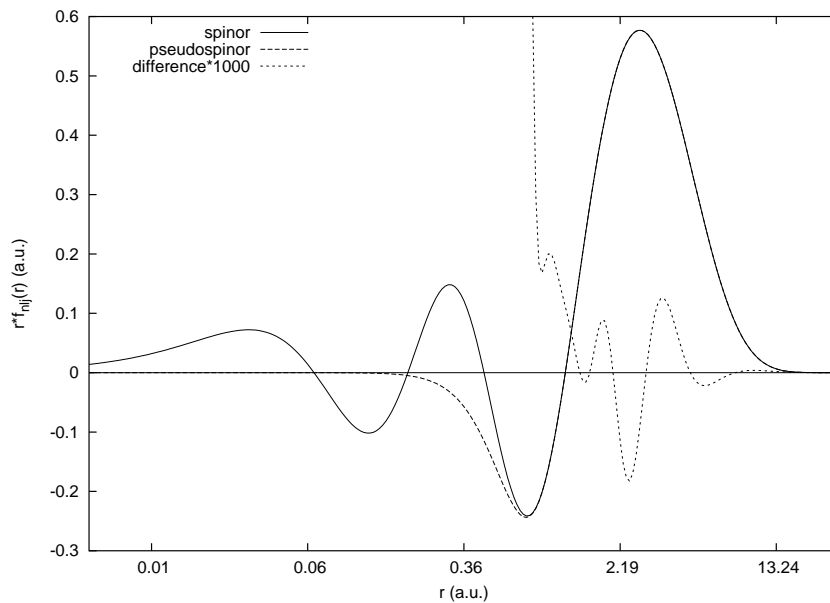
$$\tilde{\phi}_p(\mathbf{x}) \approx \sum_{l=0}^{L_{\text{max}}} \sum_{j=|l-1/2|}^{|l+1/2|} \sum_{n,m} c_{nljm}^p \tilde{f}_{nlj}(r)\chi_{ljm} , \quad (4)$$

where  $\mathbf{x}$  denotes spatial and spin variables. Note that for linear molecules only one value of  $m$  survives in the sum for each  $\phi_p$ .

- Finally, the atomic two-component pseudospinors in the molecular basis are replaced by equivalent four-component spinors and the expansion coefficients from Eq. (4) are preserved:

$$\phi_p(\mathbf{x}) \approx \sum_{l=0}^{L_{\max}} \sum_{j=|l-1/2|}^{|l+1/2|} \sum_{n,m} c_{nljm}^p \begin{pmatrix} f_{nlj}(r)\chi_{ljm} \\ g_{nlj}(r)\chi_{2j-l,jm} \end{pmatrix}. \quad (5)$$

The molecular four-component spinors constructed this way are orthogonal to the inner core spinors of the atom, because the atomic basis functions used in Eq. (5) are generated with the inner core shells treated as frozen.



**Fig. 1.** The radial parts of the large component of the  $6p_{1/2}$  bispinor and the corresponding pseudospinor obtained in equivalent Dirac-Fock and 21-electron GRECP/SCF calculations for the state averaged over the relativistic  $6s_{1/2}^2 6p_{1/2}^1$  configuration of thallium. Their difference is multiplied by 1000. The GRECP is generated for the state averaged over the nonrelativistic  $6s^1 6p^1 6d^1$  configuration.

#### *Variational one-center restoration*

In the variational technique of one-center restoration (VOCR) [84, 85], the proper behavior of the four-component molecular spinors in the core regions

of heavy atoms can be restored as an expansion in spherical harmonics inside the sphere with a restoration radius,  $R_{\text{VOCR}}$ , that should not be smaller than the matching radius,  $R_c$ , used at the RECP generation. The outer parts of spinors are treated as frozen after the RECP calculation of a considered molecule. This method enables one to combine the advantages of two well-developed approaches, molecular RECP calculation in a gaussian basis set and atomic-type one-center calculation in numerical basis functions, in the most optimal way. This technique is considered theoretically in [85] and some results concerning the efficiency of the one-center reexpansion of orbitals on another atom can be found in [80].

The VO CR scheme can be used for constructing the core parts of the molecular spinors (orbitals) instead of using equivalent basis sets as in the NOCR technique. A disadvantage of the NOCR scheme is that molecular pseudorbitals are usually computed in a spin-averaged GRECP/SCF molecular calculation (i.e. without accounting for the effective spin-orbit interaction) and the reexpansion of molecular pseudospinorbitals on one-center atomic pseudospinors can be restricted in accuracy, as was noticed in the GRECP/RCC/NOCR calculations [22] of the TIF molecule (see below). With the restored molecular bispinors, the two-electron integrals on them can be easily calculated. Thus, the four-component transformation from the atomic basis that is a time-consuming stage of four-component calculations of heavy-atom molecules can be avoided. Besides, the VO CR technique developed in [97] for molecular *pseudospinors* can be reformulated for the case of molecular *pseudospinorbitals* to reduce the complexity of the molecular GRECP calculation as is discussed in section 4.

However, the most interesting direction in the development of the two-step method is the possibility to “split” the correlation structure calculation of a molecule into two sequential correlation calculations: first, in the valence region, where the *outer core and valence* electrons are explicitly involved in the GRECP calculation; and then, in the core region, when the *outer and inner core* space regions are only treated at the restoration stage. Correlation effects in the valence and outer core regions (not only valence parts of molecular orbitals but also configuration coefficients) can be calculated, for example, by a combination of RCC and CI methods (see section 9) with very high accuracy. Then correlation effects in the inner and outer core regions (including the dipole-type relaxation of atomic inner core shells in a molecule) can be taken into account using the Dirac-Coulomb(-Breit) Hamiltonian and the one-center expansion. By increasing the one-center restoration radius  $R_{\text{VOCR}}$ , one can take into account correlation effects in the intermediate region (outer core in our case) with the required accuracy. Roughly speaking, the computational efforts for the correlation structure calculations in the core and valence regions are added when using the two-step approach, whereas in the conventional one-step scheme, they have multiplicative nature.

*Two-step calculation of molecular properties*

To evaluate one-electron core properties (hyperfine structure, P,T-odd effects etc.) employing the above restoration schemes it is sufficient to obtain the one-particle density matrix,  $\{\widetilde{D}_{pq}\}$ , after the molecular RECP calculation in the basis of pseudospinors  $\{\widetilde{\phi}_p\}$ . At the same time, the matrix elements  $\{W_{pq}\}$  of a property operator  $\mathbf{W}(\mathbf{x})$  should be calculated in the basis of equivalent four-component spinors  $\{\phi_p\}$ . The mean value for this operator can be then evaluated as

$$\langle \mathbf{W} \rangle = \sum_{pq} \widetilde{D}_{pq} W_{pq} . \quad (6)$$

Only the explicitly treated valence shells are used for evaluating a core property when applying Eq. (6) since the atomic frozen core (closed) shells do not usually contribute to the properties of practical interest. However, correlations with the core electrons explicitly excluded from the RECP calculation can be also taken into account if the effective operator technique [119] is applied to calculate the property matrix elements  $\{W_{pq}^{\text{Ef}}\}$  in the basis set of bispinors  $\{\phi_p\}$ . Then, in expression (6) one should only replace  $\{W_{pq}\}$  by  $\{W_{pq}^{\text{Ef}}\}$ . Alternatively, the correlations with the inner core electrons can be, in principle, considered within the variational restoration scheme for electronic structure in the heavy atom cores. Strictly speaking, the use of the effective operators is correct when the molecular calculation is carried out with the ‘‘correlated’’ GRECP (see [75]), in which the same correlations with the excluded core electrons are taken into account at the GRECP generation as they are in constructing  $\{W_{pq}^{\text{Ef}}\}$ . Nevertheless, the use of the (G)RECP that does not account for the core correlations at the molecular calculation stage can be justified if these correlations do not influence dramatically the electronic structure in the valence region. The latter approximation was applied in the calculations of YbF and BaF molecules described in the following section.

When contributions to  $\langle \mathbf{W} \rangle$  are important both in the core and valence regions, the scheme for evaluating the mean value of  $\mathbf{W}(\mathbf{x})$  can be as follows:

- calculation of matrix elements with the molecular pseudospinorbitals (which are usually linear combinations of atomic gaussians) over the entire space region using conventional codes for molecular RECP calculations (although the operator  $\mathbf{W}$  can be presented in different forms in calculations with the RECP and Dirac-Coulomb(-Breit) Hamiltonians),

$$\langle \widetilde{\mathbf{W}} \rangle = \sum_{pq} \widetilde{D}_{pq} \int_{r < \infty} \widetilde{\phi}_p(\mathbf{x}) \mathbf{W}(\mathbf{x}) \widetilde{\phi}_q(\mathbf{x}) d\mathbf{x} ; \quad (7)$$

- calculation of the inner part of the matrix element of the operator with the same molecular pseudospinorbitals using the one-center expansion for  $\{\widetilde{\phi}_p\}$  ( $R_{\text{ocr}}$  stands for  $R_{\text{noocr}}$  or  $R_{\text{voocr}}$  below,  $R_{\text{ocr}} \geq R_c$ ):



$$\langle \widetilde{\mathbf{W}} \rangle^< = \sum_{pq} \widetilde{D}_{pq} \int_{r < R_{\text{ocr}}} \widetilde{\phi}_p(\mathbf{x}) \mathbf{W}(\mathbf{x}) \widetilde{\phi}_q(\mathbf{x}) d\mathbf{x} ; \quad (8)$$

- calculation of the inner part of the matrix element of the operator with the restored molecular four-component spinors using the one-center expansion for  $\{\phi_p\}$ :

$$\langle \mathbf{W} \rangle^< = \sum_{pq} \widetilde{D}_{pq} \int_{r < R_{\text{ocr}}} \phi_p^<(\mathbf{x}) \mathbf{W}(\mathbf{x}) \phi_q^<(\mathbf{x}) d\mathbf{x} . \quad (9)$$

The matrix element  $\langle \mathbf{W} \rangle$  of the  $\mathbf{W}(\mathbf{x})$  operator is evaluated as

$$\langle \mathbf{W} \rangle = \langle \widetilde{\mathbf{W}} \rangle - \langle \widetilde{\mathbf{W}} \rangle^< + \langle \mathbf{W} \rangle^< . \quad (10)$$

Obviously, the one-center basis functions can be numerical (finite-difference) for better flexibility.

The mean values of the majority of operators for the valence properties can be calculated with good accuracy without accounting for the inner parts of the matrix elements (8) and (9). As discussed above, for calculating the mean values of the operators heavily concentrated on or near nuclei it is sufficient to account only for the inner parts (9) of the matrix elements of  $\mathbf{W}(\mathbf{x})$  on the restored functions  $\phi_p^<(\mathbf{x})$ , whereas the other contributions, (7) and (8), can be neglected.

Calculation of properties using the finite-field method [120, 121] and Eq. (6) within the coupled-cluster approach is described in section 8.

## 6 Calculations of PbF and HgF

The ground states of the diatomic radicals PbF and HgF are  ${}^2\Pi_{1/2}$  and  ${}^2\Sigma_{1/2}$ , respectively. Here the superscript denotes spin multiplicity,  $\Pi$  and  $\Sigma$  are the projections of the electron orbital angular momentum on the molecular axis and the subscript is the projection of the total electron angular momentum on the molecular axis directed from the heavy atom to fluorine. It is convenient to describe the spin-rotational spectrum of the ground electronic state in terms of the effective spin-rotational Hamiltonian  $\mathbf{H}_{\text{eff}}^{sr}$ , following [95, 122]:

$$\begin{aligned} \mathbf{H}_{\text{eff}}^{sr} = & B\mathbf{J}^2 + \Delta\mathbf{S}' \cdot \mathbf{J} + \mathbf{S}' \cdot \mathbf{A} \cdot \mathbf{I} \\ & + \mu_0\mathbf{S}' \cdot \mathbf{G} \cdot \mathbf{B} - D\boldsymbol{\lambda} \cdot \mathbf{E} \\ & + W_A k_A \boldsymbol{\lambda} \times \mathbf{S}' \cdot \mathbf{I} + (W_d d_e + W_S k_S) \mathbf{S}' \cdot \boldsymbol{\lambda} \end{aligned} \quad (11)$$

The first line in this expression describes the rotational structure with  $\omega$ - or spin-doubling and the hyperfine interaction of the effective electron spin  $\mathbf{S}'$  with the nuclear spin  $\mathbf{I}$ .  $B$  is the rotational constant,  $\mathbf{J}$  is the electron-rotational angular momentum,  $\Delta$  is the  $\omega$ -doubling constant. The second line

describes the interaction of the molecule with the external fields  $\mathbf{B}$  and  $\mathbf{E}$ , ( $\boldsymbol{\lambda}$  is the unit vector directed from the heavy nucleus to the light one). The last line corresponds to the P-odd electromagnetic interaction of the electrons with the anapole moment of the nucleus described by the constant  $k_A$  [45], P,T-odd interaction of the electron EDM  $d_e$  with the intermolecular field, and P,T-odd scalar interactions of the electrons with the heavy nucleus [95].

The parameter  $\Delta$ , tensors  $\mathbf{A}$  and  $\mathbf{G}$ , molecular dipole moment  $D$  and the constants  $W_i$  are expressed in terms of one-electron matrix elements; concrete expressions for the above parameters can be found in [95], and for  $W_d$  and  $A_{\parallel}$  they are also given in the next sections. The results of the calculations are presented in Table 2.

**Table 2.** Parameters of the spin-rotational Hamiltonian for the ground states of  $^{199}\text{HgF}$  and  $^{207}\text{PbF}$  ( $I=1/2$ ); (a) experimental data [123]; (b) semiempirical results from [29]; (c) *ab initio* calculations [95]; (d),(e) *ab initio* calculations [31] with semiempirical accounting for the “minimal” and “maximal” spin-orbit mixing models, respectively, and  $\Delta/2B$  from [124] (the  $W_i$  values in [31] have wrong sign).

	$A_{\parallel}$	$A_{\perp}$	$G_{\parallel}$	$G_{\perp}$	$W_S$	$W_d$
	(MHz)	(MHz)			(kHz)	$(10^{25} \frac{\text{Hz}}{\text{e cm}})$
HgF (a)	22621	21880	1.993	1.961		
(b)					-191	-4.8
(c)	24150	23310	1.996	1.960	-185	-4.8
PbF (d)	8690	-7460	0.034	-0.269	51	1.0
(e)	9550	-8240	0.114	-0.438	99	1.8
(c)	10990	-8990	0.040	-0.326	55	1.4

In [95] the conclusion was made, that the accuracy in calculations of the parameters of the effective spin-rotational Hamiltonian is close to 20%. However, further *ab initio* calculations showed the situation is more complicated.

As was understood in calculations of YbF [97], a fortuitous cancellation of effects of different types took place in the above calculations. Accounting for the polarization of the  $5s$ ,  $5p$ -shells leads to an enhancement of the contributions of the valence shells to the  $A_{\parallel}$ ,  $A_{\perp}$  and PNC constants on the level of 50% of magnitude. A contribution of comparable magnitude but of opposite sign takes place when the relaxation-correlation effects of the  $5d$ -shell are taken into account. This was confirmed in [125] when accounting for electron correlation both in the valence and core regions of HgF as compared to the YbF case.

## 7 Calculations of YbF and BaF

The results of two-step calculations for the YbF molecule (1996,1998) [97,99] and for the BaF molecule (1997) [98] are presented in Table 3 Table 3, where they are compared with other semiempirical and four-component results. For the isotropic hyperfine constant  $A = (A_{\parallel} + 2A_{\perp})/3$ , the accuracy of our calculation is about 3%, as determined by comparison to the experimental datum. The dipole constant  $A_d = (A_{\parallel} - A_{\perp})/3$  (which is much smaller in magnitude), though better than in all previous calculations known from the literature, is still underestimated by almost 23%. After a semiempirical correction for a perturbation of  $4f$ -shell in the core of Yb due to the bond making, this error is reduced to 8%. Our value for the effective electric field on the unpaired electron is  $W = W_d |\mathbf{S}' \cdot \boldsymbol{\lambda}| = 4.9$  a.u. =  $2.5 \times 10^{10}$  V cm $^{-1}$  (see section 3 and Eq. (11)).

In Table 3 the values of the  $W_d$  constant

$$W_d d_e = 2W d_e = 2 \langle {}^2\Sigma_{1/2} | \sum_i H_d(i) | {}^2\Sigma_{1/2} \rangle, \quad (12)$$

where  $H_d$  describes interaction of the electron EDM  $d_e$  with the internal molecular electric field  $\mathbf{E}^{\text{mol}}$ :

$$H_d = 2d_e \begin{pmatrix} 0 & 0 \\ 0 & \sigma \end{pmatrix} \cdot \mathbf{E}^{\text{mol}},$$

from various calculations are tabulated. These include the unrestricted Dirac-Fock calculation of Parpia (1998) [101], four-component calculations of Quiney *et al.* (1998) [100] accounting for correlation, the most recent semiempirical calculation of Kozlov (1997) [126] and our latest GRECP/RAS-SCF/EO calculation (EO stands for the effective operator technique in the framework of the second-order perturbation theory; see section 5 and paper [105] for more details). All results are in very close agreement now. It should be noted that the valence electron contribution to  $W_d$  in [101] differs by only 7.4% from the corresponding RECP-based calculation of Titov *et al.* (1996) [97].

A similar increase in the values for the hyperfine constants and parameters of the P,T-odd interactions when the correlations with the core shells (primarily,  $5s, 5p$ ) are taken into account is also observed for the BaF molecule [98], as one can see in Table 3. Of course, the corrections from the  $4f$ -electron excitations are not required for this molecule. The enhancement factor for the P,T-odd effects in BaF is three times smaller than in YbF mainly because of the smaller nuclear charge of Ba.

**Table 3.** The hyperfine structure constants  $A = (A_{\parallel} + 2A_{\perp})/3$  (isotropic) and  $A_d = (A_{\parallel} - A_{\perp})/3$  (dipole) and PNC parameters  $W_i$  (i.e.  $W_d$ ,  $W_A$ , and  $W_S$ ) described in Eqs. (11) and (12) for the  $^{171}\text{YbF}$  and  $^{137}\text{BaF}$  molecules.

	$A$	$A_d$	$W_d$	$W_A$	$W_S$
	(MHz)	(MHz)	( $10^{25} \frac{\text{Hz}}{\text{e cm}}$ )	(Hz)	(kHz)
<b>The <math>^{171}\text{YbF}</math> molecule</b>					
Experiment [127]	7617	102			
Semiempirical [126]			-1.5	730	-48
Semiempirical [128] (with $4f$ -correction)			-1.26		-43
GRECP/SCF/NOCR [97]	4932	59	-0.91	484	-33
GRECP/RASSCF/NOCR [97]	4854	60	-0.91	486	-33
Restricted DF (Quiney, 1998) [100] <sup>1</sup>	5918	35	-0.62	326	-22
Rescaled <sup>1,2</sup> restricted DF			-1.24	652	-44
Restricted DF + core polarization <sup>1</sup>	7865	60	-1.20	620	-42
Unrestricted DF (Parpia, 1998) [101]					
(unpaired valence electron)			-0.962		
Unrestricted DF [101]			-1.203		-44 <sup>1</sup>
GRECP/RASSCF/NOCR/EO [99]	7842	79	-1.206	634	
GRECP/RASSCF/NOCR/EO [99]					
(with $4f$ -correction)	7839	94	-1.206	634	
<b>The <math>^{137}\text{BaF}</math> molecule</b>					
Experiment [129] <sup>3</sup>	2326	25			
Semiempirical [29]			-0.41	240	-13
Experiment [130] <sup>4</sup>	2418	17			
Semiempirical [29]			-0.35	210	-11
GRECP/SCF/NOCR [98]	1457	11	-0.230	111	-6.1
GRECP/RASSCF/NOCR [98]	1466	11	-0.224	107	-5.9
GRECP/SCF/NOCR/EO [98]	2212	26	-0.375	181	
GRECP/RASSCF/NOCR/EO [98]	2224	24	-0.364	175	

<sup>1</sup> The results of Quiney *et al.* and Parpia have been adjusted by a factor of two to be consistent with the definition of  $W_i$  used here, see Eqs. (11) and (12).

<sup>2</sup> The  $W_i$  values are rescaled from the “restricted DF” results employing the calculated and experimental  $A$  and  $A_d$  values by the factor  $\sqrt{(A^{\text{expt}} \cdot A_d^{\text{expt}})/(A^{\text{calc}} \cdot A_d^{\text{calc}})}$ , which are in good agreement with the “restricted DF + core polarization” values.

<sup>3</sup> The hyperfine constants are measured in an inert gas matrix [129] and the semiempirical  $W_i$  values [29] are based on these data.

<sup>4</sup> The hyperfine constants are measured in a molecular beam [130].

## 8 Calculation of $^{205}\text{TlF}$ molecule.

### *Effective Hamiltonian.*

Here we consider the P,T-odd interaction of the  $^{205}\text{Tl}$  nucleus (which has one unpaired proton) with the electromagnetic field of the electrons in the  $^{205}\text{TlF}$  molecule [22]. This molecule is one of the best objects for measurements of the proton EDM. The effective interaction with the EDM of the Tl nucleus in TlF is written in the form

$$H^{\text{eff}} = (d^V + d^M)\mathbf{I}/I \cdot \boldsymbol{\lambda} , \quad (13)$$

where  $\mathbf{I}$  is the Tl nuclear spin operator;  $\boldsymbol{\lambda}$  is the unit vector along  $z$  (from Tl to F);  $d^V$  and  $d^M$  are the *volume* and *magnetic* constants [131]:

$$d^V = 6SX = (-d_p R + Q)X , \quad (14)$$

where  $S$  is the nuclear Schiff moment;  $d_p$  is the proton EDM;  $R$  and  $Q$  are the factors determined by the nuclear structure of  $^{205}\text{Tl}$  (see [22]);

$$X = \frac{2\pi}{3} \left[ \frac{\partial}{\partial z} \rho_\psi(\mathbf{r}) \right]_{x,y,z=0} ; \quad (15)$$

$\rho_\psi(\mathbf{r})$  is the electronic density calculated from the electronic wavefunction  $\psi$ ,

$$d^M = 2\sqrt{2}(d_p + d_N) \left( \frac{\mu}{Z} + \frac{1}{2mc} \right) M , \quad (16)$$

where  $d_N$  is the nuclear EDM arising due to P,T-odd forces between the nucleons;  $\mu$ ,  $m$  and  $Z$  are the magnetic moment, mass and charge of the Tl nucleus;  $c$  is the velocity of light;

$$M = \frac{1}{\sqrt{2}} \langle \psi | \sum_i \left( \frac{\boldsymbol{\alpha}_i \times \mathbf{l}_i}{r_i^3} \right)_z | \psi \rangle ; \quad (17)$$

$\mathbf{l}_i$  is the orbital momentum of  $i$ -th electron;  $\boldsymbol{\alpha}_i$  are its Dirac matrices. Accounting for  $H_{\text{eff}}$  leads to a difference in the hyperfine splitting of TlF in parallel and antiparallel electric and magnetic fields. The level shift  $h\nu = 4(d^V + d^M)\langle \mathbf{I} \cdot \boldsymbol{\lambda} \rangle / I$  is measured experimentally (for the latest results see [21]).

The parameters  $X$  of Eq. (15) and  $M$  of Eq. (17) are determined by the electronic structure of the molecule. They were calculated in 1997 for the ground  $0^+$  state of TlF by Parpia [94] and by Laerdahl, Saue, Faegri Jr., and Quiney [93] using the Dirac-Fock method with gaussian basis sets of large sizes (see Table 4). Below we refer to paper [132] with the calculations presented in details and not to the brief communication [93] of the same authors. There was also a preliminary calculation of electronic structure in TlF performed by Wilson *et al.* in [133]. In paper [22] the first calculation of  $^{205}\text{TlF}$  that accounts for correlation effects was performed (see also [14] where the limit on the Schiff moment of  $^{205}\text{Tl}$  was recalculated).

*Results.*

Calculations were carried out at two internuclear separations, the equilibrium  $R_e = 2.0844 \text{ \AA}$  as in Ref. [94], and  $2.1 \text{ \AA}$ , for comparison with Ref. [132]. The relativistic coupled cluster (RCC) method [134, 135] with only single (RCC-S) or with single and double (RCC-SD) cluster amplitudes is used (for review of different coupled cluster approaches see also [136, 137] and references). The RCC-S calculations with the spin-dependent GRECP operator take into account effects of the 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 results obtained with the one-center expansion of the molecular spinors in the Tl core in either  $s; p$ ,  $s; p; d$  or  $s; p; d; f$  partial waves are collected in Table 4. The first point to notice is the difference between spin-averaged SCF values and RCC-S values; the latter include spin-orbit interaction effects. These effects increase  $X$  by 9% and decrease  $M$  by 21%. The RCC-S function can be written as a single determinant, and results may therefore be compared with DF values, even though the RCC-S function is not variational. The GRECP/RCC-S values of  $M$  indeed differ only by 1–3% from the corresponding DF values [94, 132] (see Table 4).

Much larger differences occur for the  $X$  parameter. There are also large differences between the two DF calculations for  $X$ , which cannot be explained by the small change in internuclear separation. The value of  $X$  may be expected to be less stable than  $M$  [132]. The conclusion in [22] is that the RCC-S value for  $X$ , which is higher than that of [94, 132], is more correct. The electron correlation effects are calculated by the RCC-SD method at the molecular equilibrium internuclear distance  $R_e$ . A major correlation contribution is observed, decreasing  $M$  by 17% and  $X$  by 22%.

The hyperfine structure constants of Tl  $6p_{1/2}^1$  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% with respect to experiment and the RCC-SD results are within 1–4% of experiment. The improvement in  $X$  and  $M$  upon inclusion of correlation is expected to be similar.

## 9 Calculations of $^{207}\text{PbO}$ molecule.

As is noted in section 1, experiments on the excited  $a(1)$  [34] or  $B(1)$  [138] states of PbO having nonzero projection of total electronic momentum on the internuclear axis can be, in principle, sensitive enough to detect  $d_e$  two or even four orders of magnitude lower than the current limit. Knowledge of the effective electric field,  $W$ , is required for extracting  $d_e$  from the measurements (see section 3). In papers [102, 103],  $W$  for the  $a(1)$  ( $^3\Sigma^+ \sigma_1^2 \sigma_2^2 \sigma_3^2 \pi_1^3 \pi_2^1$ ) and  $B(1)$  ( $^3\Pi_1 \sigma_1^2 \sigma_2^2 \sigma_3^1 \pi_1^4 \pi_2^1$ ) states of the PbO molecule was calculated by the RCC-SD [106, 107] and configuration interaction (CI) [108–110, 139] methods.

**Table 4.** Calculated  $X$  (15) and  $M$  (17) parameters (in a.u.) for the  $^{205}\text{TlF}$  ground state, compared with DF values [94,132]. GRECP/RCC-S results include spin-orbit interaction, and GRECP/RCC-SD values also account for electron correlation.

Expansion	$R_e = 2.0844 \text{ \AA}$			$R = 2.1 \text{ \AA}$		
	$s, p$	$s, p, d$	$s, p, d, f$	$s, p$	$s, p, d, f$	$s, p$
	$M$			$X$		
SCF (spin-averaged)	19.67	17.56	17.51	8967	19.52	17.43
GRECP/RCC-S	16.12	13.84	9813	16.02	13.82	9726
DF [94]	15.61			7743		
DF [132]				13.64 <sup>1</sup>		
GRECP/RCC-SD	11.50			7635		

<sup>1</sup>  $M$  is calculated in Ref. [132] using two-center molecular spinors, corresponding to infinite  $L_{max}$  in Eq. (5).

To provide an accuracy check for the calculation of the electronic structure near the Pb nucleus the hyperfine constant,  $A_{\parallel}$ , was also calculated.

### Results.

CI calculations [103] were performed at two internuclear distances:  $R = 3.8$  a.u. (as in RCC calculations), and  $R = 4.0$  a.u. (which is close to the equilibrium distances of the  $a(1)$  and  $B(1)$  states). In the RCC calculations [102] the internuclear distance  $R = 3.8$  a.u. was used because of problems with convergence at larger distances. The calculated values with the one-center expansion of the molecular spinors in the Pb core in either  $s; p$  or  $s; p; d$  partial waves are collected in Table 5.

Let us consider the  $5s, 5p, 5d$  orbitals of lead and  $1s$  orbital of oxygen as the outercore and the  $\sigma_1, \sigma_2, \sigma_3, \pi_1, \pi_2$  orbitals of PbO (consisting mainly of  $6s, 6p$  orbitals of Pb and  $2s, 2p$  orbitals of O) as valence. Although in the CI calculations we take into account only the correlation between valence electrons, the accuracy attained in the CI calculation of  $A_{\parallel}$  is much better than in the RCC-SD calculation. The main problem with the RCC calculation was that the Fock-space RCC-SD version used there was not optimal in accounting for nondynamic correlations (see [140] for details of RCC-SD and CI calculations of the Pb atom). Nevertheless, the potential of the RCC approach for electronic structure calculations is very high, especially in the framework of the intermediate Hamiltonian formulation [107,135].

Next we estimate the contribution from correlations of valence electrons with outercore ones (which also account for correlations between outercore electrons) as the difference between the results of the corresponding 10- and 30-electron GRECP/RCC calculations (see also [140] where this correction is applied to the Pb atom). We designate such correlations in Table 5 as

“outercore correlations”. When taking into account outercore contributions at the point  $R = 4.0$  a.u. we used the results of the RCC calculation at the point  $R = 3.8$  a.u. Since these contributions are relatively small and because the correlations with the outercore electrons are more stable than correlations in the valence region when the internuclear distance is changed, this approximation seems reasonable. Finally, we have linearly extrapolated the results of the calculations to the experimental equilibrium distances,  $R_e = 4.06$  a.u. for  $a(1)$  [141] and  $R_e = 3.91$  a.u. for  $B(1)$  [124]. The final results are:  $A_{\parallel} = -3826$  MHz,  $W = -6.1 \cdot 10^{24} \text{Hz}/(e \cdot \text{cm})$  for  $a(1)$  and  $A_{\parallel} = 4887$  MHz,  $W = -8.0 \cdot 10^{24} \text{Hz}/(e \cdot \text{cm})$  for  $B(1)$ . The estimated error for the final  $W$  value is 20% for the  $B(1)$  state. For  $a(1)$  the estimated error bounds put the actual  $W$  value between 90% and 130% of our final value (for details see [103]).

**Table 5.** Calculated parameters  $A_{\parallel}$  (in MHz) and  $W$  (in  $10^{24} \text{Hz}/(e \cdot \text{cm})$ , see section 3 and Eq. (12)) for the  $a(1)$  and  $B(1)$  states of  $^{207}\text{PbO}$  at the internuclear distances 3.8 and 4.0 a.u. The experimental value of  $A_{\parallel}$  in  $a(1)$  is  $-4113$  MHz [142]. The preliminary experimental value of  $A_{\parallel}$  for  $B(1)$  is  $5000 \pm 200$  MHz [143].

State	$a(1)$	$\sigma_1^2 \sigma_2^2 \sigma_3^2 \pi_1^3 \pi_2^1$	$^3\Sigma_1$	$B(1)$	$\sigma_1^2 \sigma_2^2 \sigma_3^1 \pi_1^4 \pi_2^1$	$^3H_1$
Parameters	$A_{\parallel}$	$W$		$A_{\parallel}$	$W$	
Expansion	s,p,d	s,p	s,p,d	s,p,d	s,p	s,p,d
<b>Internuclear distance <math>R = 3.8</math> a.u.</b>						
10e-RCC-SD [102]	-2635	-2.93	-3.05	3878	-11.10	-10.10
30e-RCC-SD [102]	-2698		-4.10	4081	-9.10	-9.70
<i>outercore: (30e-10e)-RCC-SD</i>	<i>-63</i>		<i>-1.05</i>	<i>203</i>		<i>0.40</i>
10e-CI [103]	-3446		-4.13	4582		-10.64
<b>FINAL [103]</b>						
(10e-CI + outercore)	<b>-3509</b>		<b>-5.18</b>	<b>4785</b>		<b>-10.24</b>
<b>Internuclear distance <math>R = 4.0</math> a.u.</b>						
10e-CI [103]	-3689		-4.81	4762		-7.18
<b>FINAL [103]</b>						
(10e-CI + outercore) <sup>1</sup>	<b>-3752</b>		<b>-5.86</b>	<b>4965</b>		<b>-6.78</b>

<sup>1</sup> It is assumed that the outercore contribution at the internuclear distance  $R=4.0$  a.u. is approximately the same as is at  $R=3.8$  a.u.

## 10 Conclusions

The P,T-parity nonconservation parameters and hyperfine constants have been calculated for the particular heavy-atom molecules which are of primary interest for modern experiments to search for PNC effects. It is found that



a high level of accounting for electron correlations is necessary for reliable calculation of these properties with the required accuracy. The applied two-step (GRECP/NOCR) scheme of calculation of the properties described by the operators heavily concentrated in atomic cores and on nuclei has proved to be a very efficient way to take account of these correlations with moderate efforts. The results of the two-step calculations for hyperfine constants differ by less than 10% from the corresponding experimental data. A comparable level of accuracy is expected for the P,T-odd spin-rotational Hamiltonian parameters, which can not be obtained experimentally.

The precision of the discussed calculations is limited by the current possibilities of the correlation methods and codes and not by the GRECP and NOCR approximations, despite the fact that the GRECP/NOCR method allows one to reduce seriously the computational expenses of the correlation treatment as compared to conventional Dirac-Coulomb(-Breit) approaches when (1) using molecular spin-orbitals instead of spinors in (G)RECP calculation; (2) employing “correlated” GRECP versions [75] to account for correlations with the core electrons explicitly excluded from (G)RECP calculations; (3) combining gaussian basis functions at the molecular (G)RECP calculation with numerical functions at the one-center restoration; and (4) splitting the correlation treatment of a molecule into two sequential steps, first in valence and then in core regions.

In turn, the accuracy attained in the calculations presented above is sufficient for a reliable interpretation of the measurements in PNC experiments on these molecules.

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