Evaluation of CP-violation in HfF$^+$

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CP violation effects produced by the nuclear magnetic quadrupole moment (MQM), electron electric dipole moment (eEDM), and scalar–pseudoscalar nucleus–electron neutral current (SP) interaction have been calculated. The role of the hyperfine interaction is investigated. It is shown that the MQM shift can be distinguished from the electron EDM and SP ones due to the explicit dependence of MQM shift on the hyperfine level. The MQM effect is expressed in terms of the proton (EDM), QCD vacuum angle $\theta$ and quark chromo-EDMs.

I. T,P-ODD INTERACTIONS HAMILTONIAN

Hafnium isotopes $^{177}$Hf and $^{179}$Hf have nuclear spin $I^1 = 7/2$ and $I^1 = 9/2$, respectively. Fluorine isotope $^{19}$F has nuclear spin $I^2 = 1/2$. For the purposes of this work it is convenient to use the coupling scheme

$$F_1 = J + I^1,$$

$$F = F_1 + I^2,$$

where $J$ is the total molecular less nuclear spins angular momentum. The field-free energy levels of the ground rotational state with the quantum number $J = 1$ splits by the hyperfine interaction with the hafnium nucleus into three groups which are characterized by $F_1 = 9/2$, $F_1 = 7/2$, $F_1 = 5/2$ for $^{177}$Hf and $F_1 = 11/2$, $F_1 = 9/2$, $F_1 = 7/2$ for $^{179}$Hf quantum numbers. The hyperfine interaction with the fluorine nucleus further splits levels with total momentum $F = F_1 \pm 1/2$. Note that $F_1$ is not exact but a good quantum number since the hyperfine interaction with the fluorine nucleus is much weaker than the hyperfine interaction with the hafnium nucleus. Finally each hyperfine level has two parity eigenstates known as the $\Omega$-doublet. These states are equal mixture of the $\Omega = \pm 1$ states, where $\Omega$ is the projection of $J$ on the internuclear $\hat{n}$ axis.

An external electric field mixes $\Omega$-doublet states of opposite parity and transforms the $\Omega$-doublet structure of each hyperfine level to the Stark doublet structure. For a sufficiently large electric field, $\Omega$ becomes a good quantum number, except $m_F = 0$ levels which are not mixed by the electric field. Here $m_F$ is the projection of $J$ on the laboratory $\hat{z}$ axis which coincides with the direction for the electric field. The state $J = 1$ in the $^{19}$Hf$^+$ molecule with the spinless hafnium isotope becomes almost fully polarized by the electric field $E > 4 \text{ V/cm}$. The molecules $^{177}$Hf$^{19}$F$^+$ and $^{179}$Hf$^{19}$F$^+$ require much larger field to be polarized (see below).

The T,P-odd electromagnetic interaction of the nuclear magnetic quadrupole moment with electrons is described...
by the Hamiltonian

$$H_{\text{MQM}} = -\frac{M}{2I(2I-1)}T_{ik} \frac{3}{2\pi} \epsilon_{ijkl} \alpha_j r_i r_k,$$

(3)

where $\epsilon_{ijkl}$ is the unit antisymmetric tensor, $\alpha$ is the vector of Dirac matrices, $r$ is the displacement of the electron from the Hf nucleus, $M$ is the Hf nuclear MQM,

$$M_{i,k} = \frac{3M}{2I(2I-1)}T_{i,k},$$

(4)

$$T_{i,k} = I_i^k I_i^k + I_i^k I_i^k - \frac{2}{3} \delta_{i,k} I_i^k (I_i^k + 1).$$

(5)

The $e$EDM interaction is described by the Hamiltonian

$$H_d = 2d_e \begin{pmatrix} 0 & 0 \\ 0 & \sigma E \end{pmatrix},$$

(6)

$E$ is the inner molecular electric field, and $\sigma$ are the Pauli matrices.

The T,P-odd SP interaction with a characteristic dimensionless constant $k_{SP}$ is described by the Hamiltonian

$$H_{SP} = i \frac{G_F}{\sqrt{2}} Z_k s_{SP} \gamma_0 \gamma_5 n(r),$$

(7)

where $G_F$ is the Fermi-coupling constant, $\gamma_0$ and $\gamma_5$ are the Dirac matrices and $n(r)$ is the nuclear density normalized to unity. For simplicity the summation over different electrons is omitted in Eqs. (3), (6) and (7).

For the field-free eigenstates the expectation value for $H_{\text{MQM}}$, $H_{\text{d}}$ and $H_{\text{SP}}$ is zero. For the completely polarized molecule and neglecting the interaction between different rotational, $J$, and hyperfine, $F_1$, levels the energy shift due to the SP, $e$EDMand MQM interactions are

$$\delta_d = d_e E_{\text{eff}} \Omega,$$

(8)

$$\delta_{SP} = k_{SP} W_{SP} \Omega,$$

(9)

$$\delta_{M}(J,F_1) = (-1)^J + F C(J,F_1) M W_{M} \Omega,$$

(10)

$$C(J,F_1) = \frac{(2J+1)}{2} \begin{pmatrix} J & 0 & 2 J & 0 \\ -J & \Omega & 0 & \Omega \\ I_1 & -2 I_1 & I_1 & -2 I_1 \end{pmatrix},$$

(11)

where (...) means the elements with the 3j-symbols and \{\} with the 6j-symbols, $E_{\text{eff}} = \langle \Psi_{\Delta i} | \sum_i H_d(i) \frac{d_e}{r} | \Psi_{\Delta i} \rangle,$

$$W_{SP} = \langle \Psi_{\Delta i} | \sum_i H_{SP}(i) \frac{k_{SP}}{\sigma} | \Psi_{\Delta i} \rangle,$$

(12)

(13)

$$W_M = \frac{3}{2} \frac{1}{\Omega} \langle \Psi_{\Delta i} \sum_i \left( \frac{\alpha_i \times r_i}{r_i^3} \right) \frac{r_i}{\zeta} | \Psi_{\Delta i} \rangle,$$

(14)

where $\Psi$ is the electronic wave function of the considered $H^2\Delta_1$ state of the HfF$^+$ cation.

Two sublevels within a Stark doublet are connected by the time reversal $m_F \rightarrow -m_F$, $\Omega \rightarrow -\Omega$ and therefore have opposite signs for both $m_F$ and $\Omega$ quantum numbers and are degenerate unless the T,P-odd interactions are not taken into account. One can see from Eqs. (3), (6) and (7) that the states with the opposite projections of $\Omega$ have the opposite MQM, $e$EDM, SP interaction energy shifts which give rise to a splitting between the Stark doublet sublevels to be measured in the experiment. The MQM shift can be distinguished from the other two ones by its dependence on $F_1$ quantum number. For given $F_1$ the energy shifts are independent of the $F$ and $m_F$ quantum numbers provided the approximations assumed above. The exception is for $m_F = 0$ levels which have zero shifts as they are equal mixture of $\Omega = \pm 1$ states.

In the present work we take into account the interactions with the external electric field, magnetic dipole and electric quadrupole hyperfine interactions which mix different rotational ($J$) and hyperfine ($F_1$) levels and modify the values of the shifts given by Eqs. (3), (6), (7).

II. EVALUATION OF T,P-ODD SHIFTS

The MQM, $e$EDM, SP interaction energy shifts have been calculated as the expectation values of the Hamiltonians (3), (6) and (7) with the wavefunctions of the $^{177}$Hf$^{19}$F$^+$ and $^{179}$Hf$^{19}$F$^+$ molecules. Following Refs. (12, 13), the energy levels and wave functions of the $^{190}$Hf$^{19}$F$^+$ ion are obtained by the numerical diagonalization of the molecular Hamiltonian ($\hat{H}_{\text{mol}}$) on the basis set of the electronic-rotational wavefunctions

$$\Psi_{\Omega \Gamma} \theta_{M,\Omega}^\Gamma(\alpha,\beta) U_{M,\Gamma}^{Hf} U_{F,\Gamma}^{F},$$

(15)

Here $\Psi_{\Omega}$ is the electronic wavefunction, $\theta_{M,\Omega}^\Gamma(\alpha,\beta) = \sqrt{(2J+1)/4\pi D_{M,\Omega}^{\Gamma}(\alpha,\beta,\gamma = 0)}$ is the rotational wavefunction, $\alpha, \beta, \gamma$ are the Euler angles, $U_{M,\Gamma}^{Hf}$ and $U_{F,\Gamma}^{F}$ are the Hf and F nuclear spin wavefunctions and $M$ ($\Omega$) is the projection of the molecule angular momentum, $\mathbf{J}$, on the laboratory $\hat{z}$ (internuclear $\hat{n}$) axis, $M^{1,2}$ are the projections of the nuclear angular momentums on the same axis. We write the molecular Hamiltonian for the $^{190}$Hf$^{19}$F$^+$ molecule in the form:

$$\hat{H}_{\text{mol}} = \hat{H}_{el} + \hat{H}_{\text{rot}} + \hat{H}_{\text{hfs}} + \hat{H}_{\text{ext}}.$$
is the hyperfine interaction between electrons and a nucleus, \( g_F \) and \( g_{HH} \) are 19^F and 177,179Hf nuclear g-factors, \( \mu_N \) is the nuclear magneton, \( \mathbf{r}_{1i} \) and \( \mathbf{r}_{2i} \) are radius-vector for the \( i \)-th electron in the coordinate system centered on the Hf(F) nucleus, \( \hat{Q}_q^S(1^I) \) is the quadrupole moment operator for the 177,179Hf nuclei. Note, that the subscript 1 is omitted in \( r_1 \) in the section III for simplicity. The hyperfine structure of the 3\( \Delta_1 \) state only was taken into account in the present study. Provided that the electronic matrix elements are known, the matrix elements of \( \hat{H}_{HH} \) between the states in the basis set \( |15\rangle \) can be calculated with the help of the angular momentum algebra \( |11\rangle \). The required electronic matrix elements are

\[
A^F = g_F \langle \Psi_{3\Delta_1} | \sum_i \left( \frac{\alpha_i \times \mathbf{r}_{2i}}{r_{2i}^3} \right) | \Psi_{3\Delta_1} \rangle, 
\]

(20)

\[
A^H = g_{HH} \langle \Psi_{3\Delta_1} | \sum_i \left( \frac{\alpha_i \times \mathbf{r}_{1i}}{r_{1i}^3} \right) | \Psi_{3\Delta_1} \rangle, 
\]

(21)

\[
eQ_{q_0} = 2eQ \langle \Psi_{3\Delta_1} | \sum_i \sqrt{\frac{2\pi}{5}} \frac{Y_{20}(\theta_{1i}, \phi_{1i})}{r_{1i}^3} | \Psi_{3\Delta_1} \rangle, 
\]

(22)

\[
eQ_{q_2} = 2\sqrt{6}eQ \langle \Psi_{3\Delta_1} | \sum_i \sqrt{\frac{2\pi}{5}} \frac{Y_{22}(\theta_{1i}, \phi_{1i})}{r_{1i}^3} | \Psi_{3\Delta_{-1}} \rangle, 
\]

(23)

where \( Q = 2\langle U^H_{11,11}|\hat{Q}_q^S(1^I)|U^H_{11,11} \rangle \) is the quadrupole moment for the 177,179Hf nuclei. The 177Hf and 179Hf isotopes have \( I^1 = 7/2, g_{HH} = 0.2267, Q = 3.365 \) b and \( I^1 = 9/2, g_{HH} = -0.1424, Q = 3.793 \) b, respectively.

The magnetic dipole hyperfine structure constants \( A^F = -620.0 \) MHz was measured in Ref. [1]. The magnetic dipole hyperfine structure constants \( A^H = 898 \) MHz for 177Hf^{19}F^+ and 179Hf^{19}F^+, respectively, were calculated in Ref. [15]. The electric quadrupole hyperfine structure constants \( eQ_{q_0} = -2100 \) MHz, \( eQ_{q_2} = 110 \) MHz and \( eQ_{q_0} = -2400 \) MHz, \( eQ_{q_2} = 125 \) MHz for 177Hf^{19}F^+ and 179Hf^{19}F^+, respectively, were calculated in the present work. The ratios for the magnetic dipole and electric quadrupole hyperfine structure constants correspond to the ratios for the nuclear g-factors and the quadrupole moments of the 177Hf and 179Hf nuclei.

III. EVALUATION OF \( eQ_{q_0} \) AND \( eQ_{q_2} \) CONSTANTS

To compute \( eQ_{q_0} \) in the 3\( \Delta_1 \) state of HfF\(^+\) we have performed relativistic coupled cluster calculations within the Dirac-Coulomb Hamiltonian using the DIRAC12 code [19]. In all the calculations the Hf–F internuclear distance in the 3\( \Delta_1 \) state was set to 3.41 Bohr [3]. In the main calculation all 80 electrons of HfF\(^+\) were included in the correlation treatment within the coupled cluster calculations with single, double and perturbative triple amplitudes, CCSD(T) using the uncontracted Dyall’s CVTZ basis set for Hf [17] and the aug-ccpVTZ basis set [19, 20] for F. We have also applied the correction on the basis set expansion up to the uncontracted Dyall’s AEQZ basis set for Hf [17] and the aug-ccpVQZ [19, 21] for F. In the calculation 1s–3d core electrons of Hf were excluded from the correlation treatment within the CCSD(T) method. Accounting of the perturbative triple cluster amplitudes contributes \( \approx 88 \) MHz in \( eQ_{q_0}(177\text{HfF}^+) \). The contribution of the higher cluster amplitudes were estimated within the two-step approach [7, 21, 25] similar to Refs. [6, 26, 29] and found to be negligible in the present case.

As it follows from Eq. (23), \( eQ_{q_2} \) has no non-zero matrix elements within a main nonrelativistic term 3\( \Delta_1 \). The main contribution to \( eQ_{q_2} \) is due to the spin-orbit admixture of II state with the leading configuration \( |55d_{5d}\rangle \) composed of 5s, 5d atomic orbitals of Hf. Then one can obtain

\[
eQ_{q_2} = 483wQ \langle 1/r^3 \rangle_{5d} \text{MHz},
\]

(24)

where \( w \) is the weight of the admixture of the II state, \( Q \) is the quadrupole moment of 177,179Hf in Barns, \( \langle 1/r^3 \rangle_{5d} \) = 4.86 a.u. as obtained from the Hartree-Fock-Dirac calculations of Hf\(^+\). The value for the \( w \) can be estimated from the sensitive to it of the body fixed g-factor

\[
G_\parallel = \frac{1}{\Omega}(3\Delta_1 | \hat{L}_n \times \hat{S}_n | 3\Delta_1) \approx (25)
\]

\[
2 - 2.002319 + w,
\]

where \( g_S = -2.002319 \) is the free-electron g-factor. The same approximation as for Eq. (23) was used in Eq. (25). Then using the experimental value \( G_\parallel = 0.011768 \) [14, 30] one obtains \( w = 0.014, eQ_{q_2} = 110 \) MHz and \( eQ_{q_2} = 125 \) MHz for 177Hf^{19}F\(^+\) and 179Hf^{19}F\(^+\), respectively.

IV. RESULTS AND DISCUSSIONS

In Figs. (1–3) results for MQM shifts as functions of \( A^H \), \( eQ_{q_0} \) and \( eQ_{q_2} \) are given for 177Hf^{19}F\(^+\). One can see that MQM shift strongly depends on \( eQ_{q_2} \) and decreases as \( eQ_{q_2} \) increases. Similar dependencies are for the SP and eEDM shifts. The reason is that the electric quadrupole hyperfine interaction causes the sublevels \( \Omega = +1 \) and \( \Omega = -1 \), which have different signs.
FIG. 1. (Color online) Calculated MQM energy shifts (in units $MW_M$) for the $J = 1, H^2\Delta_1^{177}$Hf$^{19}$F$^+$ as functions of $A^H_f$. Bold solid (red), bold dashed (green), bold dotted (blue) lines correspond to $F_1 = 9/2$, $F_1 = 7/2$, $F_1 = 5/2$, respectively. Horizontal thin solid (red), thin dashed (green), thin dotted (blue) correspond to values obtained by Eq. (10). Vertical black lines correspond to values $A^H_f = 0$ and $A^H_f = -1429$ MHz obtained in calculation. $E = 20$ V/cm, $eQq_0 = 0$ and $eQq_2 = 0$ in calculations.

for T,P-odd shifts, to mix. The coupling of the states with the different signs of $\Omega$ is proportional to $eQq_2$ as it follows from Eq. (23). The least dependence is observed for the $eQq_0$ constant. Hamiltonians (6) and (7) do not mix different rotational levels and therefore are almost independent of the $A^H_f$ and $eQq_0$ constants. In Table I the calculated T,P-odd shifts accounting for the hyperfine and Stark interactions between different rotational levels compared with the ones obtained from Eqs. (3)-(10) are given. The values are quite different and the former demonstrate a large dependence on the electric field.

For the completely polarized Hf$^+$ the eEDM and SP interaction energy shifts approach $d_eE_{\text{eh}}^n$ and $k_{\text{SP}}W_{\text{SP}}$ values, respectively, which are independent of the $F_1$ quantum number. As evident from Table II the MQM shifts depend on $F_1$. This fact has to be used to distinguish MQM from the scalar T,P-odd effects. Eq. (10) gives approximately a factor of three difference between the largest and the smallest shifts for both $^{177}$Hf$^{19}$F$^+$ and $^{179}$Hf$^{19}$F$^+$ ions. One can see from Table III that more accurate numerical calculations give approximately factors two and four for $^{177}$Hf$^{19}$F$^+$ and $^{179}$Hf$^{19}$F$^+$, respectively. MQM can be expressed in terms of the proton and neutron EDms $d_p$ and $d_n$, QCD vacuum angle $\theta$, chromo-EDMs $d_p$ and $d_n$. Using these data [2], the calculated value $W_M = 0.494\times10^{-33}\text{Hz}/e\text{cm}$ [26], and data from Table I one obtains that current limits $|d_p| < 2.0\times10^{-25}e\text{cm}$, $|\theta| < 1.5\times10^{-10}$, $|d_p - d_n| < 5.7\times10^{-27}e\text{cm}$ correspond to energy shifts less than $6\mu$Hz, $8\mu$Hz, $18\mu$Hz for $^{177}$Hf$^{19}$F$^+$ and less than $3\mu$Hz, $5\mu$Hz, $11\mu$Hz for $^{179}$Hf$^{19}$F$^+$, respectively.

V. CONCLUSION

We have calculated the T,P-odd energy shifts produced by the MQM, eEDM, and SP interactions for the ground rotational $J = 1$ hyperfine levels of the $^3\Delta_1$ electronic state of the $^{177}$Hf$^{19}$F$^+$ and $^{179}$Hf$^{19}$F$^+$ ions. It is found that taking into account the hyperfine interaction is critically important for the accurate evaluation of the effects. The MQM shifts depend on a hyperfine sublevel of the $J = 1$ rotational state. We found that there is factor of two and four difference between the largest and the smallest shifts for $^{177}$Hf$^{19}$F$^+$ and $^{179}$Hf$^{19}$F$^+$, respectively. The experiment on $^{177}$Hf$^{19}$F$^+$ and $^{179}$Hf$^{19}$F$^+$, similarly to the one on $^{180}$Hf$^{19}$F$^+$ [24], can be performed using rotating electric and magnetic fields which trap the cation. We have shown that $^{177}$Hf$^{19}$F$^+$ and $^{179}$Hf$^{19}$F$^+$ require much larger than $^{180}$Hf$^{19}$F$^+$ electric field to be polarized. However, our calculations have shown that the $F_1 = 9/2, 5/2$ and $F_1 = 11/2, 7/2$ states of $^{177}$Hf$^{19}$F$^+$ and $^{179}$Hf$^{19}$F$^+$ respectively, for the electric filed $\sim 20$ V/cm used in the experiment [11], are almost completely polarized.

VI. ACKNOWLEDGEMENT

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FIG. 2. (Color online) Calculated MQM energy shifts (in units \(MW_M\)) for the \(J = 1\), \(H^3\Delta_t \textsuperscript{177} \text{HI}^{20}\text{F}^+\) as functions of \(eQq_0\). Bold solid (red), bold dashed (green), bold dotted (blue) lines correspond to \(\Delta t = 9/2\), \(\Delta t = 7/2\), \(\Delta t = 5/2\), respectively. Vertical black lines correspond to the values \(eQq_0 = 0\) and \(eQq_0 = -2100\) MHz obtained in the calculation. \(E = 20\) V/cm, \(A^{\parallel}_{||} = -1429\) MHz and \(eQq_0 = 0\) in the calculations.

FIG. 3. (Color online) Calculated MQM energy shifts (in units \(MW_M\)) for the \(J = 1\), \(H^3\Delta_t \textsuperscript{177} \text{HI}^{20}\text{F}^+\) as functions of \(eQq_2\). Bold solid (red), bold dashed (green), bold dotted (blue) lines correspond to \(\Delta t = 9/2\), \(\Delta t = 7/2\), \(\Delta t = 5/2\), respectively. \(E = 4, 20, 100\) V/cm, \(A^{\parallel}_{||} = -1429\) MHz and \(eQq_0 = -2100\) MHz in calculations.

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TABLE I. $\delta_M$, $\delta_d$ and $\delta_{SP}$ shifts (in units $MW_M$, $d_eE_e^{\text{eff}}$ and $k_{SP}W_{SP}$, respectively) for the $J = 1$, $H^2\Delta_1$. Numerical calculations take into account interaction between different rotational levels.

| $F_1$ | Electric field(V/cm) | Eq. (10) | $\delta_M$ | $\delta_d$($\delta_{SP}$) |
|-------|----------------------|----------|-------------|------------------------|
|       |                      | numerical calculation | numerical calculation  |
| 9/2   | 4                    | 0.05000  | 0.07879     | 0.90804                |
|       | 20                   | 0.08651  |             | 0.99577                |
|       | 100                  | 0.08742  |             | 0.99933                |
| 7/2   | 4                    | 0.14286  | 0.02278     | 0.14581                |
|       | 20                   | 0.09268  |             | 0.59325                |
|       | 100                  | 0.15050  |             | 0.96511                |
| 5/2   | 4                    | 0.10714  | 0.02864     | 0.36015                |
|       | 20                   | 0.07048  |             | 0.88791                |
|       | 100                  | 0.07789  |             | 0.99466                |
| 11/2  | 4                    | 0.05000  | 0.02165     | 0.72080                |
|       | 20                   | 0.02961  |             | 0.98200                |
|       | 100                  | 0.03074  |             | 0.99926                |
| 9/2   | 4                    | 0.13333  | 0.00446     | 0.03696                |
|       | 20                   | 0.02195  |             | 0.18187                |
|       | 100                  | 0.08213  |             | 0.67962                |
| 7/2   | 4                    | 0.09167  | 0.06467     | 0.53716                |
|       | 20                   | 0.11499  |             | 0.95405                |
|       | 100                  | 0.12101  |             | 0.99603                |

a $\delta_d$ and $\delta_{SP}$ are equal.

b Values obtained using Eq. (10) are independent of the values of the electric field.

c If the hyperfine interaction with the hafnium nucleus is not taken into account (or we consider $^{180}$Hf$^{19}$F$^+$ ion where it is identically zero) then the $\delta_d$ and $\delta_{SP}$ shifts are equal to unity for the fields used in the table.