

## Marked Influence of the Nature of the Chemical Bond on $CP$ -Violating Signature in Molecular Ions $\text{HBr}^+$ and $\text{HI}^+$

Boris Ravaine, Sergey G. Porsev,\* and Andrei Derevianko<sup>†</sup>

*Department of Physics, University of Nevada, Reno, Nevada 89557, USA*

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Heavy polar molecules offer a great sensitivity to the electron electric dipole moment (EDM). To guide emerging searches for EDMs with molecular ions, we estimate the EDM-induced energy corrections for hydrogen halide ions  $\text{HBr}^+$  and  $\text{HI}^+$  in their respective ground  $X^2\Pi_{3/2}$  states. We find that the energy corrections due to EDM for the two ions differ by an unexpectedly large factor of 15. We demonstrate that a major part of this enhancement is due to a dissimilarity in the nature of the chemical bond for the two ions: the bond that is nearly of ionic character in  $\text{HBr}^+$  exhibits predominantly a covalent nature in  $\text{HI}^+$ . We conclude that because of this enhancement the  $\text{HI}^+$  ion may be a potentially competitive candidate for the EDM search.

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A nonvanishing permanent electric dipole moment (EDM) of a particle simultaneously violates two discrete symmetries: parity ( $P$ ) and time reversal ( $T$ ). By virtue of the  $CPT$  theorem, the  $T$  violation would imply  $CP$  violation [1]. Searches for EDMs of atoms and molecules [2] provide important constraints on competing extensions to the standard model of elementary particles. For example, the most stringent limits on electron EDM come from a tabletop experiment with atomic Tl [3]. As with atoms, the internal energy states of heavy polar molecules can show evidence of EDMs of the constituents. Compared to atomic experiments, where application of a strong external  $E$  field is required to enhance sensitivity, the experiments with polar molecules rather rely on the inner electric molecular field  $\mathcal{E}_{\text{int}}$  exerted upon the heavier atom. This field can be several orders of magnitude larger than the attainable laboratory fields. This notion, first elucidated by Sandars [4], has been exploited in experiments with YbF [5] and TlF [6–8] molecules. We also mention an ongoing experiment with the metastable PbO molecule [9].

A relatively small laboratory field is still required in the EDM experiments to polarize the molecule. Since the  $E$  field would accelerate a charged particle out of an apparatus, EDM experiments are typically carried out using neutrals. It has been recently realized by Stutz and Cornell [10] that this limitation may be overcome with ion traps: electrostatic force exerted upon the ion by the polarizing  $E$  field can average to zero if the polarizing field rotates rapidly in space, with the requisite spectroscopy then being performed in a rotating frame of reference. Moreover, the long coherence times in the trap would improve statistics compared to traditional beam and gas-cell approaches. Because of this improved statistics, molecular ions with a relatively weak sensitivity to electron EDM could provide competitive constraints. In particular, the hydrogen halide ions  $\text{HBr}^+$  and  $\text{HI}^+$  in their lowest rovibrational state of the ground  $X^2\Pi_{3/2}$  term are considered as attractive candidates for the proposed experiment [10].

The goal of this Letter is twofold. First, we provide guidance to emerging EDM searches with molecular ions [10] by computing EDM-induced energy corrections. Second, we elucidate the important role of the chemical bond in enhancement of electron EDM in molecular systems. While both  $\text{HBr}^+$  and  $\text{HI}^+$  ions have a similar electronic structure, the chemical bond in  $\text{HBr}^+$  is of ionic nature, while for heavier  $\text{HI}^+$  it is predominantly covalent [11,12]. We find that this evolution in the character of the chemical bond has a marked effect on the EDM-induced energy corrections. From the experimental point of view, our computed EDM-induced energy correction for  $\text{HBr}^+$  is too small to produce competitive bounds on the electron EDM in experiment [10]. By contrast, the pronounced covalent bond enhancement for the  $\text{HI}^+$  ion, illuminated here, makes it a potentially competitive candidate for the electron EDM search.

*Molecular structure and EDM-induced corrections.*— The molecular structure of low-lying rotational states of hydrogen halide ions  $\text{HBr}^+$  and  $\text{HI}^+$  can be well classified by Hund's case (a). Relativistic effects split the ground  $X^2\Pi$  electronic term into two components:  $^2\Pi_{3/2}$  and  $^2\Pi_{1/2}$ , distinguished by  $\Omega$ , projection of the total electronic angular momentum along the molecular axis.  $^2\Pi_{3/2}$  is the ground electronic term and is considered as a possible candidate for the EDM experiment. In the estimates below we employ the following values of the equilibrium internuclear separations [11,12]:  $R_e \approx 1.448 \text{ \AA}$  for  $\text{HBr}^+$  and  $R_e \approx 1.632 \text{ \AA}$  for  $\text{HI}^+$ . Unless noted otherwise, atomic units,  $\hbar = |e| = m_e \equiv 1$ , are used throughout the Letter.

In Hund's case (a) the molecular eigenfunctions including the nuclear rotation can be described as  $|\Lambda\Sigma\Omega; JM_J\rangle = |JM_J\Omega\rangle|\Lambda\Sigma\Omega\rangle$ , where  $\Lambda$  and  $\Sigma$  are projections of the electronic orbital momentum and spin onto the internuclear axis,  $J$  is the total molecular momentum (including nuclear rotation), and  $M_J$  is the laboratory

frame projection of  $J$ . The rotational part  $|JM_J\Omega\rangle$  may be expressed in terms of the Wigner  $D$  functions. While in the lowest order  $|\Lambda\Sigma\Omega; JM_J\rangle$  and  $|-\Lambda-\Sigma-\Omega; JM_J\rangle$  states have the same energies, at the finer level each rotational state of the  ${}^2\Pi_\Omega$  terms splits into a so-called  $\Lambda$  doublet [13] due to rotational and spin-orbit perturbations. The eigenstates of the field-free molecular Hamiltonian (disregarding EDM) are  $e/f$  parity states, composed of linear combinations of the two above states.

An externally applied electric field  $\mathcal{E}_0$  couples the  $e/f$  parity states. For a sufficiently strong  $E$  field the eigenstates can be classified by a definite value of  $\Omega$ , rather than by the  $e/f$  parity label. In this case the correction to the energy due to electron EDM can be parametrized as [14]  $\delta W(J, M, \Omega) = W_d\Omega$ . It is defined as an expectation value,

$$\begin{aligned} W_d\Omega &= \langle \Lambda\Sigma\Omega; JM_J | H_e | \Lambda\Sigma\Omega; JM_J \rangle \\ &= \langle \Lambda\Sigma\Omega | H_e | \Lambda\Sigma\Omega \rangle. \end{aligned} \quad (1)$$

Here  $H_e = -d_e(\gamma_0 - 1)\Sigma \cdot \mathcal{E}$  is the pseudoscalar coupling [2] of an electron EDM  $d_e$  to an electric field  $\mathcal{E}$  (this internal molecular field is to be distinguished from the externally applied field). The expectation value (1) is accumulated in the region of strong fields, i.e., mainly in the vicinity of the nucleus of the heavier halogen atom. A common approximation is that the electric field is produced by a spherically symmetric charge distribution  $\mathcal{E}(\mathbf{r}) \approx Z/r^2\hat{\mathbf{r}}$ , where  $Z$  is the nuclear charge of the heavier atom, and  $\mathbf{r} = 0$  coincides with its center.

*Chemical bond.*—In the following we make an order-of-magnitude estimate of the EDM factor  $W_d$  using a qualitative model of an isolated atomic particle perturbed by its molecular counterpart. In this regard it is important to discuss the nature of the chemical bond in the hydrogen halide  $HX^+$  ions. It can be described by two limiting cases [12]: ionic ( $H^+ : X$ ) and covalent ( $H \cdots X^+$ ) bonds. In the case of the ionic bond the halogen atom is electrostatically perturbed by a proton. When the bond is covalent, the halogen atom is singly ionized ( ${}^3P$  state), while the hydrogen atom is in its ground state.

Although both  $HBr^+$  and  $HI^+$  ions dissociate to the covalent limit, the chemical bond at intermediate separations can be better characterized from molecular spectra. In particular, the hyperfine structure is of significance to our consideration, because both the EDM coupling and the hyperfine interaction are sensitive to behavior of the molecular orbitals near the nuclei. An analysis of the hyperfine structure in Ref. [11] indicates that the bond for the  $HBr^+$  ion can be adequately described as being of the ionic nature. As to the  $HI^+$  ion, the hyperfine-structure analysis by the same authors [12] shows that the bond is predominantly of the covalent character.

Below we consider both ionic and covalent bonds. Our semiquantitative calculations follow a general scheme similar to those described in Refs. [2,15]. First, we determine the effective molecular electric field  $\mathcal{E}_{\text{int}}$  exerted upon the

heavier halogen atom/ion. Then we use the first-order perturbation theory in the interaction with  $\mathcal{E}_{\text{int}}$  to determine mixing of the atomic states of opposite parity. Finally we compute the expectation value of the EDM-coupling operator using *ab initio* relativistic atomic-structure codes.

*Ionic bond approximation for the  $HBr^+$  ion.*—In the case of the ionic bond the halogen atom is electrostatically perturbed by a proton. In the spirit of the linear combination of atomic orbitals method we expand the electronic wave function in terms of atomic states  $\Phi_i$  of the halogen atom

$$|\Lambda\Sigma\Omega\rangle = \sum_i c_i |\Phi_i\rangle, \quad (2)$$

where the total angular momentum  $J_{e,i}$  of the atomic state  $\Phi_i$  and its projection on the molecular axis  $M_{e,i}$  are constrained to  $J_{e,i} \geq |\Omega|$  and  $M_{e,i} = \Omega$ . We determine the expansion coefficients  $c_i$  using the first-order perturbation theory in the interaction  $V$  due to the electrostatic field exerted upon the halogen atom by the proton

$$|\Lambda\Sigma\Omega\rangle \approx |\Phi_0\rangle + \sum_{i \neq 0} |\Phi_i\rangle \frac{\langle \Phi_i | V | \Phi_0 \rangle}{E_0 - E_i}, \quad (3)$$

where  $\Phi_0$  is the ground atomic state of the proper symmetry and  $E_i$  are the energies of atomic states.

Keeping only the leading dipole term in the multipole expansion of the interaction of atomic electrons of the halogen atom with the proton, the perturbation  $V \approx -\mathbf{D} \cdot \mathcal{E}_{\text{int}}$ ,  $\mathcal{E}_{\text{int}}$  being the electric field of the proton at the position of the atom and  $\mathbf{D}$  the atomic electric dipole operator. It is this strong electric field that produces an enhancement of the electron EDM in molecular ions.

Finally, the EDM-induced energy correction is

$$W_d\Omega = \frac{2}{R_e^2} \sum_{i \neq 0} \frac{\langle \Phi_0 | H_e | \Phi_i \rangle \langle \Phi_i | D_z | \Phi_0 \rangle}{E_0 - E_i}. \quad (4)$$

In the following we use a shorthand notation

$$T = H_e(E_0 - H_a)^{-1}D_z, \quad (5)$$

with  $H_a$  being the atomic Hamiltonian so that

$$W_d\Omega = \frac{2}{R_e^2} \langle \Phi_0 | T | \Phi_0 \rangle. \quad (6)$$

It is worth noting that all the quantities (except for empirical  $R_e$ ) in Eq. (4) are atomic ones and we employ atomic-structure methods to evaluate this sum. First we employ Dirac-Hartree-Fock (DHF) approximation and then the more elaborate configuration-interaction (CI) method. All calculations carried out here are *ab initio* relativistic.

The halogen atoms Br and I are open-shell systems with one hole in the outer  $np_{3/2}$  shell,  $n = 4$  for bromine, and  $n = 5$  for iodine. In the DHF approximation the atomic orbitals  $|i\rangle$  satisfy the eigenvalue equation  $h_{\text{DHF}}|i\rangle = \varepsilon_i|i\rangle$ , where the Dirac Hamiltonian  $h_{\text{DHF}}$  includes an interaction with the field of the nucleus and the self-consistent field of

the electrons. In the DHF approximation we obtain

$$W_d\Omega = \frac{2}{R_e^2} \sum_i \frac{\langle g|h_e|i\rangle\langle i|d_z|g\rangle}{\varepsilon_i - \varepsilon_g}, \quad (7)$$

where  $g$  denotes the  $np_{3/2}$  hole state and the summation over  $i$  extends over a complete set of orbitals, including both core and virtual orbitals.

Numerically we carried out the summation using the  $B$ -spline pseudospectrum technique [16]. The pseudospectrum was generated using the DHF potential of the ground  $^2P_{3/2}$  atomic state. In a typical calculation we used a set of basis functions expanded over 100  $B$ -splines, which provided numerical accuracy sufficient for the goals of this Letter. Among other technical details it is worth mentioning that, while integrating the radial Dirac equation, we used the potential produced by a nucleus of the finite size.

To investigate a potentially large correlation effect beyond the DHF approximation, we have also carried out CI calculations for Br within the active space of seven  $4s^24p^5$  valence electrons. In this method, the many-electron wave functions were obtained as linear combinations of determinants composed from single and double excitations of the valence electrons from the active space. Finally, following the Dalgarno-Lewis-Sternheimer method [17], we carried out the summation over intermediate states in Eq. (12) by solving the inhomogeneous many-body Dirac equation inherent to the method and computed the sum (4). More details will be provided elsewhere.

The resulting DHF value of the EDM-induced energy correction (hole in the  $4p_{3/2}$  shell)

$$W_d\Omega[\text{HBr}^+, \text{ionic, DHF, } X^2\Pi_{3/2}] = -1.5 \times 10^{-2}d_e. \quad (8)$$

A similar DHF calculation assuming a hole in the  $4p_{1/2}$  shell leads to a 100-fold increase in the value of the EDM correction,

$$W_d\Omega[\text{HBr}^+, \text{ionic, DHF, } X^2\Pi_{1/2}] = 1.6d_e. \quad (9)$$

A large difference in the values of the  $W_d\Omega$  parameter for the two cases can be explained as follows. The EDM-coupling operator  $H_e$  is a pseudoscalar: it does not change the total angular momentum of a state, but flips its parity. For example, if the hole state  $g$  has  $p_{3/2}$  angular character, then the intermediate states in Eq. (7) are  $d_{3/2}$  orbitals. Similarly, the  $p_{1/2}$  hole state requires  $s_{1/2}$  intermediate states. It is well known [2] that since the states of lower orbital momentum have a larger probability to be found close to the nucleus, this selection rule has a profound effect on the order of magnitude of the EDM factor  $W_d$ .

One may argue that an enhancement of the EDM factor for the  $X^2\Pi_{3/2}$  state may arise due to particle-hole excitations, when the  $s_{1/2}$  ( $p_{1/2}$ ) electron is excited from the core to the  $p_{1/2}$  ( $s_{1/2}$ ) orbital. It is easy to demonstrate in the DHF approximation that, while the individual contri-

butions from such excitations are certainly large, their sum vanishes. It is the reason why the closed-shell systems are largely insensitive to the electron EDM [2], i.e., the EDM-induced energy correction arises only due to an unpaired electron. Correlations (many-body effects beyond DHF) may potentially spoil the presented argument and we have carried out the correlated CI calculations. The result,

$$W_d\Omega[\text{HBr}^+, \text{ionic, CI, } X^2\Pi_{3/2}] = -2.6 \times 10^{-2}d_e, \quad (10)$$

is of the same order as the DHF value.

As a reference, here we also present the DHF value for the  $\text{HI}^+$  ion in the ionic bond approximation,

$$W_d\Omega[\text{HI}^+, \text{ionic, DHF, } X^2\Pi_{3/2}] = -7.0 \times 10^{-2}d_e. \quad (11)$$

*Covalent bond approximation for  $\text{HI}^+$ .*—From the preceding discussion it is clear that a participation of the unpaired  $p_{1/2}$  or  $s_{1/2}$  orbital in the ground-state configuration of the heavier molecular constituent is important for gaining a large  $W_d$  parameter. Qualitatively we can hope that such an enhancement for the  $X^2\Pi_{3/2}$  component may arise when the chemical bond acquires a covalent character (case of the  $\text{HI}^+$  ion). Indeed, in the covalent bond approximation, the halogen atom becomes singly ionized, its ground state being  $^3P$ . The ground state has two  $p$  holes in the outer shell, so that the corresponding relativistic many-body states are composed from the linear combination of  $p_{1/2}^{-1}p_{1/2}^{-1}$ ,  $p_{3/2}^{-1}p_{1/2}^{-1}$ , and  $p_{3/2}^{-1}p_{3/2}^{-1}$  single-electron configurations (the superscript  $-1$  designates a hole state). Therefore the unpaired  $j = 1/2$  orbital becomes involved in the calculations, and, indeed, as shown below, this leads to a significantly larger EDM-induced energy correction for the  $X^2\Pi_{3/2}$  term.

The  $\text{HI}^+$  ion may be pictured as the iodine ion  $\text{I}^+$  in the  $^3P$  state perturbed by the neutral hydrogen atom in its ground state. First let us derive the internal electric field  $\mathcal{E}_{\text{int}}$  and the associated mixing of opposite parity states of the iodine ion. Qualitatively, the field of  $\text{I}^+$  induces a dipole moment of the hydrogen atom  $|D_{\text{H}}| = \alpha_0/R_e^2$ , where  $\alpha_0 = 9/2$  is the polarizability of the hydrogen ground state. In turn, the induced dipole moment exerts a field at the position of the iodine ion  $\mathcal{E}_{\text{int}} = 2\alpha_0/R_e^5\hat{z}$ . Thus the iodine ion is perturbed by  $V \approx -2\alpha_0 D_z/R_e^5$ , where  $D$  is the atomic dipole moment operator for  $\text{I}^+$ .

Again we limit our consideration to a qualitative estimate and use the first-order perturbation theory in the molecular field, so that the EDM-induced energy correction is

$$W_d\Omega = -\frac{4\alpha_0}{R_e^5} \langle \Phi_0 | T | \Phi_0 \rangle, \quad (12)$$

where the operator  $T$  is given by Eq. (5), except now all the participating operators in that expression are to be understood as being for the iodine ion and  $\Phi_0$  is its properly symmetrized ground state. The above expression differs

from the analogous formula (6) for the ionic bond by a prefactor characterizing the internal molecular field  $\mathcal{E}_{\text{int}}$  acting upon the halogen atom/ion. Compared to the ionic bond, this perturbing field becomes 70% weaker.

In order to carry out the calculations with the relativistic operator  $H_e$ , we express the unperturbed nonrelativistic molecular wave function in terms of the relativistic wave functions of the iodine ion,  $|^3P_J, M_{I^+}\rangle$ , and the hydrogen,  $|1s_{1/2}, M_H\rangle$ ,

$$|^2\Pi_{3/2}\rangle_{\text{covalent}}^{(0)} = \sqrt{\frac{2}{3}}|^3P_2, 2\rangle \left| 1s_{1/2}, -\frac{1}{2} \right\rangle + \sqrt{\frac{1}{6}} \left( |^3P_2, 1\rangle \left| 1s_{1/2}, \frac{1}{2} \right\rangle + |^3P_1, 1\rangle \left| 1s_{1/2}, \frac{1}{2} \right\rangle \right). \quad (13)$$

Since the expectation value of the EDM-coupling operator  $H_e$  is accumulated close to the nucleus of the heavy iodine ion,  $H_e$  is essentially a one-center operator, and a generalization of Eq. (12) for the two-center wave function (14) reads

$$\left( -\frac{4\alpha_0}{R_e^5} \right)^{-1} \langle ^2\Pi_{3/2} | H_e | ^2\Pi_{3/2} \rangle_{\text{covalent}} = \frac{3}{2} \langle ^3P_2, 1 | T | ^3P_2, 1 \rangle + \frac{1}{6} \langle ^3P_1, 1 | T | ^3P_1, 1 \rangle + \frac{1}{6} \langle ^3P_2, 1 | T | ^3P_1, 1 \rangle + \frac{1}{6} \langle ^3P_1, 1 | T | ^3P_2, 1 \rangle. \quad (14)$$

We calculated the values of matrix elements for the iodine ion within the CI approach similar to the one described above for Br. The computed values are  $\langle ^3P_2, 1 | T | ^3P_2, 1 \rangle = 6.4d_e$ ,  $\langle ^3P_1, 1 | T | ^3P_1, 1 \rangle = -13.4d_e$ ,  $\langle ^3P_1, 1 | T | ^3P_2, 1 \rangle = -11.2d_e$ , and  $\langle ^3P_2, 1 | T | ^3P_1, 1 \rangle = 2.5d_e$ . Finally,

$$W_d \Omega[\text{HI}^+, \text{covalent}, \text{CI}, X^2\Pi_{3/2}] = -0.4d_e. \quad (15)$$

We notice a sizable enhancement compared to the value of  $-7 \times 10^{-2}d_e$  obtained in the ionic bond approximation.

**Conclusions.**—First of all, the EDM-induced energy correction for the  $X^2\Pi_{3/2}$  state of  $\text{HI}^+$  is about 15 times larger than for  $\text{HBr}^+$ . A lesser part of this enhancement comes from the well-known  $Z^3$  scaling of  $CP$ -violating matrix elements [2], when bromine ( $Z = 35$ ) is replaced by the heavier iodine ( $Z = 53$ ). A more substantial factor, illuminated in this work, is the evolution in the nature of the chemical bond. To reiterate, the  $CP$ -violating matrix elements are much larger for the  $p_{1/2}$  states than for  $p_{3/2}$ , due to the fact that the values of the relevant matrix elements are accumulated close to the nucleus. In the ionic bond case of  $\text{HBr}^+$ , the EDM correction arises from an unpaired  $p_{3/2}$  hole state in the outer shell and  $CP$ -violating effects are suppressed. By contrast, the covalent bond of  $\text{HI}^+$  in addition opens the  $p_{1/2}$  shell, leading to a marked enhancement.

Typical values [14,18] of the EDM-induced energy corrections for heavy *neutral* polar molecules  $\text{PbO}$  and  $\text{YbF}$  are on the order of  $10d_e$  atomic units. Our computed value for  $\text{HI}^+$  is an order of magnitude smaller. Yet, when compared with the conventional beam and gas-cell experiments, the proposed trapping experiment [10] has a better statistical sensitivity so that molecular ions with smaller enhancement parameters, such as  $\text{HI}^+$ , may suffice. By contrast, the EDM correction for  $\text{HBr}^+$  is too small to be of experimental interest. As shown here, it is the covalent bond of  $\text{HI}^+$  that makes this ion a potentially competitive candidate for the emerging searches for EDMs with molecular ions.

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\*Petersburg Nuclear Physics Institute, Gatchina, Leningrad district, 188300, Russia.

†Electronic address: andrei@unr.edu

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