Zeeman interaction in the $^3\Delta_1$ state of HfF$^+$ to search for the electron electric dipole moment

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A theoretical study devoted to suppression of magnetic systematic effects in HfF$^+$ cation for an experiment to search for the electron electric dipole moment is reported. The g factors for $J = 1$, $F = 3/2$, $|M_F| = 3/2$ hyperfine levels of the $^3\Delta_1$ state are calculated as functions of the external electric field. The minimal value for the difference between the g factors of Ω-doublet levels, $\Delta g = 3 \times 10^{-6}$, is attained at the electric field 7 V/cm. The body-fixed g factor, $G_\parallel$, was obtained both within the *ab initio* electronic structure calculations and with our fit of the experimental data [H. Loh, K. C. Cossel, M. C. Grau, K.-K. Ni, E. R. Meyer, J. L. Bohn, J. Ye, and E. A. Cornell, Science **342**, 1220 (2013)]. For the electronic structure calculations we used a combined scheme to perform correlation calculations of HfF$^+$, which includes both the direct four-component all-electron and generalized relativistic effective core potential approaches. The electron correlation effects were treated using the coupled cluster methods. The calculated value $G_\parallel = 0.0115$ agrees very well with the $G_\parallel = 0.0118$ obtained with our fitting procedure. The calculated *ab initio* value $D_\parallel = -1.53$ a.u. for the molecule-frame dipole moment (with the origin in the center of mass) is in agreement with the experimental datum $D_\parallel = -1.54(1)$ a.u. [H. Loh, Ph.D. thesis, Massachusetts Institute of Technology, 2006].

I. THEORY

Search for the electron electric dipole moment (eEDM), d_e, is an important test of the standard model and its extensions [1,2]. The best current limit on the electron EDM, $|d_e| < 9 \times 10^{-29}$ e cm, was set with a molecular beam of the thorium monoxide (ThO) molecules by the ACME Collaboration [3] using the theoretical data from Ref. [4]. This and other neutral systems are considered for further search for the eEDM and other manifestations of effects of time-reversal (T) and spatial parity (P) symmetries violations of the fundamental interactions [4–9].

Cornell and Ye's group has suggested use of the trapped molecular ions for the eEDM search [10,11]. One of the most promising systems for the search is the HfF$^+$ cation [10,12–17], which is also of interest for other fundamental experiments [18–20]. It has the long-lived metastable $^3\Delta_1$ electronic state with lifetime $\sim 2s$ [12,15], which means a very large coherence time is achievable in the experiment. The other main feature of the $^3\Delta_1$ state is that it has a very small g factor (zero in the nonrelativistic limit in approximation with the free-electron g factor g_S equal to –2.0) which leads to the suppression of the magnetic systematic effects. It was shown that further suppression of systematics is possible due to existence of the Ω-doublet structure of molecules in the $^3\Delta_1$ electronic state [21–24]. For preparation and implementation of the eEDM experiment one should investigate the dependence of upper and lower Ω-doublet state g factors on the strength of the laboratory electric field. And this is the goal of the present paper.

We define the g factors such that Zeeman shift is equal to

$$E_{\text{Zeeman}} = -g\mu_B \mathcal{B} M_F, \tag{1}$$

where μ_B is the Bohr magneton, M_F is the projection of the total angular momentum on the laboratory z axis, and $\mathbf{B} = \mathcal{B}\hat{z}$ is the external magnetic field. This definition matches the ones in the papers [13,22]. Using the angular momentum algebra [25], one can calculate that in the adiabatic approximation and in the limit of zero hyperfine interaction g factors of hyperfine sublevels of the $^3\Delta_1$ state of HfF$^+$ are determined by

$$
\begin{aligned}
g = &-G_\parallel \frac{F(F+1) + J(J+1) - 3/4}{2F(F+1)J(J+1)} \\
&+ g_F \frac{\mu_N}{\mu_B} \frac{F(F+1) - J(J+1) + 3/4}{2F(F+1)}.
\end{aligned} \tag{2}
$$

Here $g_F = 5.257\,73$ is ^{19}F nucleus g factor and μ_N is the nuclear magneton. The first term in the right-hand side of Eq. (2) is the electronic contribution [26] and the second term is contribution from the magnetic moment of the ^{19}F nucleus.

Equation (2) does not take into account the hyperfine interaction between different rotational levels and nonadiabatic interaction with other electronic states. To take these effects into account, following Refs. [26] and [22], the g factors are obtained by numerical diagonalization of the molecular Hamiltonian ($\hat{\mathbf{H}}_{\text{mol}}$) in external electric $\mathbf{E} = \mathcal{E}\hat{z}$ and magnetic $\mathbf{B} = \mathcal{B}\hat{z}$ fields over the basis set of the electronic-rotational wave functions

$$\Psi_\Omega \theta_{M,\Omega}^J(\alpha,\beta) U_{M_I}^F. \tag{3}$$

Here Ψ_Ω is the electronic wave function, $\theta_{M,\Omega}^J(\alpha,\beta) = \sqrt{(2J+1)/4\pi} D_{M,\Omega}^J(\alpha,\beta,\gamma = 0)$ is the rotational wave function, α,β,γ are Euler angles, $U_{M_I}^F$ is the F nuclear-spin-wave functions, M (Ω) is the projection of the molecule angular

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momentum on the laboratory $\hat{z}$ (internuclear $\hat{n}$) axis, and $M_I = \pm 1/2$ is the projection of the nuclear angular momentum on the same axis. Note that $M_F = M_I + M$.

We represent the molecular Hamiltonian for ^{180}Hf^{19}F$^+$ as

$$\hat{\mathbf{H}}_{\text{mol}} = \hat{\mathbf{H}}_{\text{el}} + \hat{\mathbf{H}}_{\text{rot}} + \hat{\mathbf{H}}_{\text{hfs}} + \hat{\mathbf{H}}_{\text{ext}}. \qquad (4)$$

Here $\hat{\mathbf{H}}_{\text{el}}$ is the electronic Hamiltonian,

$$\hat{\mathbf{H}}_{\text{rot}} = B_{\text{rot}}\mathbf{J}^2 - 2B_{\text{rot}}(\mathbf{J} \cdot \mathbf{J}^e) \qquad (5)$$

is the rotational Hamiltonian,

$$\hat{\mathbf{H}}_{\text{hfs}} = g_{\text{F}}\mathbf{I}\cdot\left[\sum_i\left(\frac{\boldsymbol{\alpha}_i \times \boldsymbol{r}_i}{r_i^3}\right)\right] \qquad (6)$$

is the hyperfine interaction between electrons and fluorine nucleus, and

$$\hat{\mathbf{H}}_{\text{ext}} = \mu_{\text{B}}(\mathbf{L}^e - g_S\mathbf{S}^e) \cdot \mathbf{B} - g_{\text{F}}\frac{\mu_N}{\mu_B}\mathbf{I} \cdot \mathbf{B} - \mathbf{D} \cdot \mathbf{E} \qquad (7)$$

describes the interaction of the molecule with external magnetic and electric fields, $B_{\text{rot}} = 0.2989$ [12] is the rotational constant, $g_S = -2.0023$ is a free-electron g factor, and $\mathbf{D}$ is the dipole moment operator.

For the current study we have considered the following low-lying electronic basis states: $^3\Delta_1$, $^3\Delta_2$, $^3\Pi_0^+$, and $^3\Pi_{0^-}$. $\hat{\mathbf{H}}_{\text{el}}$ is diagonal on the basis set (3). Its eigenvalues are transition energies of these states. They were calculated and measured in Ref. [12]:

$$^3\Delta_1 : T_e = 976.930 \text{ cm}^{-1},$$
$$^3\Delta_2 : T_e = 2149.432 \text{ cm}^{-1},$$
$$^3\Pi_{0^-} : T_e = 10\,212.623 \text{ cm}^{-1},$$
$$^3\Pi_{0^+} : T_e = 10\,401.723 \text{ cm}^{-1}. \qquad (8)$$

Other terms of the molecular Hamiltonian $\hat{\mathbf{H}}_{\text{mol}}$ are determined by the parameters given in Eqs. (9)–(20) below. We have performed electronic calculations for the following matrix elements of the basis electronic states:

$$G_\perp^{(1)} = \langle^3\Delta_1|\hat{L}_-^e - g_S\hat{S}_-^e|^3\Delta_2\rangle = -2.617, \qquad (9)$$

$$D_\perp^{(1)} = \langle^3\Delta_1|\hat{D}_-|^3\Delta_2\rangle = 0.034 \text{ a.u.}, \qquad (10)$$

$$\Delta^{(1)} = 2B_{\text{rot}}\langle^3\Delta_1|J_-^e|^3\Delta_2\rangle = -0.737\,087\,4 \text{ cm}^{-1}, \qquad (11)$$

$$D_\parallel = \langle^3\Delta_1|\hat{D}_{\hat{n}}|^3\Delta_1\rangle = -1.53 \text{ a.u.}, \qquad (12)$$

$$D_\perp^{(2a)} = \langle^3\Delta_1|\hat{D}_+|^3\Pi_{0^+}\rangle = 0.457 \text{ a.u.}, \qquad (13)$$

$$D_\perp^{(2b)} = \langle^3\Delta_1|\hat{D}_+|^3\Pi_{0^-}\rangle = 0.447 \text{ a.u.}, \qquad (14)$$

where $D_\pm = D_x \pm iD_y$ and the same is for other vectors. Matrix element (13) is in a good agreement with the value $D_\perp^{(2a)} = 0.467$ a.u. calculated in Ref. [15]. The spin-orbit direct configuration interaction with configuration selection method was used in Ref. [15], and the multireference complete active space configuration interaction method with single and double excitations is used in this work to calculate matrix elements (13) and (14). The calculated permanent dipole moment $D_\parallel$ is in a good agreement with the experimental

value $D_\parallel = -1.54(1)$ a.u. [27]. The matrix elements

$$G_\perp^{(2a)} = \langle^3\Delta_1|\hat{L}_+^e - g_S\hat{S}_+^e|^3\Pi_{0^+}\rangle = 1.3456, \qquad (15)$$

$$G_\perp^{(2b)} = \langle^3\Delta_1|\hat{L}_+^e - g_S\hat{S}_+^e|^3\Pi_{0^-}\rangle = 1.5524, \qquad (16)$$

$$\Delta^{(2a)} = 2B_{\text{rot}}\langle^3\Delta_1|J_+^e|^3\Pi_{0^+}\rangle = 0.8044 \text{ cm}^{-1}, \qquad (17)$$

$$\Delta^{(2b)} = 2B_{\text{rot}}\langle^3\Delta_1|J_+^e|^3\Pi_{0^-}\rangle = 0.9280 \text{ cm}^{-1}, \qquad (18)$$

were chosen to reproduce the experimental value

$$0.369J(J + 1)\text{MHz} = \frac{J(J + 1)}{2}\left(\frac{\left(\Delta^{(2a)}\right)^2}{T_e(^3\Delta_1) - T_e(^3\Pi_{0^+})}\right.$$
$$\left. - \frac{\left(\Delta^{(2b)}\right)^2}{T_e(^3\Delta_1) - T_e(^3\Pi_{0^-})}\right)$$

for Ω doubling of $^3\Delta_1$. We have estimated from our calculations that the matrix elements $\langle^3\Delta_1|S_+^e|^3\Pi_{0\pm}\rangle$ are much smaller than $\langle^3\Delta_1|J_+^e|^3\Pi_{0\pm}\rangle$ by absolute value. Therefore for matrix elements (15) and (16) we can write $G_\perp^{(2a)} = \Delta^{(2a)}/2B_{\text{rot}}$, $G_\perp^{(2b)} = \Delta^{(2b)}/2B_{\text{rot}}$. A similar situation is for ThO [22] and WC [28] molecules which have similar electronic structure. The choice of matrix elements (17),(18) is not unique, since we need to approximate Ω doubling (defined by one number) by two independent parameters. However, accounting for the close relation between $\Delta^{(2a)}, \Delta^{(2b)}$ and $G_\perp^{(2a)}, G_\perp^{(2b)}$ described above, it can be shown [28] that ambiguity in $\Delta^{(2a)}$ and $\Delta^{(2b)}$ does not lead to an ambiguity in the g-factor difference of Ω doublets. It is natural, however, to take matrix elements (17) and (18) close to the value $2B_{\text{rot}}\sqrt{2} = 0.845$ cm^{-1} calculated on leading configurations of $^3\Delta_1$, $^3\Pi_{0\pm}$ states [22]. Note that the described procedure of estimating of matrix elements (17),(18) using experimental value of Ω doubling effectively can take into account interaction with higher electronic states.

The matrix element

$$A_\parallel = g_{\text{F}}\langle\Psi_{^3\Delta_1}|\sum_i\left(\frac{\boldsymbol{\alpha}_i \times \boldsymbol{r}_i}{r_i^3}\right)_\zeta|\Psi_{^3\Delta_1}\rangle = -58.1 \text{ MHz} \qquad (19)$$

has been taken from Ref. [15]. The hyperfine structure only of the $^3\Delta_1$ state was taken into account. $G_\parallel$ is given by the following formula:

$$G_\parallel = \frac{1}{\Omega}\langle^3\Delta_1\big|\hat{L}_{\hat{n}}^e - g_S\hat{S}_{\hat{n}}^e\big|^3\Delta_1\rangle. \qquad (20)$$

To perform electronic structure calculations of the diagonal matrix elements (12) and (20) we have used the combined computational scheme similar to that used in Refs. [8,19,29], which includes electronic structure treatment within the generalized relativistic effective core (GRECP) potential approach [30,31] and the relativistic four-component Dirac-Coulomb approach. Note that the GRECP operator [30,31] allows one to take account of the Breit interaction very effectively. The applied computational scheme includes the following stages: (i) a two-component 52-electron relativistic correlation calculation using the coupled cluster with single, double, and noniterative triple cluster amplitudes, CCSD(T), method. For this we have used the semilocal version of the 44-electron GRECP operator [30,31]. The 28 inner core $1s..3d$ electrons

of Hf have been excluded from the correlation treatment by the GRECP operator and all other (outer core and valence) electrons were included in the correlation calculation. (ii) To treat the correlation contribution from the inner core electrons we have performed direct four-component calculations at the level of the coupled cluster with single amplitudes (CCS) method as the difference in the calculated properties within the 80-electron (i.e., all-electron) CCS versus the 52-electron CCS. (iii) Calculation of vibration correction for $G_\parallel$. (iv) Calculation of the correction on high-order correlation effects.

For the stage (i) we have generated the uncontracted basis set for Hf that includes 25 s-, 25 p-, 21 d-, 14 f-, 10 g-, 5 h-, and 5 i-type Gaussians. For fluorine the augmented correlation consistent-polarized valence quadruple zeta (aug-ccpVQZ) basis set [32,33] was used which contains 6 s-, 5 p-, 4 d-, 3 f-, and 2 g-contracted Gauss functions and can be briefly written as (13,7,4,3,2)/[6,5,4,3,2]. Note that the reduction of the basis set on Hf to 15 s-, 10 p-, 8 d-, 7 f-, 4 g-, 2 h-, and 1 i-type Gaussians (g-, h-, and i-type basis functions were contracted using the code from Ref. [34]) leads to only slight changes in the calculated values.

For stage (ii) the uncontracted core-valence double zeta (CVDZ) [35,36] basis set for Hf and the correlation consistent-polarized valence double zeta (ccpVDZ) [32,33] basis set for F were used. At stage (iv) the high-order correlation effects were considered as a difference in the values of considered properties calculated within the coupled cluster with single, double, triple, and noniterative quadruple amplitudes and the CCSD(T) method. In the calculations 20 valence and outer core electrons of HfF$^+$ were correlated.

To calculate off-diagonal matrix elements (9), (10), and (11) we have used the 12-electron version of the GRECP operator for Hf used earlier in Refs. [14,15,18] to perform two-component 20-electron correlation calculations. For the calculations we have used the [12,16,16,10,8]/(6,5,5,3,1) basis set for Hf and [14,9,4,3]/(4,3,2,1) atomic natural orbital (ANO-I) basis set for F [37]. Calculations of the matrix elements (9), (10), and (11) were performed within the linear-response coupled cluster with single and double cluster amplitudes (LR-CCSD) method.

Electronic calculations were performed within the DIRAC12 [38] and MRCC [39] codes. The code to calculate matrix elements of the g-factor operator over the four-component molecular bispinors has been developed in the present paper, while the code for matrix elements over two-component molecular spinors was developed earlier in Refs. [7,40].

II. RESULTS AND DISCUSSIONS

$G_\parallel$ obtained from the electronic structure calculation is equal to 0.0115 and is in very good agreement with the value $G_\parallel = 0.011\,768$ obtained by fitting the $g_{fit} = -0.003\,06$ value. In Ref. [13] the experimental value $g_{exp} = +0.003\,06$ obtained in the external electric field $\mathcal{E} = 11.6$ V/cm is given. The electronic structure calculation is in agreement with the experiment only if the sign of the g factor be changed. Thus, for consistency with the experiment, in this work we further use the g-factor value $g_{fit} = -g_{exp}$ with the sign reversed from that in Ref. [13]. Only the $G_\parallel$ parameter was optimized in the fitting procedure. Equation (2) gives $G_\parallel = 0.012\,043$.
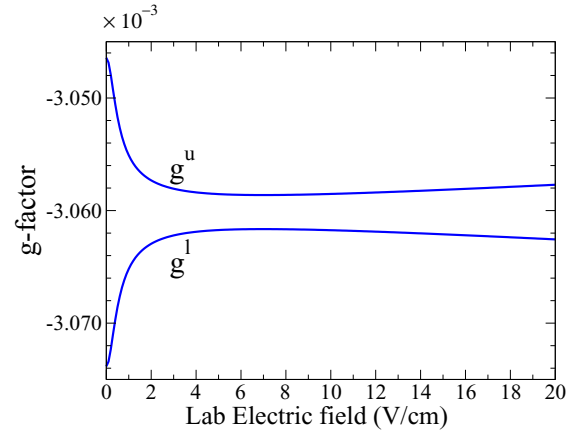

FIG. 1. Calculated g factors for upper (g^u) and lower (g^l) levels of Ω doublets for the $J = 1, F = 3/2, M_F = 3/2$ levels of the $^3\Delta_1$ state of HfF$^+$ as functions of the electric field.

In Fig. 1 the calculated g factors for the $J = 1, F = 3/2, M_F = 3/2$ levels of the HfF$^+$ $^3\Delta_1$ state are shown as functions of the laboratory electric field. The calculated difference $\Delta g = g^u - g^l = 3.4 \times 10^{-6}$ between the g factors of the upper (g^u) and lower (g^l) levels of Ω doublets is consistent with the experimental value $-1(2) \times 10^{-5}$ [13]. Note that for zero electric field the difference is zero in the adiabatic approximation.

In the eEDM experiment the energy splittings for $J = 1$, $F = 3/2$, $|M_F| = 3/2$ hyperfine levels of the $^3\Delta_1$ electronic state of the ^{180}Hf^{19}F$^+$ ion are measured in the presence of the *rotating* electric and magnetic fields being parallel or antiparallel to each other [13,41]. The eEDM-induced contribution to the splitting is $2d_e\mathcal{E}_{eff}$, where $\mathcal{E}_{eff} = 22.5$ GV/cm [14,15,20] is the effective electric field in the molecule acting on the eEDM. The eEDM-induced contribution to the splitting there is the Zeeman contribution $3\mu_B g\mathcal{B}$. Thus insufficient control of the magnetic field is a source of systematic errors in the experiment. In addition to the small value of g factor, HfF$^+$ (similarly to ThO [3], WC [28], and some other molecules) has a possibility to suppress the systematic due to the existence of closely spaced levels of Ω doublets. It can be shown (see [22] and references) that Ω doublets have equal, by absolute value, but opposite eEDM-induced shifts. Therefore, the splittings of two Ω-doublet states can be subtracted from each other, which suppresses many effects related to the spurious magnetic field $\tilde{B}$ [21] but doubles the eEDM signal. However, the upper and lower Ω-doublet states have slightly different magnetic g factors. The minimal value for the difference, $\Delta g = 3 \times 10^{-6}$, is attained at the electric field $\mathcal{E} = 7$ V/cm. The smaller Δg, the smaller the systematics $\sim 3\mu_B \Delta g\tilde{B}$ coming from a spurious magnetic field $\tilde{B}$.

In summary, we have considered the g factors of the HfF$^+$ $^3\Delta_1$ state, including dependence on Ω doublets and external electric field, and have found the value of the field which will minimize magnetic systematic errors. Systematic effects related to magnetic field imperfections can manifest themselves as a false EDM. Provided no systematic corrections are applied, the magnetic field control at the level of μG would lead to systematic error $\delta d_e = \frac{3\mu_B\Delta g}{2\mathcal{E}_{eff}}1\mu G \approx 10^{-30}e$ cm. Additionally, the calculated Δg is a good source of data to test

an eEDM measurement procedure [22]. At the same time, the calculated values of $G_{||}$ and $D_{||}$ parameters for the $^3\Delta_1$ electronic state are found to be in excellent agreement with the experimental data. The latter is also essential for probing the accuracy of the electronic wave function for the considered state that is used to calculate other parameters (effective electric field, etc.) as well; these parameters cannot be measured but are required to extract the fundamental value of the electron electric dipole moment [20]. Of course, it is not a strict test of the effective electric field [40,42], but the more calculated parameters are compared with experiment the better.

Note added. Recently, we became aware of a paper [43] which also addresses the sign error of the Cornell and Ye group.

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