Enhancement of the electric dipole moment of the electron in the BaF molecule

M. G. Kozlov, A. V. Titov, N. S. Mosyagin, and P. V. Souchko

Petersburg Nuclear Physics Institute, Gatchina, St. Petersburg District, 188350, Russia

(Received 14 July 1997)

We report results of *ab initio* calculation of the spin-rotational Hamiltonian parameters including P- and P,T-odd terms for the BaF molecule. The ground-state wave function of BaF molecule is found with the help of the relativistic effective core potential method followed by the restoration of molecular four-component spinors in the core region of barium in the framework of a nonvariational procedure. Core polarization effects are included with the help of the atomic many-body perturbation theory for the Barium atom. For the hyperfine constants the accuracy of this method is about 5–10 %. [S1050-2947(97)50311-8]

INTRODUCTION

It is well known that possible P- and P,T-odd effects are strongly enhanced in heavy diatomic radicals (see, for example, [1,2]). In the molecular experiment with the TlF molecule [3] stringent limits on the Schiff moment of the Tl nucleus and on the tensor constant of the electron nucleus P,T-odd interaction were obtained. In the experiments with the polar diatomics with the unpaired electron one can search for the P,T-odd effects caused by the permanent electric dipole moment (EDM) of the electron d_e [4] and by the scalar electron-nuclear P,T-odd interaction [5]. The most stringent limit on the electron EDM was obtained in the experiment with atomic thallium [6] (for the review of the theoretical predictions for d_e, see [7]). Heavy polar diatomic molecules provide enhancement of the electron EDM, which is several orders of magnitude larger than in Tl. An experimental search for the EDM of the electron is now underway on the YbF molecule [8]. The P-odd effects associated with the anapole moment of the nucleus are also strongly enhanced in diatomic radicals [9,10].

The first calculations of the P,T-odd interactions in molecules were carried out for TlF molecule with the use of a ''relativistic matching'' of the nonrelativistic one-configurational wave function [11]. Then a semiempirical scheme [12,13] and *ab initio* method based on the relativistic effective core potential (RECP) calculation of the molecular wave function [14] were developed. The first RECP-based calculations of the P,T-odd spin-rotational Hamiltonian parameters for PbF and HgF molecules were carried out in the framework of the one-configurational approximation with minimal atomic basis sets; i.e., the correlation structure was not taken into account. In calculations of the YbF molecule [15], a flexible atomic basis set was used and the correlation effects were considered within the restricted active space self-consistent-field (RASSCF) method [16,17].

It was concluded in [15] that, in order to perform more accurate calculations of the hyperfine and the P,T-odd constants, the spin-correlation of the unpaired electron with the outermost core shells $5s$ and $5p$ of ytterbium should be taken into account. Such correlations can hardly be efficiently considered within multiconfigurational SCF-like methods because of the necessity of correlating too many electrons.

Here we suggest using an effective operator (EO) technique to account for the most important types of the core-valence correlations. EOs for the valence electrons are formed with the help of the atomic many-body perturbation theory. This method allows one to include correlations not only with the outermost core shells, but with all core electrons, which appears to be quite important for the hyperfine and P,T-odd interactions. The EO technique was recently developed for atoms [18] and proved to be very efficient for the calculations of the hyperfine structure of the heavy atoms [19]. This technique is naturally and easily combined with the RECP method for the molecular calculations. As a result, a significant improvement of accuracy is achieved. Below we report the results of application of this method to calculation of the BaF molecule.

SPIN-ROTATIONAL HAMILTONIAN

Molecular spin-rotational degrees of freedom are described by the following spin-rotational Hamiltonian (see [2]):

$$H_{SR} = B\mathbf{N}^2 + \gamma \mathbf{S}\cdot\mathbf{N} - D_e\mathbf{n}\cdot\mathbf{E} + \mathbf{S}\cdot\hat{\mathbf{A}}\mathbf{I} + W_A k_A \mathbf{n}\times\mathbf{S}\cdot\mathbf{I}$$
$$+ (W_S k_S + W_d d_e)\mathbf{S}\cdot\mathbf{n}. \tag{1}$$

In this expression $\mathbf{N}$ is the rotational angular momentum, B is the rotational constant, $\mathbf{S}$ and $\mathbf{I}$ are the spins of the electron and the Ba nucleus, and $\mathbf{n}$ is the unit vector directed along the molecular axis from Ba to F. The spin-doubling constant γ characterizes the spin-rotational interaction. D_e and $\mathbf{E}$ are the molecular dipole moment and the external electric field. The axial tensor $\hat{\mathbf{A}}$ describes magnetic hyperfine structure. It can be determined by two parameters: $A = (A_\parallel + 2A_\perp)/3$ and $A_d = (A_\parallel - A_\perp)/3$. The last three terms in Eq. (1) account for the P- and P,T-odd effects. The first of them describes the interaction of the electron spin with the anapole moment of the nucleus k_A [10]. The second one corresponds to the scalar P,T-odd electron-nucleus interaction with the dimensionless constant k_S. The third one describes the interaction of the electron EDM d_e with the molecular field. The constant W_d characterizes an effective electric field on the unpaired electron.

TABLE I. Excitation energies for low-lying states of Ba averaged over nonrelativistic configurations (finite-difference SCF calculations).

Transition	DF Transition energy (a.u.)	GRECP Absolute error (a.u.)	GRECP Relative error (%)
$6s^2 \rightarrow 6s^1 6p^1$	0.04813	-0.00003	0.06
$6s^1 5d^1$	0.03942	0.00010	0.24
$6s^1$	0.15732	-0.00002	0.01
$6p^1$	0.24473	0.00002	0.01
$5d^1$	0.18742	0.00017	0.09

It is important to note that all P- and P,T-odd constants W_i mostly depend on the electron spin density in the vicinity of the heavy nucleus. The same, of course, can be said about hyperfine constants A and A_d. So, the comparison of the theoretical results for the hyperfine constants with the experiment is a good test for the accuracy of the whole calculation.

RECP CALCULATION OF THE ELECTRONIC WAVE FUNCTION

The scheme of the RECP calculation for the BaF molecule is very similar to that for YbF described in [15] (see also [14]), and below we will focus only on specific features of the present calculations. The generalized RECP (GRECP) [20] (with the inner core $1s^2[\cdots]4s^2 4p^6 4d^{10}$ shells, which were not included explicitly in the RECP calculations) was selected from a few other RECP variants for calculations of BaF because our test electronic structure calculations showed that it combined high accuracy with quite small computational expenses (see Table I and the spectroscopic data below).

Numerical pseudospinors derived from the GRECP-SCF calculations of some electronic configurations for Ba, Ba$^+$, and Ba^{2+} were approximated by generally contracted s, p, d, and f Gaussian functions forming the $(10,8,6,2) \rightarrow [6,5,4,2]$ basis set for barium.[1] For fluorine we used basis sets $(14,9,4) \rightarrow [6,5,2]$ and $[4,3,3]$ from the ANO-I Library [17]. These basis sets proved to be sufficiently flexible to reproduce electronic structure in valence region of BaF as compared to other basis sets involved in our test SCF and RASSCF calculations.

The RASSCF calculations of the spectroscopic constants were performed with the spin-averaged part of the GRECP (AREP), and the contribution of a relatively small spin-orbit interaction (i.e., effective spin-orbit potential or ESOP as a part of GRECP) was estimated in the framework of the perturbation theory. The results of our AREP-RASSCF calcula-

tions with 79 558 configurations[2] for the equilibrium distance and vibration constant ($R_e = 2.25$ Å, $\omega_e = 433$ cm^{-1}) are in a good agreement with the experimental data [21] ($R_e = 2.16$ Å, $\omega_e = 469$ cm^{-1}). For the dipole moment we have obtained $D_e = 2.93D$.

RESTORATION OF THE FOUR-COMPONENT SPINOR FOR THE VALENCE ELECTRON

In order to evaluate matrix elements of the operators that are singular near the nucleus of barium, we have performed GRECP-SCF and GRECP-RASSCF calculations of BaF where the pseudospinors corresponding to $5s_{1/2}$, $5p_{1/2}$, and $5p_{3/2}$ shells were ''frozen'' with the help of the level-shift technique (which is also known as the Huzinaga-type ECP; see Ref. [22] and references therein). It was necessary to do this because polarization of these shells was taken into account by means of the EO technique (see below). Spin-orbit interaction was neglected for the explicitly treated electrons because of its smallness (see [15]). Thus, only core molecular pseudo-orbitals occupying mainly atomic $1s$, $2s$, and $2p$ orbitals of fluorine and the valence pseudo-orbital of the unpaired electron (which is mainly the $6s,6p$-hybridized orbital of barium) were varied. RASSCF calculations with 5284 configurations were performed for 11 electrons distributed in RAS 1=(2,0,0,0), RAS 2=(2,1,1,0), and RAS 3=(6,4,4,2) subspaces.

The molecular relativistic spinor for the unpaired electron was constructed from the molecular pseudo-orbital $\widetilde{\varphi}_u^M$,

$$\widetilde{\varphi}_u^M = \sum_i C_i^s \widetilde{\varphi}_i^s + \sum_i C_i^p \widetilde{\varphi}_i^{p,m_l=0} + \cdots, \qquad (2)$$

so that the atomic s and p pseudo-orbitals of barium in Eq. (2) were replaced by the unsmoothed four-component Dirac-Fock (DF) spinors derived for the same atomic configurations that were used in the generation of basis s,p pseudo-orbitals. The MO LCAO coefficients were preserved after the RECP calculations. Since the spin-orbit interaction for the unpaired electron is small, the ''spin-averaged'' valence atomic p pseudo-orbital was replaced by the linear combination of the corresponding spinors with $j = l \pm 1/2$ (see [15,14] for details).

EFFECTIVE OPERATORS FOR VALENCE ELECTRONS

It is well known that the accuracy of the hyperfine-structure calculations for heavy atoms is not high if core polarization effects are not taken into account. In [23] it was suggested that correlations, which are not included in the active space, can be treated with the help of the EO. The latter is constructed by means of the atomic many-body perturbation theory (for the application of the perturbation theory to the calculations of the P,T violation in atoms, see, for example, [24]). The main advantage of this method is that there is no need to extend the active space to include core electrons.

In [23] it was supposed that the EO is constructed in the active space, which includes only few interacting levels. On the contrary, in [18,19] it is suggested that one use the single EO for the whole (infinite-dimensional) valence space. Thus,

---

[1] See [15] for details. Gaussian expansions for these pseudospinors, GRECP components and molecular orbital linear combination of atomic orbitals coefficients from BaF calculations can be found on http://www.qchem.pnpi.spb.ru.

[2] We used C_{2v} point group with (a_1,b_1,b_2,a_2) irreducible representations; 17 electrons were distributed on active orbitals within RAS 1=(3,1,1,0), RAS 2=(3,1,1,0) and RAS 3=(5,3,3,1) subspaces.

all correlations between valence electrons are treated explicitly, while the EO accounts only for the core excitations. In this case, the EO is energy dependent, but this dependence is weak if the energy gap between the core and the valence space is not too small. This makes the EO method much more flexible and allows us to use one EO for different quantum systems, provided that they have the same core. In particular, it is possible to form an EO for the atom (or ion) and then use it in a molecular calculation.

Generally speaking, the EO for the hyperfine interaction (as well as for any other one-electron operator) is no longer a one-electron operator, even in the lowest order of the perturbation theory. On the other hand, the one-electron part of the EO includes the two most important correlation corrections and in many cases appears to be a very good approximation. The first correction corresponds to the random phase approximation (RPA), and the second one corresponds to the substitution of the Dirac-Fock orbitals by the Brueckner orbitals.

To illustrate how the EO works for atomic barium, let us look at the hyperfine constant of the $^3P_1(6s6p)$ level of ^{137}Ba. The two-electron multiconfigurational Dirac-Fock calculation gives $A = 804$ MHz [25], which should be compared to the experimental value 1151 MHz. The two-electron configuration-interaction calculation with RPA and Brueckner corrections included gives $A = 1180$ MHz.

In this work we calculated EOs for the magnetic hyperfine interaction, for the EDM of the electron, and for the anapole moment. Both RPA equations and Brueckner equations were solved for a finite basis set in the V^{N-2} approximation (which means that the SCF corresponds to Ba^{2+}), and matrix elements of the EOs were calculated. The basis set included Dirac-Fock orbitals for $1s, \ldots, 6s, 6p$ shells. In addition, $7-21s$, $7-21p$, $5-20d$, and $4-15f$ orbitals were formed in analogy to the basis set $N2$ of [18]. Molecular orbitals were reexpanded in this basis set to find matrix elements of EOs for the molecular wave function.

RESULTS

Expressions for the electronic matrix elements that correspond to the parameters A, A_d, and W_i of the operator (1) can be found in [2]. All radial integrals and atomic four-component spinors were calculated for the finite nucleus in a model of a uniformly charged ball.

Results for the parameters of the spin-rotational Hamiltonian are given in Table II. There are two measurements of the hyperfine constants for ^{137}BaF [26,27]. The first of them was made for a matrix-isolated molecule and second was performed in a molecular beam. Results of these measurements were used in the semiempirical calculations [12,2] of P- and P,T-odd parameters of the spin-rotational Hamiltonian. These calculations were based on the similarity between electronic matrix elements for the hyperfine-structure interaction and for the P- and P,T-odd interactions. All of these operators mainly depend on the electron spin density in the vicinity of the nucleus. As a result, in a one-electron approximation, parameters W_i are proportional to $\sqrt{AA_d}$ [12]. Electronic correlations can break this proportionality.

TABLE II. Parameters of the spin-rotational Hamiltonian for BaF.

	A (MHz)	A_d (MHz)	W_d (10^{25} Hz/ e cm)	W_A (KHz)	W_S (Hz)
Expt. I–semiemp. [a]	2326	25	-0.41	240	-13
Expt. II–Semiemp. [b]	2418	17	-0.35	210	-11
SCF	1457	11	-0.230	111	-6.1
RASSCF	1466	11	-0.224	107	-5.9
SCF-EO	2212	26	-0.375	181	
RASSCF-EO	2224	24	-0.364	175	

[a]Hyperfine-structure constants measured for the matrix-isolated molecule [26] and semiempirical calculation of constants W_i based on this experiment [2].
[b]Hyperfine-structure constants measured for the free molecule [27] and semiempirical calculation based on this experiment [2].

In Table II we give results of the SCF and RASSCF calculations for 11 electrons with the restoration procedure described above. It is seen that in these calculations parameters A and A_d, are significantly smaller than in experiments [26,27]. At the next stage we used EOs to account for the core polarization effects. That led to the 50% growth for the constant A, while the constant A_d increased by 130%. Our final numbers for the hyperfine constants are very close to experiment [26] (the difference being less than 5%) but differ more significantly from [27].

Our SCF and RASSCF results for all three constants W_i are much smaller than results of the semiempirical calculations [12,2]. When core polarization effects are taken into account with the help of corresponding EOs, our values for W_d and W_A dramatically increase (at present we do not have an RPA for the constant W_S). There is good agreement between our final value for W_d and that from the semiempirical calculation, but for the constant W_A, our result is noticeably smaller. It can be explained by the fact that proportionality between W_d and $\sqrt{AA_d}$ holds within a 10% accuracy, but for the constant W_A deviation from proportionality reaches 30%. Almost half of this deviation is caused by the finite nuclear-size corrections to radial integrals. Electron-correlation corrections for both constants are about 15%.

Two conclusions can be made from the results of this work. First, as was suggested in [15], core polarization effects play a very important role in calculations of parameters of the spin-rotational Hamiltonian for heavy diatomic radicals. Second, results of the *ab initio* calculations, with core polarization included, are close to the results of the semiempirical calculations, correlation corrections being about 15%. The fact that two very different methods give similar results confirms that it is possible to make reliable calculations for such molecules.

[1] I. B. Khriplovich, *Parity Non-conservation in Atomic Phenomena* (Gordon and Breach, New York, 1991).

[2] M. G. Kozlov and L. N. Labzowsky, J. Phys. B **28**, 1933 (1995).

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

[4] O. P. Sushkov and V. V. Flambaum, Zh. Eksp. Teor. Fiz. **75**, 1208 (1978) [Sov. Phys. JETP **48**, 608 (1978)].

[5] V. G. Gorshkov, L. N. Labzowsky, and A. N. Moskalev, Zh. Eksp. Teor. Fiz. **76**, 414 (1979) [Sov. Phys. JETP **49**, 209 (1979)].

[6] E. Commins, S. Ross, D. DeMille, and B. Regan, Phys. Rev. A **50**, 2960 (1994).

[7] S. M. Barr, Int. J. Mod. Phys. A **8**, 209 (1993).

[8] B. E. Sauer, S. K. Peck, G. Redgrave, and E. Hinds, Phys. Scr. **T70**, 34 (1997); for preliminary studies of the YbF molecule, see B. E. Sauer, J. Wang, and E. A. Hinds, Phys. Rev. Lett. **74**, 1554 (1995).

[9] L. N. Labzowsky, Zh. Eksp. Teor. Phys. **75**, 856 (1978) [Sov. Phys. JETP **48**, 434 (1978)].

[10] V. V. Flambaum and I. B. Khriplovich, Phys. Lett. **110A**, 12 (1985).

[11] E. A. Hinds and P. G. H. Sandars, Phys. Rev. A **21**, 471 (1980); P. V. Coveney and P. G. H. Sandars, J. Phys. B **16**, 3727 (1983).

[12] M. G. Kozlov, Zh. Eksp. Teor. Fiz. **89**, 1933 (1985) [Sov. Phys. JETP **62**, 1114 (1985).]

[13] M. G. Kozlov and V. F. Ezhov, Phys. Rev. A **49**, 4502 (1994).

[14] Yu. Yu. Dmitriev, M. G. Kozlov, L. N. Labzowsky and A. V. Titov, Leningrad Nuclear Physics Institute, Report No. 1046, 1985 (unpublished); A. V. Titov, Ph.D. thesis, Leningrad University, 1986 (unpublished); M. G. Kozlov, V. I. Fomichev, Yu. Yu. Dmitriev, L. N. Labzowsky, and A. V. Titov, J. Phys. B **20**, 4939 (1987); Yu. Yu. Dmitriev *et al.*, Phys. Lett. **167A**, 280 (1992).

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

[16] J. Olsen and B. O. Roos, J. Chem. Phys. **89**, 2185 (1988).

[17] K. Andersson, M. R. A. Blomberg, M. P. Fülscher, V. Kellö, R. Lindh, P.-Aa Malmqvist, J. Noga, J. Olsen, B. O. Roos, A. J. Sadlej, P. E. M. Siegbahn, M. Urban, and P.-O. Widmark, MOLCAS, Version 2, University of Lund, Sweden, 1991.

[18] V. A. Dzuba, v. V. Flambaum, and M. G. Kozlov, JETP Lett. **63**, 882 (1996); Phys. Rev. A **54**, 3948 (1996).

[19] V. A. Dzuba, V. V. Flambaum, M. G. Kozlov, and S. G. Porsev (unpublished).

[20] I. I. Tupitsyn, N. S. Mosyagin, and A. V. Titov, J. Chem. Phys. **103**, 6548 (1995); N. S. Mosyagin, A. V. Titov, and Z. Latajka, Int. J. Quantum Chem. **63**, 1107 (1997).

[21] K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand, New York, 1979).

[22] V. Bonifacic and S. Huzinaga, J. Chem. Phys. **60**, 2779 (1974).

[23] I. Lindgren, Rep. Prog. Phys. **47**, 345 (1984).

[24] A.-M. Martensson-Pendrill, Meth. Comp. Chem. **5**, 99 (1992).

[25] T. Olsson, A. Rosen, B. Frike, and G. Torbohm, Phys. Scr. **37**, 730 (1988).

[26] L. B. Knight, W. C. Easley, and W. Weltner, J. Chem. Phys. **54**, 322 (1971).

[27] Ch. Ryzlewicz *et al.*, Chem. Phys. **71**, 389 (1982).