In search of the electron electric dipole moment: relativistic correlation calculations of the P,T-violation effect in the ground state of HI+

T.A. Isaev† A.N. Petrov, N.S. Mosyagin, and A.V. Tito†
Petersburg Nuclear Physics Institute, Gatchina, 188300, Russia

We report the first results of ab initio relativistic correlation calculation of the effective electric field on the electron, $E_{\text{eff}}$, in the ground state of the HI$^+$ cation. This value is required for interpretation of the suggested experiment on search for the electron electric dipole moment. The generalized relativistic effective core potential, Fock-space relativistic coupled cluster with single and double cluster amplitudes and spin-orbit direct configuration interaction methods are used, followed by nonvariational one-center restoration of the four-component wavefunction in the iodine core. The calculated value of $E_{\text{eff}}$ by the coupled cluster method is $E_{\text{eff}} = 0.345 \times 10^{24}$ Hz/e·cm. Configuration interaction study gives $E_{\text{eff}} = 0.336 \times 10^{24}$ Hz/e·cm (our final value). The structure of chemical bonding and contributions to $E_{\text{eff}}$ in HI$^+$ is clarified and significant deviation of our value from that obtained in Ravaine et al. Phys. Rev. Lett. 94, 013001 (2005) is explained.

Introduction. It is known [12] that existence of the permanent electric dipole moments (EDM) of the elementary particles violate two fundamental symmetries: space parity (P) and time reversal (T). Considerable experimental efforts invested recently to the search for the electron EDM $d_e$ (see [3, 4, 5, 6, 7]) are primarily connected with the high sensitivity of $d_e$ to the “new physics” beyond the Standard Model (see [2] and references). Polar heavy-atom diatomics with nonzero projection of the total electronic momentum on the molecular axis (see below) are currently considered as the most prospective objects to search for $d_e$ because of the great value of the effective electric field acting on the unpaired electrons in the ground or excited states of such molecules [8, 9].

The only nonzero component of the effective electric field in the ground or excited states of such molecules [8, 9] is $E_\parallel$, which is determined for the HI$^+$ ground state. The “covalent” limit corresponds to the I$^+$ ion perturbed by the electrostatic field from the dipole of the polarized neutral H. We are using inverted commas to mark the approximations since from the traditional point of view they both correspond rather to a van der Waals–type interaction between ion and induced dipole. It was found in [10] that the value of $E_{\text{eff}}$ is greatly changed (about six times) depending on the approximation made, either “ionic” or “covalent”.

Model consideration. We calculated molecular dipole moment $D$ of the ground HI$^+$ state with the molecular axes origin at the iodine nucleus using the restricted active space self-consistent field (RASSCF) method. The details of that calculation can be found on [19]. Our calculation shows that the highest doubly occupied $\sigma$-orbital is bonding and most “mixed” one among occupied orbitals. It is formed mainly by the iodine 5p$_0$ and hydrogen 1s orbitals, where subscript denotes the projection of the angular momentum on the molecular axis. Though this is not the highest by energy from the occupied orbitals, it gives 77% of the calculated electronic part of $D$, $D_{\text{el}} = -2.610$ (the contribution from the hydrogen nucleus is, obviously, 1$R_e = 3.08$; here and below we use atomic units unless the opposite is stated explicitly).

On the other hand, the valence $\pi_{-1}$ and $\pi_{+1}$ orbitals are formed mainly by the iodine 5p$_{-1}$ and 5p$_{+1}$ orbitals (mixture of the 5p$_{1/2, \pm1/2}$, 5p$_{3/2, \pm1/2}$, and 5p$_{3/2, \pm3/2}$ spinors) and their contribution to $D_{\text{el}}$ is about 7%.

The distinctions of the “covalent” and “ionic” approximations from our consideration can be illustrated on the one-configurational model of the chemical bond in HI$^+$. The leading (SCF) configuration of this molecule in the ground $^2\Pi_3/2$ state with $\Omega = +3/2$ (having weight 0.9 in the correlated wavefunction) can be presented as $\ldots |\sigma^2(\pi_{-1,\alpha}\pi_{+1,\beta})\pi_{+1,\alpha}^\dagger\pi_{+1,\beta}^\dagger|$. Where $\alpha$ and $\beta$ correspond
to the spin projections $+1/2$ and $-1/2$, the degenerate $\pi_{-1,\alpha}$ and $\pi_{+1,\beta}$ spin-orbitals constitute a shell in the used relativistic classification, and the unpaired $\pi'_{1,\alpha}$ state is mainly the $5p_{3/2,1/2}$ spinor of iodine (we distinguish $\pi'$ from $\pi$ just to emphasize their different behavior at the iodine nucleus). Let us consider contributions of the bonding spin-orbitals $|\sigma_{\alpha,\beta}\rangle = C_I|\sigma^I_{\alpha,\beta}\rangle + C_H|\sigma^H_{\alpha,\beta}\rangle$ to the hyperfine structure (HFS) properties at the iodine nucleus. The occupied $\sigma^2$ shell can be presented as

$$\sigma^2 = \alpha,\beta \sigma^2 = C_I^2 \sigma^2_{\alpha,\beta} + C_I C_H \left( \sigma^I_{\alpha,\beta} \sigma^H_{\alpha,\beta} + \sigma^H_{\alpha,\beta} \sigma^I_{\alpha,\beta} \right) + C_H^2 \sigma^H_{\alpha,\beta} \sigma^H_{\alpha,\beta},$$

where the operator of asymmetrization is omitted, $|\sigma^I\rangle$ is mainly $5p_{3/2}$-orbital of iodine, $|\sigma^H\rangle$ is mainly $1s$-orbital of hydrogen, and $C_I^2 + C_H^2 = 1$ (assume for simplicity that $|\sigma^I\rangle$ and $|\sigma^H\rangle$ are orthogonal and $C_I$, $C_H$ are real; $C_I \approx 0.83$, $C_H \approx 0.56$ in our calculations). In the spin-orbit representation, the atomic $5p_0$ orbital can be approximately presented as a combination of the $5p_{1/2}$ and $5p_{3/2}$ spinors of iodine with weights $1/3$ and $2/3$, respectively.

The contribution in the first line of Eq. (1) corresponds to the “ionic” model in [16, 17] (when $|C_I| \approx 1$), two terms in the second line can be compared to their “covalent” model (the maximum $|C_I C_H| = 1/2$ is, obviously, attained for $|C_I| = |C_H| = 1/\sqrt{2}$ and the term in the third line corresponds to the conventional ion model $I^{++} - H^{-}$ ($|C_H| \approx 1$) that is not considered there. Both terms from the second line equally contribute to the electric quadrupole HFS constant on iodine (dependent on the space-inhomogeneous part of electronic density with respect to the iodine nucleus) whereas their contributions are completely compensated for the spin-dependent magnetic dipole HFS constants as well as for $E_{\text{eff}}$ (see below). The latter is a consequence of the fact that closed shells do not influence on those spin-dependent properties; their contributions can become nonzero only when polarization and correlation effects are considered. So, the only open shell $\pi'_{1,\alpha}$ ($5p_{3/2,1/2}$) should be considered when calculating spin-dependent properties within our simple one-conﬁguration model. The weight of the rest configurations (obviously, orthogonal to the leading one and accounting for correlation without any restriction on the occupancy of $\pi_{\pm 1,\alpha}, \pi_{\pm 1,\beta}, \sigma_{\alpha}^H, \sigma_{\beta}^H$ etc.) is only 0.1 (as is obtained in the calculations discussed below). Even if one suggests that all the correlating conﬁgurations contain singly-occupied $1s$-orbital of hydrogen and $\sigma^H$ is also $1s$, the maximal weight of the $I^+$ conﬁgurations of type $[\ldots] 1s^2 I^+$ is smaller than 0.7 that can be compared to the weight 1.0 in the “covalent” model of Chanda et al. [17] and Ravaine et al. [16]. Moreover, in the “covalent” model by Ravaine et al. the contributions with the weights $2/3$ and $1/3$ (see Eq. (13) in [16]) in the front of the wavefunction terms containing $\sigma^H_{\alpha}$ and $\sigma^H_{\beta}$ ($1s$ of hydrogen) are ﬁxed in accord to the spin-coupling rules (with the lowest lying $^3\Pi_{2,1}$ states of $I^+$ and proper dissociation limit) and not varied. This induces a large artificial asymmetry in contributions of the $5p_{1/2, \pm 1/2}$ states when calculating $E_{\text{eff}}$ within the “covalent” model both at the one-conﬁguration and correlation levels. Such asymmetry could be attained in the correlation calculations only if the conﬁguration in which the singlet $\sigma^2$ pair replaced in the leading conﬁguration by the triplet $\sigma^I_{\alpha,\beta} \sigma^H_{\alpha,\beta}$ state would have weight $\approx 0.1$, thus leaving nothing to other correlation conﬁgurations.

Effective P, T-odd Hamiltonian. The terms of our interest for $H^+$ in the effective spin-rotational Hamiltonian may be written following Refs. [11, 20]. The P,T-odd interaction of $d_e$ with the effective electric field is

$$H_d = W_d d_e (J \cdot n),$$

where $J$ is the total electronic momentum and $n$ is the unit vector along the molecular axis from I to H. In [11] slightly different form of $H_d$ is used:

$$H_d = W_d (J \cdot n),$$

so the value of $d_e$ appears explicitly in their final result for $E_{\text{eff}}$. The effective operator

$$H_e = 2d_e \left( \begin{array}{cc} 0 & 0 \\ 0 & \sigma E \end{array} \right)$$

is used to express the interaction of $d_e$ with the inner molecular electric field $E$ ($\sigma$ are the Pauli matrices), to avoid large numerical cancellation of the terms with opposite signs because of Schiff’s theorem [21, 22]. After averaging over the electronic coordinates in the molecular wavefunction, one obtains

$$W_d \Omega = \frac{1}{d_e} \langle \Psi_{\Omega} | \sum_i H_e(i) | \Psi_{\Omega} \rangle,$$

de is wavefunction for the $X^2\Pi_{3/2}$ state.

To check the accuracy of calculating the wavefunction in the vicinity of the iodine nucleus we computed the hyperﬁne constant $A_{\parallel}$ (see [24]) and quadrupole coupling constant $eQq_0$, where $Q = -710$ millibarn is quadrupole moment of $^127I$ [23], $q_0$ is electric field gradient along molecular axis. Note, however, that the errors in calculated $A_{\parallel}$, $eQq_0$ and $E_{\text{eff}}$ are not related closely. As our recent calculations showed [13, 14], the error for $A_{\parallel}$ presents rather a lower bound estimate for the $E_{\text{eff}}$ error. The quadrupole interaction constant is capable to provide useful information about space-inhomogeneous part of the electronic density near a nucleus. Unfortunately, the $eQq_0$ value is not a better measure of the calculation accuracy of the effective field on the electron than the $A_{\parallel}$, first of all because it doesn’t depend directly (like $E_{\text{eff}}$ and $A_{\parallel}$) on the electronic spin density near the heavy nucleus. In [17] the parameters of the Frosch-Foley effective spin-rotational Hamiltonian [24] were obtained for
the ground state of HI\(^+\). The connection of the Frocht-Foley parameters \(a, b, c\) to \(A_{||}\) is \(38\):

\[
A_{||} = \frac{1}{\Omega} (a\Lambda + (b + c)\Sigma),
\]

where \(\Lambda\) is the projection of the angular electronic momentum on the molecular axis and \(\Sigma = S_z\) is the projection of the electronic spin. Accounting for the calculated value of \(G_1\)-factor that is 2.0001 and \(|\Omega| = 1.4998\), the ground state of HI\(^+\) can be reliably classified as \(^2\Pi_{3/2}\).

**Methods and calculations.** A 25-electron generalized relativistic effective core potential (GRECP) \(25\) for iodine (its Gaussian expansion can be found on our website \(19\)) is used at the first step of the two-step calculations of HI\(^+\), so that the inner shells of iodine, \(1s - 3d\), are absorbed into the GRECP and the \(4s, 4p, 4d, 5s,\) and \(5p\) electrons (as well as an electron of hydrogen) are treated explicitly. Two calculations are carried out. In the first one, only seven external electrons of iodine are correlated whereas its 4s, 4p, 4d shells are “frozen” within the GRECP approach when employing the level-shift technique \(22\). Thus, a 7-electron GRECP version is, in fact, used in the first series of the HI\(^+\) calculations. In the other calculation, all 25 electrons are explicitly correlated. The terms with the leading configurations \(\sigma^2\pi^3\) are calculated where \(\sigma\) and \(\pi\) are the highest occupied molecular orbitals. The correlation spin-orbit basis sets are optimized in atomic two-component relativistic coupled cluster calculations of iodine with single and double cluster amplitudes (RCC-SD) using the scheme suggested in \(26, 27\). As a result, the basis \([5s5p3d2f1g]\) was generated. As our investigation shows removing of \(g\)-function from the basis set changes the RCC-SD results for \(A_{||}\) and \(E_{eff}\) on the level of 1%. Thus, contribution from \(g\)-function to the calculated values can be negligible and the basis reduced to \([5s5p3d2f]\) without loss of accuracy. Such iodine basis was used in 25 electron configuration interaction (CI) calculations of HI\(^+\). For hydrogen, the reduced \([4s3p2d]\) correlation-consistent basis \(28\) was used.

The HI\(^+\) calculations start from a one-component closed shell SCF computation of the ground state of the neutral HI molecule using the spin-averaged GRECP for iodine. Two-component Fock-space RCC-SD molecular calculations or spin-orbit direct CI (SODCI) calculations are then performed.

**RCC-SD method:** The details on the Fock-space RCC-SD method can be found in Ref. \(21, 30\) and references therein. The program package rccsd is used in all RCC calculations mentioned further in the article. The Fock-space RCC calculations start from the ground state of HI and use the scheme:

\[
\text{HI} \rightarrow \text{HI}^+ \quad (6)
\]

with an electron removed from the \(\pi, \pi'\) orbitals.

**SODCI method:** Spin-orbit direct CI approach with the selected single- and double-excitations from some multiconfigurational reference states \(31, 32\) is employed on the sets of different AS many-electron spin- and space-symmetry adapted basis functions (SAFs). In the SODCI code, the double \(C_{2v}\) group, \(C_{2v}^*\), is used to account for the spin and space symmetry of the HI\(^+\) molecule, instead of the more restrictive symmetry group \(C_{\infty v}\), which could, in principle, be employed. In the \(C_{2v}^*\) classification scheme, the doubly degenerate ground state has the components only in the irreducible representation \(E^*\).

The SODCI calculations exploiting relativistic scheme of configuration selection \(33\) start from some space of the reference functions: for 25 correlated electrons 4415 SAFs (see Table \(\text{II}\)) were included in the reference space (“main” configurations). These SAFs had the largest coefficients in the probing CI calculation. The single and double excitations from this reference space produce about \(3 \times 10^9\) SAFs. Only the most important of them, selected by second-order perturbation theory for chosen thresholds \(T_i\) (see Table \(\text{II}\)), were included in the subsequent CI calculation. About 1.6, 5.7 and 13 millions of SAFs were selected for thresholds \(T_1 = 0.01, T_2 = 0.001, T_3 = 0.0003\), correspondingly.

Since we are interested in the spin-dependent properties determined mainly by the electronic wavefunction near the iodine nucleus, the shape of the valence and outer core four-component molecular spinors are restored in the inner core of iodine that is done in the paper within the nonvariational one-center restoration scheme (NOCR) (see \(12, 25, 34, 35\) and references therein). The RCC calculation of \(E_{eff}\) employs the finite field method (see Refs. \(35, 36, 37\)). In the SODCI calculations conventional approach with the density matrix calculation for CI wavefunction was used \(14\).

**Results and discussion.** The results of the RCC and SODCI calculations for 7 and 25 correlated electrons of HI\(^+\) are presented in Table \(\text{II}\). The internuclear distance is 3.08 a.u. in accord to the experimental datum \(17\).

It should be noted that the authors of paper \(10\) considered their “covalent” result as the final one and presented their “ionic” result only for comparison. The results of our RCC and SODCI calculations give essentially different \(E_{eff}\) value than the one obtained in \(10\) by the configuration interaction calculation for the “covalent” approximation. Particularly, the sign of \(E_{eff}\) is opposite to that by Ravaine et al. One can see that accounting for correlations with the iodine core electrons (occupying the shells \(4s, 4p\) and \(4d\)) practically doesn’t change the value of \(E_{eff}\). The importance of accounting for correlations can be seen by comparing the results of RCC-S and RCC-SD calculations. In the RCC-S calculations (only with the single-body cluster amplitudes) effect of “spin-polarization” is taken into account analogously to “unrestricted” Dirac-Hartree-Fock (DHF) calculation. Inclusion of electron correlations in the RCC-SD calculation
TABLE I: Calculated $E_{\text{eff}}$ (in $10^{24}$ Hz/(e-cm)), $A_\parallel$ (in MHz) and quadrupole interaction value $eQ_0$ (in MHz) for the ground state $X^2Π_{3/2}$ of $^{127}\text{I}^+$. The one-center expansion by s, p, d spinors within the iodine core is used in the NOCR scheme. Experimental values for $A_\parallel$ is 1021 MHz and for quadrupole coupling constant $eQ_0$ is $-712.6$ MHz.

| Method                                                                 | $E_{\text{eff}}$ | $A_\parallel$ | $eQ_0$ |
|-----------------------------------------------------------------------|-----------------|--------------|--------|
| work [16] “ionic” approx. DHF                                          | -0.09           |              |        |
| work [16] “covalent” approx. CI                                        | -0.49           |              |        |
| AGRECP/SCF/NOCR calculations                                           |                 |              |        |
| restricted SCF                                                         | 0.008           | 949          | -647   |
| 7 electrons                                                           | 0.010           | 1024         | -667   |
| GRECP/RCC/NOCR calculations                                           |                 |              |        |
| RCC-S                                                                 | 0.206           | 863          | -719   |
| RCC-SD                                                                | 0.347           | 881          | -708   |
| 25 electrons                                                          | 0.226           | 906          | -807   |
| RCC-SD                                                                | 0.345           | 962          | -752   |
| GRECP/SODCI/NOCR calculations                                         |                 |              |        |
| Threshold (mHartree)                                                  | SAF number      |              |        |
| Mains only                                                            |                 |              |        |
|                           $7$ electrons                                  |                 |              |        |
| 0.001                    | 7786            | 0.294        | 984     | -687   |
| 0.0001                   | 676397          | 0.335        | 895     | -711   |
| 0.0001                   | 1911282         | 0.336        | 892     | -709   |
|                           $25$ electrons                                |                 |              |        |
| 0.01                     | 4415            | 0.333        | 1063    | -778   |
| 0.001                    | 1600012         | 0.299        | 975     | -738   |
| 0.0001                   | 5712946         | 0.329        | 971     | -743   |
| 0.0003                   | 12678133        | 0.336        | 968     | -745   |

Our results of the SODCI calculation (our final values) for the $E_{\text{eff}}$, $A_\parallel$ and $eQ_0$ properties are in close agreement with the RCC-SD values. It means that higher-order correlations practically do not influence on the value of $E_{\text{eff}}$. On the other hand the value of $A_\parallel$ is increased for about 10% when outercore correlations are taken into account. It was noticed before that rather good accuracy in the calculated $A_\parallel$ value gives us just a lower bound for the accuracy of $E_{\text{eff}}$. Taking into account weak dependence of $E_{\text{eff}}$ from the outercore-valence correlations we estimate the accuracy of $E_{\text{eff}}$ calculation in 10%.

In any case our calculations show that the absolute value for $E_{\text{eff}}$ in $X^2Π_{3/2}$ of HI$^+$ is much lower than that in YbF, $6.0\times10^{24}$ Hz/(e-cm), and in the metastable $a(1)$ state of PbO, $6.1\times10^{24}$ Hz/(e-cm). Thus, HI$^+$ can be perspective candidate for experiments on the EDM search provided that the experimental scheme is improved to reach much better statistics or coherence time, than that in on-going experiments on YbF and PbO.

Acknowledgments. The authors are grateful to M. Kozlov for drawing our attention to the suggested EDM experiment on HI$^+$. This work is supported by the RFBR grant 03–03–3235 and, in part, by the CRDF grant RP2–2339–GA–02. N.M. is also supported by grants of Russian Science Support Foundation and the governor of Leningrad district.

Changes $E_{\text{eff}}$ on about 60%. At the same time value of $A_\parallel$ is changed only on 5%, that shows that the structure of correlation contributions to $A_\parallel$ and $E_{\text{eff}}$ is very different. The same is valid for the $eQ_0$ constant, which correlations contribute less than 10%.

The restricted open shell SCF calculations presented in Table I were performed with the spin-averaged GRECP (AGRECP) for iodine. The value of $E_{\text{eff}}$ is more than order of magnitude smaller in AGRECP/SCF/NOCR calculations than in GRECP/RCC-S/NOCR ones that indicates critical importance of accounting for one-electron spin-orbit and polarization effects on valence shells in calculation of $E_{\text{eff}}$. Similar situation was observed in calculations on the $a(1)$ state in PbO [13]. We would like to emphasize that after applying the NOCR procedure the proper, four-component shapes of molecular spinors in the core of Pb are restored having appropriate relativistic behavior at the Pb nucleus both after GRECP and AGRECP calculations. In the experiment on HI$^+$ in the rotating electric field [15] the knowledge of the hyperfine coupling value of the proton spin to the molecular axis can be useful. We calculated the value of $A_\parallel$ on the H nucleus in the framework of above-described AGRECP/SCF/NOCR scheme, the value is 0.6 MHz.

[1] I. B. Khriplovich and S. K. Lamoraux, CP Violation without Out-Strangeness. The Electric Dipole Moments of Particles, Atoms, and Molecules (Springer-Verlag, Berlin, 1997).

[2] E. D. Commins, Adv. At. Mol. Opt. Phys. 40, 1 (1999).

[3] M. V. Romanis, W. C. Griffith, J. P. Jacobs, and E. N. Fortson, Phys. Rev. Lett. 86, 2505 (2001).

[4] B. C. Regan, E. D. Commins, C. J. Schmidt, and D. DeMille, Phys. Rev. Lett. 88, 071805/1 (2002).

[5] J. J. Hudson, B. E. Sauer, M. R. Tarbutt, and E. A. Hinds, Phys. Rev. Lett. 89, 023003 (2002).

[6] B. E. Sauer, P. C. Condylis, J. J. Hudson, M. R. Tarbutt, and E. A. Hinds, in 36th DAMOP Meeting (APS, Lincoln, Nebraska, 2005).

[7] D. DeMille, F. Bay, S. Bickman, D. Krause, Jr., S. E. Maxwell, and L. R. Hunter, Phys. Rev. A 61, 052507 (2000).

[8] O. P. Sushkov and V. V. Flambaum, Sov. Phys.–JETP 48, 608 (1978).

[9] V. G. Gorshkow, L. N. Labzovsky, and A. N. Moskalyov, Sov. Phys.–JETP 49, 209 (1979).

[10] M. Kozlov and L. Labzovsky, J. Phys. B 28, 1931 (1995).

[11] A. V. Titov, N. S. Mosyagin, A. N. Petrov, and T. A. Isaev, Progr. Theor. Chem. Phys. (2005), in press; arXiv:
[12] A. V. Titov, N. S. Mosyagin, A. N. Petrov, and T. A. Isaev, Int. J. Quantum Chem. 104, 223 (2005).

[13] T. A. Isaev, A. N. Petrov, N. S. Mosyagin, A. V. Titov, E. Eliav, and U. Kaldor, Phys. Rev. A 69, 030501(R) (2004).

[14] A. N. Petrov, A. V. Titov, T. A. Isaev, N. S. Mosyagin, and D. P. DeMille, Phys. Rev. A (2005), in press; arXiv: physics/0409045.

[15] R. Stutz and E. Cornell, Bull. Amer. Phys. Soc. 49, 76 (2004).

[16] B. Ravaine, S. G. Porsev, and A. Derevianko, Phys. Rev. Lett. 94, 013001 (2005).

[17] A. Chanda, W. C. Ho, M. B. Dalby, and I. Ozier, J. Chem. Phys. 102, 8725 (1995).

[18] K. Andersson, M. R. A. Blomberg, M. P. Fülscher, G. Karlström, R. Lindh, P.-A. Malmqvist, P. Neogrady, J. Olsen, B. O. Roos, A. J. Sadlej, et al. (1999), quantum-chemical program package “MOLCAS”, Version 4.1.

[19] A.-M. Martensson-Pendrill, in Atomic and Molecular Properties, edited by S. Wilson (Plenum Press, New York, 1992), pp. 99–156.

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

[21] J. Bieron, P. Pyykkö, D. Sundholm, V. Kellö, and A. J. Sadlej, Phys. Rev. A 64, 052507 (2001).

[22] R. A. Frosch and H. M. Foley, Phys. Rev. A 88, 1337 (1952).

[23] A. V. Titov and N. S. Mosyagin, Int. J. Quantum Chem. 71, 359 (1999).

[24] N. S. Mosyagin, E. Eliav, A. V. Titov, and U. Kaldor, J. Phys. B 33, 667 (2000).

[25] A. N. Petrov, N. S. Mosyagin, and D. P. DeMille, Phys. Rev. A (2005), in press; arXiv: physics/0409045.

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

[27] T. H. Dunning, Jr, J. Chem. Phys. 90, 1007 (1989).

[28] T. A. Isaev, in Recent Advances in Coupled-Cluster Methods, edited by R. J. Bartlett (World Scientific, Singapore, 1997), pp. 125–153.

[29] U. Kaldor, E. Eliav, and A. Landau, in Recent Advances in Relativistic Molecular Theory, edited by K. Hirao and Y. Ishikawa (World Scientific, Singapore, 2004), p. 283.

[30] R. J. Buenker and S. Krebs, in Recent Advances in Multi-reference Methods, edited by K. Hirao (World Scientific, Singapore, 1999), pp. 1–29.

[31] A. B. Alekseyev, H.-P. Liebermann, and R. J. Buenker, in Recent Advances in Relativistic Molecular Theory, edited by K. Hirao and Y. Ishikawa (World Scientific, Singapore, 2004), pp. 65–105.

[32] A. V. Titov, N. S. Mosyagin, A. B. Alekseyev, and R. J. Buenker, Int. J. Quantum Chem. 81, 409 (2001).

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

[34] A. N. Petrov, N. S. Mosyagin, T. A. Isaev, A. V. Titov, V. F. Ezhov, E. Eliav, and U. Kaldor, Phys. Rev. Lett. 88, 073001 (2002).

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

[36] H. J. Monkhorst, Int. J. Quantum Chem.: Quantum Chem. Symp. 11, 421 (1977).

[37] The relation can be obtained by comparing the expression for the Frosch-Foley spin-rotational Hamiltonian with the term \((I_z S_z + \frac{1}{2} (I_+ S_+ + I_- S_-))\) used in [10].