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Determination of molecular hyperfine-structure constant using the second-order relativistic many-body perturbation theory

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The spin-rotational Hamiltonian parameters $A_{\parallel}$ and $A_{\perp}$ for the BaF molecule are calculated using four-component relativistic spinors at the second-order many-body perturbation theory (MBPT) level via the **Z**-vector technique. The second-order MBPT is applied to assess the accuracy of the computed hyperfine-structure constants before studying the problem with the *state-of-the-art* coupled cluster with single and double excitations (CCSD) method which is highly accurate but computationally more expensive than MBPT. The hyperfine-structure constants A and A_d resulted from these calculations agree favorably well with experimental findings and with other correlated calculations. The convergence behavior of A and A_d with respect to the number of active orbitals used in the perturbative calculations suggests that our estimated A and A_d values should be accurate.

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I. INTRODUCTION

Paramagnetic radicals, such as BaF, YbF, thallium fluoride, etc., have been the subject of interest in experimental physics for the search of a permanent electric dipole moment (EDM) of the electron which for an atomic and/or molecular state can only arise when both parity (P) and time reversal (T) invariance are broken. The existence of a nonzero permanent EDM is, therefore, regarded as a signature of behavior beyond that described by the standard model (SM) of particle physics. Extensive theoretical investigations have been carried out over the past few decades to determine the P,T-odd interaction constant W_d (which is used to determine the electron EDM) for the previously mentioned diatomic systems. However, in order to interpret the measured data in terms of fundamental constants of the P,T-odd interaction, one must calculate specific properties of the systems to establish a connection between the measured data and the studied fundamental constants. These properties are described by the operators that are *prominent in the nuclear region*. It is pertinent to note that the accuracy of the theoretically estimated P,T-odd interaction constants can be directly assessed from the accuracy of a theoretical estimate of hyperfine constant (A and A' or $A_{\parallel}$ and $A_{\perp}$) as the operator from which hyperfine constants are determined is more or less similar to that used for the computation of P,T-odd interaction constants.

The first calculations of the P,T-odd interaction constants in molecules were carried out at the self-consistent field (SCF) level for the TlF molecule by Hinds *et al.* [1] and Coveney *et al.* [2] using *relativistic matching* nonrelativistic wave function. A semiempirical and *ab initio* method based on the relativistic effective core potential (RECP) calculation of the molecular wave function were subsequently developed by Kozlov and co-workers [3,4] for more accurate estimation of the P,T-odd interactions constants. Titov *et al.* [5,6] have also applied the RECP basis to determine the spin-rotational parameters including hyperfine-structure constant (A) for PbF and HgF molecules at the SCF level with minimal basis set. Note that the electron correlation effects were not taken into account in these pilot applications because of the complexity of the problem. The first correlated relativistic calculations were carried out by Titov *et al.* [7] for the YbF molecule. In their calculations, Titov *et al.* employed the restricted active space SCF (RASSCF) method [8] [a subset of complete active space (CAS) SCF] to incorporate the electron correlation effect. They concluded that for accurate calculations of the hyperfine and the P,T-odd interaction constants, the spin correlation of the unpaired electron must be taken into account. However, such a procedure is computationally cumbersome as too many electrons need to be correlated. In a later article, Kozlov *et al.* [3] showed that a significant portion of the core-valence electron correlation can be incorporated via the effective operator (EO) technique. They have successfully applied this technique to compute the P,T-odd interaction and hyperfine structure constants of BaF. Although the EO method offers a reasonably accurate estimate of spin-rotational Hamiltonian parameters, it only includes partial electron correlation. Thus, from a theoretical point of view, a rigorous *ab initio* relativistic correlated treatment is necessary to assess the accuracy of the P,T-odd interaction constants and related molecular properties such as equilibrium geometry, hyperfine-structure constant, dipole moment, etc. At this juncture, it is worth noting that the *analytic energy gradient* approaches are the most efficient and powerful tools to facilitate the study of equilibrium geometries, vibrational frequencies, transition states of molecular systems by determining the derivatives of the adiabatic potential energy surface(s) (for both ground and excited states) of a molecule with respect to the nuclear coordinate(s). Analytic derivatives also provide important applications to the calculations of various electrical and magnetic properties where the derivatives are taken with respect to the external field.

The seminal work of Pulay in developing a practical method for evaluating analytical gradients [9] of the SCF energy has opened fresh avenues for the study of molecular force fields [10]. Subsequent extensions by Pople *et al.* [11] of this approach treat contributions to the correlation energy by implementing analytical gradients for the second-order many-body perturbation theory method. Genuinely important breakthroughs in the early 1980s enabled simplified gradient calculations for correlated many-body methods, including the state-of-the-art **Z**-vector technique of Handy and Schaefer [12] for eliminating the terms involving derivatives of the molecular orbital coefficients in many-body perturbation theory (MBPT) and coupled-cluster (CC) methods. [13] These developments essentially provide the foundation for tremendous progress, culminating in the genesis of theoretical methods for evaluating the gradients, for example, of the MBPT energy all the way through fourth order [14–19]. The study of analytic derivatives for CC methods [20] has recently culminated in analytic gradient theories for equations of motion CC [21] (EOMCC) and propagator approaches [22] that are appropriate for specialized studies of excited electronic states and certain open-shell systems.

The analytic gradient method is nowadays routinely used in quantum chemistry to determine equilibrium geometries, vibrational frequencies, electric and magnetic properties, etc., for nonrelativistic molecular systems. It is widely accepted that the analytic energy derivative approaches are essential for a quantum chemical theory to be of practical use, and these techniques should be available for every standard many-body methods. In fact, analytic energy derivatives at the SCF, CASSCF, and MBPT levels are available in almost all quantum chemistry packages. However, despite tremendous methodological and computational advances, the gradient method is hardly applied for systems which must be treated relativistically. Thus, from a theoretical as well as a computational point of view, it is relevant to extend the analytic gradient approach to the relativistic regime to study atomic and/or molecular systems containing at least one heavy atom.

In our earlier communication [23], we employed the analytic gradient technique at the level of second-order many-body perturbation theory (MBPT) to study the P,T-odd interaction constants W_s for BaF and YbF molecules. The P,T-odd interaction constants W_s resulted from this approach were encouraging. The present paper is a continuation of our preceding studies on the numerical applications of the relativistic gradient approach at the second-order perturbation theory level. The goal of the present work is to extend the gradient approach to compute the hyperfine-structure constants for the ground state of the BaF molecule using all-electron relativistic spinors [i.e., Dirac-Fock (DF) orbitals]. The hyperfine constants for this system have been reported earlier by Kozlov *et al.* [24] at the EO-RASSCF level of theory. At this point, we reiterate that a rigorous *ab initio* study is necessary to assess the results obtained from *ab initio* many-body methods as the earlier schemes do not include the electron correlation in an effective and balanced manner. Ideally, energy gradient should be determined *analytically* for highly correlated and sophisticated many-body methods, such as the single or multireference-based coupled-cluster method with single and double (SR-CCSD or MR-CCSD) [25–34] excitation as these methods are known to be capable of providing a highly accurate estimate of atomic and molecular properties. Here, the energy gradient method at the level of second order is employed to assess the accuracy before studying the problem with the *state-of-the-art* CCSD methods.

The outlay of the paper is as follows. Sections II and III provide a brief outline of the hyperfine matrix elements and the scheme for evaluation of the analytic energy gradient with respect to external field via the **Z**-vector technique. The calculated results are presented and discussed in the subsequent section.

II. SPIN-ROTATIONAL HAMILTONIAN

Kozlov and Labzowsky [35] have shown that the molecular spin-rotational degrees of freedom can be described by the spin-rotational Hamiltonian as

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

where $\mathbf{N}$ is the rotational angular momentum and B is the rotational constant. The variables $\mathbf{S}$ and $\mathbf{I}$ are spin of the electron and Ba nucleus, $\mathbf{n}$ is the unit vector directed along the molecular axis from Ba to F, and γ is the spin-doubling constant which characterizes the spin-rotational interaction. The parameters D_e and $\mathbf{E}$ appearing in the previous expression are the molecular dipole moment and the external electric field. The magnetic hyperfine structure is described by the axial vector $\hat{\mathbf{A}}$ and the last three terms represent the P-odd and P,T-odd effects.

The one-electron one-center radial matrix elements of the magnetic hyperfine tensor interaction, $\mathbf{t}^1$ is given by [36]

$$\mathbf{t}^1_q = -\alpha(\kappa+\kappa')(-1)^{m-1/2}\sqrt{(2j+1)(2j'+1)} \times \begin{pmatrix} j & 1 & j' \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix} \begin{pmatrix} j & 1 & j' \\ -m & q & m' \end{pmatrix} R_{\kappa,\kappa'}(r), \tag{2}$$

where the radial integral $R_{\kappa,\kappa'}(r)$ is given by

$$R_{\kappa,\kappa'}(r) = \int_0^\infty [P_\kappa(r)Q_{\kappa'}(r) + Q_\kappa(r)P_{\kappa'}(r)]dr, \tag{3}$$

in which $P_\kappa(r)$ and $Q_\kappa(r)$ are the *large* and *small* component of the radial part of the atom-centered basis of symmetry label κ. Now, the magnetic hyperfine interactions $A_\parallel$ and $A_\perp$ can be defined as

$$A_\parallel = \frac{g\mathbf{N}}{m_p}\langle\omega|t^1_0|\omega\rangle, \tag{4}$$

and

$$A_\perp = \frac{g\mathbf{N}}{m_p}\langle\omega|\sqrt{2}t^1_1|-\omega\rangle = \frac{g\mathbf{N}}{m_p}\langle\omega|\sqrt{2}t^1_{-1}|-\omega\rangle, \tag{5}$$

respectively, where ω denotes the projection of electronic total angular momentum along the molecular symmetry axis. With the aid of these definitions, the magnetic hyperfine-structure constants A and A_d can be written as

$$A = \frac{1}{3}(A_\parallel + 2A_\perp), \tag{6}$$

and

$$A_d = \frac{1}{3}(A_\parallel - A_\perp). \tag{7}$$

III. METHODOLOGY

Once the molecular electronic wave function Ψ is known, the properties of interest can be computed from the expectation value,

$$\langle O\rangle = \langle\Psi|H'|\Psi\rangle, \tag{8}$$

where H' is an appropriate operator for the property of interest. For one-electron properties, Eq. (8) reduces to the contraction of a density matrix with property integrals. The property values can also be computed using perturbation theory. In this case, the property associated with H' is given by

$$\langle O\rangle = dE/d\lambda|_{\lambda=0}, \tag{9}$$

where

$$E(\lambda) = \langle\Psi|H_0 + \lambda H'|\Psi\rangle, \tag{10}$$

in which H_0 is the unperturbed Hamiltonian. Differentiating Eq. (10), w.r.t λ, we get

$$dE/d\lambda|_{\lambda=0} = \langle\Psi|H'|\Psi\rangle + \left\langle\frac{d\Psi}{d\lambda}\right|H_0|\Psi\rangle|_{\lambda=0} + \langle\Psi|H_0\left|\frac{d\Psi}{d\lambda}\right\rangle\bigg|_{\lambda=0}, \tag{11}$$

which reduces to Eq. (8) when Ψ is an exact eigenfunction of H_0 (i.e., when $d\Psi/d\lambda = 0$). Under these circumstances the wave function is said to obey the Hellmann-Feynmann theorem [37] for H'.

The simplest approach to compute the property is the finite difference approach [38], where $dE/d\lambda|_{\lambda=0}$ is estimated by finite differences, that is,

$$\left.\frac{dE}{d\lambda}\right|_{\lambda=0} = \frac{E(\bar\lambda) - E(0)}{\bar\lambda}, \tag{12}$$

for small $\bar\lambda$. However, this approach is neither convenient nor simple for general application. The alternative to Eq. (12) is the "coupled perturb" approach where the non-Hellmann-Feynmann terms are computed explicitly via

$$\left.\frac{dE}{d\lambda}\right|_{\lambda=0} = \left.\frac{\partial E}{\partial\lambda}\right|_{\lambda=0} + \sum_k \left.\frac{\partial E}{\partial\alpha_k}\right|_{\alpha_k=\alpha_0} \left.\frac{d\alpha_k}{d\lambda}\right|_{\lambda=0}, \tag{13}$$

where $\{\alpha_0\}$ is the set of parameters in the optimization of unperturbed wave function Ψ. It immediately follows from the previous equation that in order to compute the non-Hellmann-Feynmann terms in Eq. (11), we have to evaluate $\partial E/\partial\alpha_k$ and $d\alpha_k/d\lambda$. In the actual calculation, this is accomplished by the **Z**-vector method [39–41].

Since the basic formalism of the **Z**-vector method is available elsewhere [39,40], we briefly review this scheme. For convenience, we restrict our discussion on the evaluation of the analytic energy derivative involving the electric field perturbation for the CI wave function. Let us consider the following first-order perturbed Hamiltonian operator H,

$$H = H_0 + \lambda_a H'_a + \lambda_f H'_f \tag{14}$$

where H_0 is the unperturbed Hamiltonian and H'_a is the first-order change in the Hamiltonian due to nuclear perturbation, and H'_f is the first-order change due to electric field. The parameters λ_a and λ_f in Eq. (14) are the nuclear coordinate and electric field perturbations, respectively. Since the atomic orbital basis set depends only on the nuclear coordinate, H'_a affects the one-electron, two-electron, and overlap integrals. On the other hand, H'_f only affects the one-electron integrals. The electric dipole moment is defined by

$$\mu_f = -\frac{\partial E_{\text{total}}}{\partial F} = -\frac{\partial E_{\text{nuc}}}{\partial F} - \frac{\partial E_{\text{elec}}}{\partial F} = \mu_f^{\text{nuc}} + \mu_f^{\text{elec}}, \tag{15}$$

where F stands for the electric field along the f axis. Now, the first derivative of the electronic energy for the CI wave function with respect to the electric field perturbation can be written as [40]

$$\frac{\partial \mathrm{E}_{\text{elec}}}{\partial F} = -\sum_{ij}^{\text{MO}} Q_{ij} h_{ij}^f - 2\sum_{ij}^{\text{MO}} U_{ij}^f X_{ij}, \tag{16}$$

where Q is the one-electron density matrix [42] and h_{ij}^f is the dipole moment matrix. The Lagrangian matrix for the CI wave function X is given by

$$\mathbf{X} = \sum_{ij}^{\text{MO}} Q_{ij} h_{ij} + \sum_{ijkl}^{\text{MO}} G_{ijkl}(ij|kl), \tag{17}$$

in which h_{ij} and $(ij|kl)$ are the one- and two-electron matrix elements and G is the two-electron density matrix [42]. The U_{ij}^f matrices, which are related to the first derivative of molecular orbital (MO) coefficients with respect to the electric field are obtained by solving the coupled perturbed Hartree-Fock (CPHF) equations in the following matrix form;

$$\mathbf{A}\mathbf{U}^f = \mathbf{B}^f. \tag{18}$$

For a closed-shell SCF wave function matrices **A** and **B** can be written as

$$A_{ij,kl} = \delta_{ij}\delta_{kl}(\epsilon_j - \epsilon_i) - [4(ij|kl) - (ik|jl) - (il|jk)], \tag{19}$$

and

$$B_{ij} = h_{ij}^f, \tag{20}$$

respectively, where ϵ's are single-particle orbital energies. The one- and two-electron integrals appearing in Eqs. (19) and (20) are defined in terms of molecular orbitals as

$$h_{ij} = \int \phi_i^*(1)\,h(1)\,\phi_j(1)\,d\tau_1, \tag{21}$$

$$(ij|kl) = \int\!\!\int \phi_i^*(1)\,\phi_j^*(1)\frac{1}{r_{12}}\phi_k(2)\,\phi_l(2)\,d\tau_1 d\tau_2. \tag{22}$$

Now the second term of Eq. (16) may be written as [40]

$$2\sum_{ij}^{\text{MO}} U_{ij}^f X_{ij} = 2\mathbf{X}^T\mathbf{U}^f, \tag{23}$$

where $\mathbf{X}^T$ is the transpose of $\mathbf{X}$ matrix. Combining Eqs. (18) and (23), the second term of Eq. (16) can be written as

$$2\sum_{ij}^{\text{MO}} U_{ij}^f X_{ij} = 2\mathbf{X}^T\mathbf{A}^{-1}\mathbf{B}^f = 2\mathbf{Z}^T\mathbf{B}^f, \tag{24}$$

where the $\mathbf{Z}$ vector in this equation is defined by

$$\mathbf{Z}^T = \mathbf{X}^T\mathbf{A}^{-1}, \tag{25}$$

which in turn may be written as

$$\mathbf{A}^T\mathbf{Z} = \mathbf{X}. \tag{26}$$

Once $\mathbf{Z}$ is known, the corrections due to first-order changes of the MO coefficients may be evaluated as

$$2\sum_{ij}^{\text{MO}} U_{ij}^f X_{ij} = 2\sum_{ij}^{\text{MO}} B_{ij}^f Z_{ij}. \tag{27}$$

The advantage of the $\mathbf{Z}$ vector is now obvious. In Eq. (18) the simultaneous equations were to be solved for three degrees (x, y, and z) of freedom, while in Eq. (26) they are solved only for one degree of freedom. It is worth noting that the $\mathbf{Z}$-vector method, *in principle*, is applicable whenever equations of the form (26) and (27) are valid.

IV. RESULTS AND DISCUSSIONS

The hyperfine-structure constants $A_\parallel$ and $A_\perp$ of the ground $^2\Sigma_{1/2}$ state of BaF are evaluated via the analytic gradient approach through the second-order MBPT using all-electron Dirac-Fock orbitals. The calculations are carried out using a $27s27p12d8f$ and $15s10p$ even-tempered Gaussian basis set at the experimental geometry ($R_e = 2.16$ Å). The hyperfine-structure constants (A and A_d) resulting from our MBPT are compared with experimental data and with other theoretical calculations in Table I. In addition, we also report the results of A and A_d determined at the RASCI level calculated using the same basis set and active orbitals. The total number of active orbitals in the RASCI and MBPT calculations is 75. The first 24 occupied orbitals are kept frozen in the calculation as their effect on W_s and μ (dipole moment) are not significant. We would like to note that preliminary calculations exhibit a sharp increase in the computed A and A_d values with an increasing number of active unoccupied orbitals which finally stabilizes for the number of active orbital $\geqslant 60$ (for 17 active-electron cases) [23].

TABLE I. Hyperfine-structure constants (in MHz) for BaF.

Methods	A	A_d
Expt. I[a]	2326	25
Expt. II[a]	2418	17
SCF [24]	1457	11
RASSCF [24]	1466	11
SCF-EO [24]	2212	26
RASSCF-EO [24]	2224	24
RASCI (This work)[b]	2176	32
MBPT (This work)[b]	2230	19
MBPT (This work)[c]	2274	20

[a] Results obtained from two different experiments (see Ref. [35] for details).

[b] Results from 17 active electrons and 75 active orbitals used in MBPT calculations.

[c] Results from 35 active electrons and 75 active orbitals used in MBPT calculations.

As can be seen in Table I that the A and A_d parameters estimated at the SCF and RASSCF levels of theories are ∼40% off from the experiment. This clearly indicates the importance of electron correlation in the estimation of A and A_d. A similar trend was observed for the P,T-odd interaction constant W_s for this molecule. It is also evident from Table I that the inclusion of electron correlation (*partially*) via the EO method and/or *ab initio* second-order MBPT significantly improves the accuracy of the theoretically estimated hyperfine constant values. A closer inspection of the results displayed in Table I shows that the MBPT estimated hyperfine A (A_d) value is off by ∼52 MHz (5 MHz) and 144 MHz (3 MHz) with respect to the first and to the second experimental values. To analyze and assess the contribution of inner core electrons, we increase the number of active electrons in the calculation by 18 [i.e., a total of 35 active electrons (freezing lowest 15 occupied orbitals)]. The hyperfine-structure constants resulted from this calculation shows that the inclusion of inner core electrons improves the theoretical estimate of A and A_d by ∼2%.

We reiterate that we have analyzed the variations of A and A_d with respect to the space of virtual orbitals but not against the level of correlation. For a reasonably accurate estimate of the uncertainty in our calculations, the variations of A and A_d with respect to the basis sets, active space and level of correlation have to be known. However, this is beyond the scope of the present work and therefore we are not in a position to comment on the uncertainty of our estimated hyperfine-structure constants A and A_d. In passing, we note that since we have used a fairly large basis set and active orbitals in the calculations. we trust that our estimated hyperfine-structure constants should be quite accurate.

We now analyze the results obtained using the RASCI method. The RASCI calculations are carried out with 17 active electrons and 75 active orbitals. As can be seen in Table I, the RASCI approach overestimates the A_d value by almost 7 MHz and underestimates A by 150 MHz with respect to the first experimental data. Nevertheless, the RASCI calculations demonstrate that the A and A_d estimate can be also improved by incorporating the nondynamical electron correlation via configuration interaction (CI) approach. However, MBPT should be more preferable over RASCI because RASCI, unlike MBPT, is not size extensive [43].

Based on the values of A and A_d (also W_s), estimated from SCF, RASSCF, SCF-EO, MBPT, etc., we conclude that although the present calculation agrees favorably with earlier theoretical results, more sophisticated theoretical treatment is still necessary to improve the accuracy of these spin-rotational Hamiltonian parameters. State-of-the-art many-body methods such as multireference many-body perturbation theory and/or coupled-cluster methods may be used to access higher order dynamical and nondynamical electron correlation effects and accuracy of the present estimate. Work in this direction is in progress and will be presented in our future communication.

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