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Nuclear quadrupole moments of bromine and iodine from combined atomic and molecular data

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The multiconfiguration Dirac-Fock (MCDF) and Hartree-Fock (MCHF) models are employed to compute the electric field gradients in the ground states of the bromine and iodine atoms. Combined with experimental electric quadrupole hyperfine interaction constants B, they yield the nuclear quadrupole moments $Q({}^{79}_{35}\mathrm{Br})$ of 313(3) millibarn ($1\ \mathrm{mb}=10^{-31}\ \mathrm{m}^2$), $Q({}^{81}_{35}\mathrm{Br})$ of 261.5(2.5) mb, and $Q({}^{127}_{53}\mathrm{I})$ of $-710(10)$ mb. "Molecular" Q values at Douglas-Kroll coupled cluster singles and doubles with perturbative triples [CCSD(T)] level using data on HBr and HI fully support these "atomic" Q values after a "picture-change" correction is applied. In conjunction with several other recent determinations, these results indicate that the previous standard Q values of 331, 276, and -789 mb for ${}^{79}\mathrm{Br}$, ${}^{81}\mathrm{Br}$, and ${}^{127}\mathrm{I}$, respectively, should be revised. Q values are also reported for ${}^{129}\mathrm{I}$ and for the Mössbauer states of ${}^{127,129}\mathrm{I}$.

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I. INTRODUCTION

The knowledge of nuclear quadrupole moments, Q, is important both in chemical or solid-state spectroscopy and in nuclear physics. Currently one of the best ways to determine them is to combine experimental nuclear quadrupole coupling constants, B, with accurate calculations of the electric field gradient (EFG) at the nucleus.

In the case of halogens, such determinations have recently been carried out for fluorine (${}^{19}_{9}\mathrm{F}$: 197 keV, $I=\frac{5}{2}$ state) using molecular calculations [1] and for chlorine using data for the atomic ground state [2]. Recent calculations [3–6] suggest that the long-time recommended tabular values [7,8] of $Q({}^{79}_{35}\mathrm{Br})$ of 331(4) mb ($1\ \mathrm{mb}=10^{-31}\ \mathrm{m}^2$) and $Q({}^{127}_{53}\mathrm{I})$ of $-789(4)$ mb should be adjusted downwards. Haas and Petrilli [5] reanalyzed the spectroscopic atomic data and obtained Q values of 308.3 mb and -711.3 mb for $Q({}^{79}_{35}\mathrm{Br})$ and $Q({}^{127}_{53}\mathrm{I})$, respectively. They based the new Q values on $\langle r^{-3}\rangle$ integrals, estimated from the experimental magnetic dipole hyperfine coupling constants, A, and combined them with measured B values. In the present work, we use the best atomic *ab initio* methods currently available to calculate the EFG, which in combination with accurate nuclear quadrupole coupling constants yield Q values worthy of future compilations. Recent examples of this multiconfiguration Dirac-Fock (MCDF) approach are the determinations of $Q({}^{90}_{39}\mathrm{Y})$ [9], $Q({}^{49}_{22}\mathrm{Ti})$ [10], and $Q({}^{131}_{55}\mathrm{Xe})$ [11]. The present multiconfiguration Hartree-Fock (MCHF) approach has previously been used for the determination of, e.g., $Q({}^{27}_{13}\mathrm{Al})$ [12], $Q({}^{69}_{31}\mathrm{Ga})$ [13], and $Q({}^{14}_{7}\mathrm{N})$ [14]. The experimental B values for the ${}^{79}_{35}\mathrm{Br}$ and ${}^{127}_{53}\mathrm{I}$ ground states were measured by Jaccarino *et al.* [15,16] with very high accuracy already in 1954. The accuracy of the final Q values depends entirely on the accuracy of present-day EFG calculations.

As a further alternative source of $Q(\mathrm{Br})$ and $Q(\mathrm{I})$, we use the available quadrupole coupling constants for HBr and HI. The determination of the nuclear quadrupole moments from molecular microwave data has a long record of success [8,17] and is known to yield highly accurate data [12,18,19]. The previous determination of $Q(\mathrm{Br})$ and $Q(\mathrm{I})$ from molecular data for HBr and HI was based on spin-averaged relativistic calculations of the electric field gradient at the halogen nucleus. However, these calculations did not take into account the so-called picture-change contribution which arises upon transformations of the four-component Dirac equation used in the derivation of approximate relativistic models [20,21]. The later investigation of the picture-change effect has shown that in contrast to some other properties [20], its contribution may considerably affect the calculated electric field gradients at heavy nuclei [22]. A similar conclusion follows from the more recent study of the electric field gradient at the coinage metal nuclei [23]. Thus, to improve upon the earlier data [4] we have carried out spin-averaged relativistic Douglas-Kroll [24,25] calculations of the electric field gradient at the halogen nuclei in HBr and HI by using a new computational method [26,27], which takes the picture-change effects into account. It will be shown that including the picture-change term of the electric field gradient operator in spin-averaged relativistic calculations for HBr and HI leads to a satisfactory agreement between the $Q(\mathrm{Br})$ and $Q(\mathrm{I})$ data derived from molecular and atomic sources.

Since the ratio of the quadrupole splittings for two isotopes of the same element can be directly measured, the Q value for one isotope will help to determine the Q values for

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other isotopes, or other nuclear states, including Mössbauer states. The Q values for Br and I isotopes are of great importance since a large amount of experimental data exists for nuclear quadrupole coupling constants of bromine and iodine containing molecules [28].

II. THEORY

A. Atoms

The theory [29,30] and the methods of calculation [11,31–39] have been described elsewhere and will not be repeated here. In order to facilitate the discussion of the results, the hyperfine Hamiltonian and its connection to the nuclear quadrupole coupling constants and the nuclear quadrupole moments will be briefly discussed.

The hyperfine contribution to the Hamiltonian can be represented by a multipole expansion

$$H_{\mathrm{hfs}}=\sum_{k\geqslant 1}\mathbf{T}^{(k)}\cdot\mathbf{M}^{(k)}, \tag{2.1}$$

where $\mathbf{T}^{(k)}$ and $\mathbf{M}^{(k)}$ are spherical tensor operators of rank k in the electronic and nuclear spaces, respectively [30]. The $k=1$ term represents the magnetic dipole interaction and the $k=2$ term the electric quadrupole interaction.

The electronic tensor operators can be written as sums of one-particle tensor operators

$$\mathbf{T}^{(k)}=\sum_{j=1}^{N}\mathbf{t}_j^{(k)},\quad k=1,2, \tag{2.2}$$

where, in atomic units,

$$\mathbf{t}^{(1)}=-i\alpha\sum_{j=1}^{N}\boldsymbol{\alpha}_j\cdot\boldsymbol{l}_j\;\mathbf{C}_j^{(1)}r_j^{-2} \tag{2.3}$$

represents the magnetic dipole interaction and

$$\mathbf{t}^{(2)}=-\sum_{j=1}^{N}\mathbf{C}_j^{(2)}r_j^{-3} \tag{2.4}$$

is the quadrupole interaction term. In the formulas above, α is the fine-structure constant, $\boldsymbol{\alpha}$ is the vector of the three Dirac matrices, N is the number of electrons, and $\mathbf{C}^{(k)}$ is a spherical tensor with the components related to the spherical harmonics as

$$C_q^{(k)}=\sqrt{\frac{4\pi}{2k+1}}Y_{kq}. \tag{2.5}$$

The magnetic dipole operator [Eq. (2.3)] represents the magnetic field due to the electrons at the nucleus. The electric quadrupole operator [Eq. (2.4)] represents the electric field gradient at the nucleus. The hyperfine interaction constant B is obtained as

$$B_J=2Q\left[\frac{2J(2J-1)}{(2J+1)(2J+2)(2J+3)}\right]^{1/2}\times\sum_{r,s}c_rc_s\langle\gamma_rJ\|\mathbf{T}^{(2)}\|\gamma_sJ\rangle, \tag{2.6}$$

where Q is the nuclear quadrupole moment, J is the total angular momentum quantum number in the electronic space, c_r are the configuration mixing coefficients obtained in the configuration-interaction calculation, and $\langle\gamma_rJ\|\mathbf{T}^{(2)}\|\gamma_sJ\rangle$ are the reduced matrix elements between the configurations $\{\gamma_rJ\}$ and $\{\gamma_sJ\}$. Calculated electric field gradients, together with experimental values of hyperfine constant B, allow one to extract the nuclear electric quadrupole moment Q using Eq. (2.6), which can be simplified to

$$B(\gamma JM)=q(\gamma JM)(eQ)/h, \tag{2.7}$$

where $q(\gamma JM)$ denotes the electric field gradient and eQ is the electric quadrupole moment of the nucleus. When B is expressed in MHz and q in atomic units, the Q can explicitly be obtained (in mb) as

$$Q=4.255\,957\,9\frac{B(\gamma JM)}{q(\gamma JM)}. \tag{2.8}$$

B. Molecules

The origin of the nuclear quadrupole coupling [40] in molecules containing quadrupolar nuclei is essentially the same as in the case of atoms. In the electrostatic approximation, the asymmetry of the nuclear charge distribution leads to the interaction term of the form [41].

$$H_Q=\frac{1}{8}\sum_{k\geqslant 1}\mathsf{Q}^{(k)}\cdot\mathsf{U}^{(k)}, \tag{2.9}$$

where Q^k and U^k are the irreducible spherical tensors of the 2^k-pole electric moment of the nucleus and the electric field gradient operator of the appropriate order in the position of the nucleus of interest, respectively [42]. For $k=2$, one obtains the interaction between the quadrupole moment of the point nucleus, say X, and the electric field gradient produced by all other charges distributed in the molecule. The first-order interaction energy arising from this perturbation depends on the rotational state of the molecule and can be determined experimentally by fitting the observed transitions. For a linear molecule with the quadrupolar nucleus, the frequency $\nu_Q(X)$, known as the quadrupole coupling constant [40], can be expressed solely in terms of the parallel component of the total electric field gradient $[q_{zz}(X)=q(X)]$ at X:

$$\nu_Q(X)=eQ(X)q(X). \tag{2.10}$$

By inverting this formula, one obtains the quadrupole moment $Q(X)$ of the nucleus X (in mb):

$$Q(X)=\frac{\nu_Q(X)}{0.234\,964\,7q(X)}, \tag{2.11}$$

where $\nu_Q(X)$ is expressed in MHz and $q(X)$ in atomic units of the electric field gradient. The total electric field gradient $q(X)=q_v(X)$ at X in the rotationless vibrational state v can be partitioned into its pure electronic $[q_e^{\mathrm{el}}(X)]$, nuclear $[q_e^n(\mathrm{X})]$, and vibrational $[q_e^v(X)]$ contributions:

$$q_v(X)=q_e^{\mathrm{el}}(X)+q_e^n(X)+q_e^v(X), \tag{2.12}$$

with all entries calculated at the equilibrium bond distance R_e. The evaluation of the electronic contribution proceeds by means of methods of the electronic structure theory. The nuclear contribution follows from the value of R_e. In the case of the vibrational correction, we shall use the approximate formula due to Buckingham [43]:

$$q_e^v(X)\approx q_1(X)\left(v+\frac{1}{2}\right), \tag{2.13}$$

where

$$q_1(X)=\frac{B_e}{\omega_e}\left[3\left(1+\frac{\alpha_e\omega_e}{6B_e^2}\right)\left(\frac{\partial q(X)}{\partial \xi}\right)_{\xi=0}+\left(\frac{\partial^2 q(X)}{\partial \xi^2}\right)_{\xi=0}\right]. \tag{2.14}$$

The symbols ω_e, B_e, and α_e denote the usual spectroscopic constants [44] in cm^{-1} and $\xi=(R-R_e)/R_e$; R denotes the internuclear distance. The evaluation of the vibrational correction (2.14) will be carried out with experimental values of spectroscopic constants for HBr and HI [44] and theoretically computed derivatives of $q(X)$.

III. METHOD OF CALCULATION

A. Atomic MCHF

The MCHF calculations were performed using the atomic finite-element code LUCAS [36]. The approach allows the use of very large configuration interaction (CI) expansions [45,46] in combination with orbital optimization in an essentially complete one-electron basis. The program is based on the restricted active space (RAS) method [45]. The configurations are selected by dividing the orbital space into inactive, active, and secondary (virtual) spaces. The active space is further subdivided into three subspaces called RAS I, RAS II, and RAS III. The RAS I space consists usually of core and deep valence orbitals; the RAS II space consists of valence orbitals and the RAS III space contains orbitals introduced to allow for dynamical correlation and polarization. A *lower* limit is given for the number of electrons in RAS I and an *upper* limit is given for the number of electrons in RAS III. Since there are no explicit restrictions on the number of electrons in RAS II, it becomes a full configuration interaction (FCI) space. The methods used in the MCHF program have been discussed in more detail in Refs. [2,37,38]. In the MCHF calculations, the point-nucleus approximation was employed.

The following notations are used for the RAS calculations: inactive orbitals// RAS I orbitals (minimum number of electrons in RAS I)/RAS II orbitals/ RAS III orbitals (maximum number of electrons in RAS III). The shells to the left of the − sign in the notation are frozen while those to the right are fully optimized in the calculation. The **+** sign in the notation indicates the border line between valence and core-valence optimized shells.

B. Atomic MCDF

In the MCDF method, systematic expansions of configuration state functions with a given parity and symmetry are generated by substitutions from reference (Dirac-Fock) orbitals to a set of correlation orbitals [34,35,47–51]. The set of correlation shells is systematically increased until the convergence of the property is obtained. Since the number of configurations must be kept at a manageable level, restrictions have to be imposed on the allowed substitutions in such a way that the most important electron correlation effects are captured. In first-order perturbation theory, only single substitutions contribute to the hfs energy correction [52,53], implying that they usually comprise the dominant part of the hfs energy. In the hfs calculations it is important that the correlation space is sufficiently saturated with orbitals optimized for single substitutions [50,54]. In the present paper, we adopted a scheme [51,55] in which the correlation orbital space is optimized for single substitutions. However, since the energy contributions from double substitutions dominate the correlation energy, the effects arising from double substitutions were later estimated in a series of configuration-interaction calculations with fixed orbitals (see Tables I and II).

The generation of the wave functions followed essentially the scheme described in Refs. [35,51]. For each state, the spectroscopic orbitals required to form a reference wave function were obtained in a single configuration calculation. The correlation orbitals were generated in several consecutive steps, with the expansions formed by single substitutions from the reference configurations. At each step, the correlation space has been extended by one layer of correlation orbitals, with all previously generated orbitals frozen, and all new orbitals made orthogonal to others of the same symmetry (see Tables III–V).

Single substitutions (as indicated by letter ‘‘*S*’’ in column 1 of Tables III and VI) promote the electrons from the Dirac-Fock orbitals listed in column 2 to the correlation space presented in column 3. Different notations have been used in the second and third columns. In the second column, the notation $3spd4sp$ denotes spectroscopic, i.e., the occupied Dirac-Fock orbitals, from which substitutions take place. In the third column, e.g., the notation $2spdf1g$ denotes two correlation shells of each of the *s*, *p*, *d*, and *f* symmetries, and one shell of the *g* symmetry.

Monitoring the dependence of an expectation value on the size of the correlation orbital space allows us to study the convergence of the atomic property and offers a tool to estimate the precision of the final expectation value. The first few lines in Tables III and VI, where letter ‘‘*S*’’ in first column indicates single substitutions, show the convergence and saturation of the calculated value for *Q*. After the correlation space has been saturated, the effects of double substitutions have been evaluated in a series of configuration-interaction

TABLE I. The nuclear electric quadrupole moment Q (in mb) of the ${}^{79}_{35}$Br isotope obtained by comparing the experimental hyperfine constant B of the $4p^5\,{}^2P_{3/2}$ ground state of Br with the EFG (in a.u.) calculated at the nonrelativistic MCHF level.

Calculation	EFG	Q
$4s3p1d$ (HF)	4.800	341.3
$3s2p1d//3s3p2d1f$	4.461	367.2
$3s2p1d//1s1p/2s2p2d1f-(1)$	4.573	358.2
Correction FCI singles	−0.112	
$3s2p1d//1s1p/2s2p2d1f-(2)$	4.527	361.8
Correction FCI doubles	−0.067	
$3s2p1d//1s1p/2s2p2d1f-(3)$	4.474	366.1
Correction FCI triples	−0.053	
$3s2p1d//1s1p/2s2p2d1f-(4)$	4.463	367.1
Correction FCI quadruples	−0.002	
$3s2p1d//1s1p/2s2p2d1f-1s1p1d1f1g(2)$	4.510	363.2
$3s2p1d//1s1p/2s2p2d1f2s2p2d2f2g(2)$	4.527	361.8
$2s1p//1s1p1d(17)/1s1p/3s3p3d-1s1p1d(2)$	5.013	326.8
$2s1p//1s1p1d(18)/1s1p/3s3p3d+1s1p1d(2)$	4.512	363.0
CV correction	0.501	
$2s1p//1s1p1d(17)/1s1p/3s3p3d-2s2p2d(2)$	5.115	320.2
$2s1p//1s1p1d(18)/1s1p/3s3p3d+2s2p2d-(2)$	4.500	364.0
CV correction	0.615	
$2s1p//1s1p1d(17)/1s1p/3s3p3d+2s2p-(2)$	5.062	323.6
$2s1p//1s1p1d(18)/1s1p/3s3p3d+2s2p-(2)$	4.500	364.0
CV correction	0.562	
$2s1p//1s1p1d(17)/1s1p/3s3p3d+2s2p-1s1p(2)$	5.084	322.2
$2s1p//1s1p1d(18)/1s1p/3s3p3d+2s2p-1s1p(2)$	4.512	363.0
CV correlation	0.571	
Contribution from the third CV sp shells	0.009	

calculations. In order to estimate the contributions of various electron shells, the configuration-interaction calculations were also performed in a systematic way, with stepwise increase of the orbital correlation space. All MCDF calculations were done with the nucleus modeled as a variable-density sphere, where a two-parameter Fermi distribution [31]

$$\rho(r)=\frac{\rho_0}{1+e^{(r-c)/a}} \tag{3.1}$$

was employed to approximate the charge distribution. The parameter c is the *half-charge-density radius*, and a is related to the *skin thickness*, the interval across which the nuclear charge density falls from $0.9\rho_0$ to $0.1\rho_0$.

In the last column of Tables III and VI, we present the calculated values of the magnetic dipole hyperfine constant A. Since the radial dependence of the magnetic dipole and electric quadrupole hyperfine operators [30] makes them sensitive to the same inner region of the electronic wave function [57], it is expected that electron correlation effects would have a similar influence on both of them. Therefore, the evaluation of the constant A serves as a useful indication of contributions of various electronic shells, and a tool to estimate the accuracy of the calculated electric field gradients. The nuclear magnetic moments have been taken from the tables of Raghavan [7].

TABLE II. The most significant EFG contributions (in a.u.) for the $4p^5\,{}^2P_{3/2}$ ground state of Br and the corresponding Q (in mb) for the ${}^{79}_{35}$Br isotope.

Contribution	EFG	Q
Hartree-Fock	4.800	341.3
MCHF valence SD limit	4.527	361.8
MCHF ΔFCI correction	−0.067	
MCHF CV correction	0.624	
Nonrelativistic value	5.084	322.2
Relativistic correction		−9.7
Breit correction		0.4
MCHF + relativistic corrections	5.235	312.9

C. Molecular calculations

The calculation of the electric field gradient at the halogen nucleus in HBr and HI closely follows the methodology described in the earlier paper [4]. Our present results have been obtained with the same set of Gaussian functions as described in Ref. [4]. The bromine basis set is the contracted Gaussian basis set of the form $[15s12p7d2f/15s12p5d2f]$. The iodine set reads $[17s14p8d2f/17s14p6d2f]$. These ba-

TABLE III. Nuclear electric quadrupole moment Q (in mb) of the ${}^{79}_{35}$Br isotope and magnetic dipole hyperfine constant A (in MHz) of the ground $4p^{5}\,{}^{2}P_{3/2}$ state of ${}^{79}_{35}$Br as a function of the size of the active set of orbitals.

Type	From	To	Q (mb)	A (MHz)
DF			331.0	865.533
S	$1s\ldots4sp$	$1spdf$	343.9	800.438
S	$1s\ldots4sp$	$2spdf1g$	316.1	872.953
S	$1s\ldots4sp$	$3spdf2g1h$	313.8	903.244
S	$1s\ldots4sp$	$4spdf3g2h$	308.8	919.937
S	$1s\ldots4sp$	$4spdf2g1h$	308.8	919.940
S	$1s\ldots4sp$	$5spdf3g2h$	309.9	921.061
S	$1s\ldots4sp$	$6spdf3g2h$	310.0	921.275
S	$1s\ldots4sp$	$4spdf2g1h$		
SD	$3spd4sp$	$1spdf$	318.0	895.699
S	$1s\ldots4sp$	$4spdf2g1h$		
SD	$3spd4sp$	$2spdf$	311.7	883.115
S	$1s\ldots4sp$	$4spdf2g1h$		
SD	$3spd4sp$	$2spdf$		
SD	$4sp$	$2spdf2g1h$	311.0	883.984
S	$1s\ldots4sp$	$4spdf2g1h$		
SD	$3spd4sp$	$2spdf$		
SD	$4sp$	$3spdf2g1h$	310.2	885.355
S	$1s\ldots4sp$	$6spdf2g1h$		
SD	$3spd4sp$	$2spdf$		
SD	$4sp$	$3spdf2g1h$	309.9	886.254
Breit			0.4	0.02
Total			310.3	886.27
Expt. value of King and Jaccarino [15]				884.810(3)

TABLE IV. The nuclear electric quadrupole moment Q (in mb) of the ${}^{127}_{53}$I isotope obtained by comparing the experimental hyperfine constant B of the $5p^{5}\,{}^{2}P_{3/2}$ ground state of I with the EFG (in a.u.) calculated at the nonrelativistic MCHF level.

Calculation	EFG	Q
$5s4p2d$ (HF)	5.949	-820.1
$4s3p2d//3s3p2d1f$	5.444	-896.2
$4s3p2d//1s1p/2s2p2d1f-(2)$	5.539	-880.8
Correction FCI doubles	-0.095	
$4s3p2d//1s1p/2s2p2d1f-1s1p1d1f1g(2)$	5.522	-883.5
$4s3p2d//1s1p/2s2p2d1f-2s2p2d2f2g(2)$	5.539	-880.8
$5s3p2d(47)/1p/3s3p3d-4s4p4d(1)$	6.601	-739.1
$5s3p2d(48)/1p/3s3p3d-4s4p4d(1)$	5.691	-857.3
CV singles correction	0.910	
$4s2p2d//1p(6)/1s1p/3s3p3d+4s4p4d-(2)$	5.529	-882.4
$4s2p2d//1p(5)/1s1p/3s3p3d+4s4p4d-(1)$	6.251	-780.5
$4s2p2d//1p(5)/1s1p/3s3p3d+4s4p4d-(2)$	6.091	-801.0
$4s3p2d//1s1p/3s3p3d+4s4p4d-(1)$	5.638	-865.4
$4s3p2d//1s1p/3s3p3d+4s4p4d-(2)$	5.528	-882.6
CV doubles correction	-0.050	
Total CV correction	0.860	
$4s2p2d//1p(6)/1s1p/3s3p3d+2s2p2d-(2)$	5.528	-882.6
$4s2p2d//1p(5)/1s1p/3s3p3d+2s2p2d-(2)$	6.080	-802.4
Singles contribution from $4p$	0.552	
$4s2p2d//1p(4)/1s1p/3s3p3d+2s2p2d-(2)$	6.076	-803.0
Doubles contribution from $4p$	-0.004	
$4s2p2d//1p(3)/1s1p/3s3p3d+2s2p2d-(2)$	6.075	-803.1
Triples contribution from $4p$	-0.001	
$4s3p1d//1d(8)/1s1p/3s3p3d+2s2p2d-(2)$	5.747	-848.9
$4s3p1d//1d(9)/1s1p/3s3p3d+2s2p2d-(2)$	5.713	-854.0
Doubles contribution from $4d$	0.035	

sis sets are essentially uncontracted in both the valence and core regions. A little stronger contraction was used for the hydrogen set $[11s7p2d/7s4p2d]$. However, the very accurate description of the hydrogen region is not necessary in calculations of the electric field gradient at the heavy nucleus.

The evaluation of electric field gradients of high enough accuracy requires a careful consideration of the electron correlation contribution. This has been computed by using the coupled-cluster method (CC) with the full iterative evaluation of the single and double excitation amplitudes (CCSD) and noniterative correction for triple excitations [CCSD(T)] [58]. This method was successfully used in most of our earlier calculations of electric field gradients in molecules of similar electronic structure and size.

In our earlier studies [3,4], the CCSD(T) evaluation of the electron correlation contribution to electric field gradients in HBr and HI was carried out only for eight valence electrons [CCSD(T)-8]. The correlation contribution due to subvalence shells and core electrons was then estimated at the level of the second-order perturbation theory (MP2) and used as a correction to the valence contribution obtained in CCSD(T) calculations. This method has been carefully verified in several earlier calculations and is known to give acceptable results. However, to increase the accuracy and reliability of correlation corrections to electric field gradients computed in the present paper, we have also performed additional series of CCSD(T) calculations including explicitly the subvalence *d* shells, with the remainder of the correlation correction es-

TABLE V. The most significant EFG contributions (in a.u.) for the $5p^{5}\,{}^{2}P_{3/2}$ ground state of I and the corresponding Q (in mb) for the ${}^{127}_{53}$I isotope.

Contribution	EFG	Q
Hartree-Fock	5.949	-820.1
MCHF valence SD limit	5.539	-880.8
MCHF ΔFCI correction	-0.095	
MCHF valence limit	5.444	-896.2
MCHF CV correction	0.860	
MCHF CC correction $(p+d)$	0.031	
Nonrelativistic value	6.335	-770.1
Relativistic correction		60.3
Breit correction		-1.3
MCHF + relativistic corrections	6.861	-711.1

TABLE VI. Nuclear electric quadrupole moment Q (in mb) of the $^{127}_{53}$I isotope and magnetic dipole hyperfine constant A (in MHz) of the ground $5p^5\,{}^2P_{3/2}$ state of $^{127}_{53}$I as a function of the size of the active set of orbitals.

Type	From	To	Q	A
DF			-756.5	880.686
S	$1s\ldots5sp$	$1spdf$	-809.4	740.085
S	$1s\ldots5sp$	$2spdf1g$	-720.6	801.894
S	$1s\ldots5sp$	$3spdf2g1h$	-713.7	833.044
S	$1s\ldots5sp$	$4spdf2g1h$	-698.0	867.820
S	$1s\ldots5sp$	$5spdf2g1h$	-697.7	869.201
S	$1s\ldots5sp$	$6spdf2g1h$	-698.1	868.007
S	$1s\ldots5sp$	$5spdf2g1h$		
SD	$5sp$	$1spdf$	-724.3	857.877
S	$1s\ldots5sp$	$5spdf2g1h$		
SD	$5sp$	$2spdfg1h$	-726.8	860.838
S	$1s\ldots5sp$	$5spdf2g1h$		
SD	$5sp$	$3spdf2g1h$	-725.3	859.061
S	$1s\ldots5sp$	$5spdf2g1h$		
SD	$4d5sp$	$1spdfg$		
SD	$5sp$	$3spdf2g1h$	-719.0	860.024
S	$1s\ldots5sp$	$5spdf2g1h$		
SD	$4d5sp$	$2spdfg$		
SD	$5sp$	$3spdf2g1h$	-710.7	862.258
S	$1s\ldots5sp$	$5spdf2g1h$		
SD	$4d5sp$	$3spdfg$		
SD	$5sp$	$3spdf2g1h$	-709.5	862.609
S	$1s\ldots5sp$	$5spdf2g1h$		
SD	$4spd5sp$	$1spdfg$		
SD	$5sp$	$3spdf2g1h$	-711.3	860.814
S	$1s\ldots5sp$	$5spdf2g1h$		
SD	$4spd5sp$	$2spdfg$	-708.2	811.412
S	$1s\ldots5sp$	$5spdf2g1h$	-706.5	813.054
SD	$4spd5sp$	$2spdfg$		
SD	$5sp$	$2spdf2g1h$		
S	$1s\ldots5sp$	$5spdf2g1h$	-706.0	816.763
SD	$4spd5sp$	$2spdfg$		
SD	$5sp$	$3spdf2g1h$		
Breit			-1.3	1.877
Total			-707.3	818.640
Expt. value of Luc-Koenig *et al.* [56]				827.1(1.5)
Expt. value of Jaccarino *et al.* [16]				827.265(3)

timated from MP2 data. The corresponding CCSD(T) results will be referred to by CCSD(T)-18.

Our earlier studies have shown that the relativistic effects can significantly contribute to the electric field gradients at the halogen nuclei in halogen hydrides [3,4,22]. The method used to obtain relativistic corrections is the spin-averaged Douglas-Kroll (DK) approximation [24,25]. The same method has been used earlier [4]. However, the present calculations take into account the so-called picture change of the electric field gradient operator [21,22], which was totally neglected in our earlier studies [3,4]. On the basis of our investigations of the picture-change contribution to the electric field gradients in two-component relativistic methods [22], one may expect that this effect is by no means negligible. This has been also confirmed in recent calculations on the coinage metal chlorides [23] and on KrH$^+$ and XeH$^+$ [59].

Including the picture-change contribution in relativistic DK CCSD(T) calculations means that the usual field gradient operator needs to be replaced by a more complicated expression [21,22]. A method to avoid explicit transformation of the field gradient operator has been recently proposed by Pernpointner *et al.* [26] and is based on modeling of the nuclear quadrupole by a set of charges. Within this model the relativistic DK calculations of electric field gradients can be formulated in terms of the finite-field perturbation approach [22,26,27]. The problem of the choice of numerical parameters of the point charge nuclear quadrupole moment (PC-NQM) has been already discussed [22,26,27] and in this respect we follow the choice of parameters recommended for DK calculations in Ref. [22].

The calculation of the pure electronic and nuclear contributions to $q(X)$ in HBr and HI has been performed for the experimental equilibrium geometries of the two molecules: $R_e(\mathrm{HBr})=2.673$ a.u. and $R_e(\mathrm{HI})=3.040$ a.u. [44]. The spectroscopic constants required to evaluate the vibrational contribution follow from the same source [44] whereas the derivatives entering Eq. (2.12) have been evaluated by fitting the $q(X)$ computed at R_e and $R_e\pm0.05$ a.u. to a parabola with respect to R.

IV. RESULTS AND DISCUSSION

A. Atomic MCHF calculations for $Q(^{79}\mathrm{Br})$

The electric field gradient of 4.527 a.u. and the corresponding nuclear quadrupole moment of 361.8 mb obtained in the $3s2p1d//1s1p/2s2p2d1f-2s2p2d2f2g(2)$ calculation are considered to be the valence singles and doubles (SD) limit. By adding the difference of -0.067 a.u. between the EFG values obtained in the largest FCI calculation and the corresponding SDCI calculation, the extrapolated valence limit becomes 4.460 a.u., which corresponds to a $Q(^{79}_{35}\mathrm{Br})$ of 367.2 mb. The core-valence correlation contribution is estimated by allowing single excitations from the $3s$, $3p$, and $3d$ shells and optimizing an additional set of shells which accommodate core-valence effects. The final core-valence contribution to the EFG of 0.624 a.u. is obtained by adding the differential core-valence correction of the $2s1p//1s1p1d(17)/1s1p/3s3p3d+2s2p(2)$ and the $2s1p//1s1p1d(17)/1s1p/3s3p3d+2s2p-1s1p(2)$ calculations to the core-valence correction of the $2s1p//1s1p1d(17)/1s1p/3s3p3d-2s2p2d(2)$ calculation. The frozen valence shells are those of the largest valence correlation calculation, while the frozen core-valence shells are taken from the largest core-valence correlation calculation. The final nonrelativistic value of 5.084 a.u. is obtained by adding the core-valence correction of 0.624 a.u. and the valence limit of 4.460 a.u. A combination of the EFG of 5.084 a.u. with the measured electric quadrupole coupling constant of $-384.878(8)$ MHz [15] yields a nuclear quadrupole moment $[Q({}^{79}_{35}\mathrm{Br})]$ of 322.2 mb. The relativistic correction of -9.7 mb can be estimated from the ratio of the EFGs calculated at the Hartree-Fock and the Dirac-Fock levels, respectively. By considering also the Breit correction obtained at the MCDF level, the final $Q({}^{79}_{35}\mathrm{Br})$ obtained from the LUCAS calculations is 312.9 mb.

B. Atomic MCDF calculations for $Q(^{79}\mathrm{Br})$

The largest MCDF calculation has been performed with single substitutions from all occupied orbitals to the correlation space spanned by six layers of correlation shells $(6spdf2g1h)$, augmented by double substitutions from $3spd4sp$ shells to the correlation space spanned by two layers of correlation shells $(2spdf)$, and double substitutions from $4sp$ shells to the correlation space spanned by three layers of correlation shells $(3spdf2g1h)$. The tests performed with limited configurational spaces indicate that the contribution of the $1s2sp$ core to the EFG is negligible. The electron-correlation contributions arising from double substitutions are also relatively small. The correlation orbital space seems to be sufficiently saturated, and we estimate that for this particular model space the MCDF procedure yields the calculated value of Q with the precision of the order of 0.1%, as can be inferred from the last two "SD" entries in Table III.

For ${}^{79}_{35}\mathrm{Br}$, our MCDF calculations yield a Q value of 310 mb as extracted from the experimental value of the electric quadrupole constant $B=-384.878(8)$ MHz [15] and from the calculated electric field gradient. The Breit contribution of 0.4 mb was estimated in a configuration-interaction calculation.

Our calculated magnetic dipole hyperfine constant A of 886.27 MHz for the ground state of bromine, as compared to the experimental value $A(\text{expt.})$ of 884.810(3) MHz [15], indicates a remarkably good agreement, within 0.1%, which appears to be fortuitous, since there are several possible sources of systematic errors, which are likely to introduce at least a one order of magnitude larger uncertainty for the EFG. Out of these, we should mention two, whose contributions to the overall error budget are probably largest. There are certain classes of omitted double substitutions, as can be seen from Table III. Their influence on the final value is small, certainly below 1%. The triple and higher-order substitutions have been entirely neglected. Their influence has been estimated from the nonrelativistic MCHF calculations as the difference between the EFG obtained in the largest valence full configuration interaction calculation and the EFG obtained in the corresponding configuration calculation allowing only single and double excitations from the valence shells to the correlation shells. This small EFG difference (-0.067 a.u., denoted ΔFCI in Table VIII), which should constitute a good approximation of higher-order effects, increases the Q value by about 4 mb. With this correction, our total MCDF value becomes 313.9 mb.

C. Atomic MCHF calculations for $Q(^{127}\mathrm{I})$

For iodine the EFG of 5.539 a.u. and the corresponding Q of -880.8 mb obtained in the $4s3p2d//1s1p/2s2p2d1f-2s2p2d2f2g(2)$ calculation is considered to be the nonrelativistic valence singles and doubles (SD) limit. By adding the difference of -0.095 a.u. between the EFG values obtained in the largest FCI calculation and the corresponding SDCI calculation, the extrapolated nonrelativistic valence limit becomes 5.444 a.u., which corresponds to a $Q({}^{127}_{53}\mathrm{I})$ of -896.2 mb. The core-valence correlation contribution is estimated by allowing single excitations from the core shells and optimizing an additional set of four s, p, and d shells which accommodate the core-valence effects. The core-valence singles contribution to the EFG of 0.910 a.u. (CV singles correction in Table IV) has been obtained as the EFG difference between the value calculated with the $5s3p2d(47)/1p/3s3p3d-4s4p4d(1)$ orbital set, and the result of the corresponding valence correlation calculation, i.e., $5s3p2d(48)/1p/3s3p3d-4s4p4d(1)$. Double excitations of the valence electrons in combination with single excitations from the core were found to be of significant importance. This effect was studied by allowing single excitations from the $4p$ shell and comparing the EFG values obtained with and without double excitations from the valence $5s5p$ shells. The double excitations reduced the CV correction of the EFG by -0.0576 a.u. yielding a final CV correlation contribution of 0.8600 a.u. In the core-valence correlation calculations, the frozen valence shells are those of the second largest valence correlation calculation. To check the contributions from higher-order excitations from the core shells, configuration interaction calculations with up to triple excitations from the $4p$ or the $4d$ shells were performed. The obtained double excitation contribution to the EFG from the $4p$ shell was only -0.004 a.u., and the contribution from the triplets was even smaller. However, the doubles contribution from $4d$ affects the EFG by 0.034 a.u. The shells of the core-core correlation CI calculations were optimized in the core-valence correlation calculation.

The nonrelativistic value for the EFG of 6.335 a.u. was obtained by adding the core-valence and core-core correlation contributions to the valence limit value. The combination of the EFG of 6.335 a.u., with the measured electric quadrupole coupling constant of $-1146.356(10)$ MHz [16] yields the MCHF value for the nuclear quadrupole moment $[Q({}^{127}_{53}\mathrm{I})]$ of -770.1 mb. The ratio of the EFGs calculated at the Hartree-Fock and the Dirac-Fock levels, respectively, yields a relativistic correction of 60.3 mb. However, such a large correction implies that relativistic correlation effects can also be important. At the valence correlation singles level, the Q values obtained at the MCDF and MCHF levels are -796.9 mb and -873.3 mb, respectively. The relativistic correction at the valence singles level becomes 76.4 mb. In addition, at the relativistic level, double excitations from the $4d$ shell contribute -19.3 mb to Q, while at the nonrelativistic level the contribution was only -3.2 mb. By adding this relativistic correlation contribution of -16.1 mb to the relativistic correction of 76.4 mb, the final relativistic correction obtained at the correlated level is also 60.3 mb. The Breit correction of -1.3 mb is still relatively small yielding the final MCHF Q value of -711.1 mb.

D. Atomic MCDF calculations for $Q(^{127}\mathrm{I})$

For iodine, the MCDF computations proceeded as for bromine. Table VI presents the sequence of MCDF calculations, and shows their convergence with respect to systematic enlargement of the correlation orbital space, as well as with respect to opening subsequent core shells for double substitutions. The contribution from the Breit interaction is 0.2% or -1.3 mb. The contribution from higher-order valence excitations amounts to -9.8 mb and has been estimated in a similar way to that for bromine, by employing the nonrelativistic ΔFCI correction (see Table IX). Together with the above two corrections, our final MCDF value for the nuclear quadrupole moment, $Q(^{127}_{53}I)$, becomes -717.1 mb, as extracted from the experimental value of B of $-1146.356(10)$ MHz [16], and from the calculated electric field gradient. The estimate of the error bar can be based on similar assumptions, as for bromine. For iodine, the expectation value of the magnetic hyperfine constant A is much more sensitive to the electron correlation than the EFG. For iodine, the double substitutions play a significant role. Furthermore, not only valence shells, but also the correlation of the $4spd$ shells have a large effect on the value of A for iodine. Our calculated A value of 818.64 MHz is 1% smaller than the experimental result of 827.265(3) MHz, and the difference thereof can be regarded as a reasonable indication of the error bar.

E. Molecular calculations of $Q(^{79}\mathrm{Br})$ and $Q(^{127}\mathrm{I})$

For both molecules investigated in this paper, the results for different contributions in Eq. (2.12) are presented in Table VII. All values of the electronic contribution are calculated by using the PCNQM model. The earlier calculations [4] without the picture-change contribution and only eight electrons correlated at the CCSD(T) level of approximation gave 7.579 a.u. and 11.953 a.u. for Br and I, respectively. Thus, taking into account the picture change for the electric field gradient lowers the $q(\mathrm{Br})$ value in HBr by about 0.27 a.u. For I in HI the corresponding lowering is much larger and amounts to 0.94 a.u.

To use these data for the determination of nuclear quadrupole moments of Br and I on the basis of highly accurate values of ν_Q, one would like to have some estimate of the accuracy of the calculated values. The nuclear and vibrational ($v=0$) contributions presented in Table VII can be, for the present purpose, considered as essentially exact. There is, however, some uncertainty in the accuracy of the pure electronic contribution which follows from the use of truncated basis sets and limited treatment of the electron correlation contribution. According to our earlier studies of the halogen hydrides [3] and calculations on similar systems [12,18,19], the basis-set extension should not affect the present data by more than ± 0.01 a.u., i.e., by much less than 1% of the total values. To estimate the saturation of the correlation contribution, one may compare the total (with the corresponding MP2 estimates of the core contribution) CCSD(T)-8 and CCSD(T)-18 values of q_e^{el}. The corresponding differences are about 0.005 a.u. for HBr and 0.025 a.u. for HI. Again they fall much below 1% of the total values.

TABLE VII. Contributions to the electric field gradient at the halogen nuclei in HBr and HF from DK CCSD(T) calculations within the PCNQM model. All results correspond to experimental values of the equilibrium bond distance and are given in a.u.

Contribution to $q_v(X)$	Br in HBr	I in HI
q_e^{el}		
CCSD(T)-8[a]	7.0287	10.6865
Core contribution, MP2[b]	0.0848	0.1223
Total electronic with CCSD(T)-8	7.1135	10.8088
q_e^{el}		
CCSD(T)-18[c]	7.0831	10.7603
Core contribution, MP2[d]	0.0352	0.0731
Total electronic with CCSD(T)-8	7.1183	10.8334
q_e^n	0.1047	0.0712
$q_e^v, v=0$	0.0900	0.1335
Total from CCSD(T)-8	7.3082	11.0135
Total from CCSD(T)-18	7.3130	11.0381

[a] DK CCSD(T) calculations with eight correlated electrons.

[b] MP2 estimate of the remaining core correlation contribution calculated as the difference between all-electron and eight-electron MP2 results.

[c] DK CCSD(T) calculations with 18 correlated electrons.

[d] MP2 estimate of the remaining core correlation contribution calculated as the difference between all-electron and 18-electron MP2 results.

There is obviously uncertainty concerning the electron correlation contribution to q_e^{el} from higher than triple excitations. This effect can only be estimated on the basis of the quality of the CCSD(T) data for other systems [12,18,19] and the present experience in calculations of electric field gradients in small molecules. A 1% inaccuracy of the present data is presumably the upper limit for the contribution of the neglected electron correlation effects.

Finally, all molecular calculations presented in this paper have been carried out in the spin-averaged DK formalism. Hence, our results do not include the spin-orbit effects. The spin-orbit contribution to $q(\mathrm{I})$ in HI has been calculated at the level of the DHF approximation by Visscher *et al.* [60] and amounts to -0.052 a.u. However, the electron correlation effects are known to quench the spin-orbit effects [61,62] and one can safely assume that the corresponding CCSD(T) result will be considerably smaller. For HBr the spin-orbit contribution should be negligible.

All these estimates of the possible inaccuracies of the calculated electric field gradients in HBr and HI indicate that reasonably safe error bars are at the level of 1%. The inaccuracies of experimental values of ν_Q are much lower, therefore the error bars of the derived values of Q remain at the level of at most 1%. Errors of this order of magnitude have been found in our earlier molecular calculations of nuclear quadrupole moments [12,18,19].

With the experimental value of $\nu_Q(^{79}\mathrm{Br})=532.3048$ MHz for the $v=0$ vibrational level of $\mathrm{H}^{79}\mathrm{Br}$ [63], the value of $q(\mathrm{Br})=7.3130$ a.u. (Table VII), and the estimated 1% error bars one obtains from Eq. (2.10) $Q(^{79}\mathrm{Br})=310(3)$ mb. The inaccuracy of the experimental value of $\nu_Q(^{79}\mathrm{Br})$ becomes irrelevant in comparison with the accuracy of the calculated value of $q(\mathrm{Br})$.

For $\mathrm{H}^{127}\mathrm{I}$ in the $v=0$ vibrational state, the experimental value of ν_Q has been reported as equal to -1828.28 MHz [63] and with $q(\mathrm{I})$ value of 11.0381 a.u. (Table VII) gives $Q(^{127}\mathrm{I})=-705(7)$ mb. Recently the quadrupole coupling constant has been reported also for $\mathrm{D}^{127}\mathrm{I}$ and is equal to $-1823.226(54)$ MHz [64]. The vibrational correction to $q_v(\mathrm{I})$ in the $v=0$ state of $\mathrm{D}^{127}\mathrm{I}$, calculated from spectroscopic constants of the $\mathrm{H}^{127}\mathrm{I}$ molecule [44] by scaling, is found to be 0.0947 a.u. This leads to the total value of $q(\mathrm{I})$ in $\mathrm{D}^{127}\mathrm{I}$ equal to 10.9992 a.u. and gives $Q(^{127}\mathrm{I})=-705(7)$ mb. The differences between the $Q(^{127}\mathrm{I})$ values derived from the experimental data for $\mathrm{H}^{127}\mathrm{I}$ and $\mathrm{D}^{127}\mathrm{I}$ are too small to be seen within the accuracy of the present calculations.

It is also worthwhile to mention that without taking into account in the molecular DK calculation the picture-change effect, the value of $Q(^{79}_{35}\mathrm{Br})$ would turn out to be equal to only about 305 mb [4]. Similarly, without this correction the molecular value of $Q(^{127}_{53}\mathrm{I})$ would be about -651 mb, i.e., less negative by almost 60 mb than the present result [4].

F. Nuclear quadrupole moments of Br and I: Final adjustment

The final Q values for the $^{79}_{35}\mathrm{Br}$ and $^{127}_{53}\mathrm{I}$ nuclei are compared with literature values in Tables VIII and IX, respectively. For Br, there is an almost perfect agreement between the Q values of 312.9 and 313.9 mb obtained in the atomic MCHF and MCDF calculations, respectively. The molecular value $Q(^{79}_{35}\mathrm{Br})$ is equal to 310(3) mb and, within the estimated error bars, agrees perfectly with the atomic values. It is possible that the true value of $Q(^{79}_{35}\mathrm{Br})$ could be closer to it. We propose 313(3) mb as our final Q value for $^{79}_{35}\mathrm{Br}$. By using the experimental ratio $Q(^{79}_{35}\mathrm{Br})/Q(^{81}_{35}\mathrm{Br})$ of 1.197 051 4(32) [72], we deduce for $Q(^{81}_{35}\mathrm{Br})$ a value of 261.5(2.5) mb. The estimated uncertainties are given in parentheses. Atomic-beam measurements [73] yield the value of 0.591 41(27) for the ratio $Q[^{80}_{35}\mathrm{Br}(17.6\ \mathrm{m},\ I=1)]/Q(^{79}_{35}\mathrm{Br})$. This yields a Q value of 185(2) mb for the $^{80}_{35}\mathrm{Br}$ $I=1$ ground state. γ-ray angular correlation measurements on solid bromine are reported by Taqqu [65] for the 37 keV 7.4 ns $I=2$ and 86 keV 4.42 h $I=5$ states of $^{80}_{35}\mathrm{Br}$. Their Q values now become ± 163 and $+709$ mb, respectively.

For $^{127}_{53}\mathrm{I}$, the agreement between the MCHF and MCDF values is remarkably good even though the relativistic correction is 60 mb, and the relativistic correlation and the higher-order valence correlation contributions are significant. The Breit correction of -1.3 mb is still relatively small. The final MCHF and MCDF Q values are -711.1 and -717.1 mb, respectively. The molecular value of $Q(^{127}_{53}\mathrm{I})$ derived in this paper from both HI and DI, without any spin-orbit corrections, is equal to $-705(7)$ mb and within the estimated error bars fully agrees with the atomic results. We quote the final $Q(^{127}_{53}\mathrm{I})$ as $-710(10)$ mb. The true value may be closer to the molecular one.

TABLE VIII. Comparison of present nuclear electric quadrupole moments Q (in mb) of the $^{79}_{35}\mathrm{Br}$ isotope with literature values.

	Q
MCDF+ΔFCI correction, this work	313.9
MCHF + relativistic corrections, this work	312.9
HBr molecule, this work	310(3)
Final value, this work	313(3)
van Lenthe and Baerends, 2000 [6]	300(10)
Haas and Petrilli, 2000 (molecular) [5]	305(5)
Haas and Petrilli, 2000 (atomic reanalysis) [5]	308.7
Kellö and Sadlej, 1996 [4]	298.9
Kellö and Sadlej, 1990 [3]	304.5
Taqqu, 1978 [65]	331(4)
Lederer and Shirley, 1978 [66]	293
Fuller, 1976 [67][a]	370
Korol'kov and Makhanek, 1962 [68]	293
King and Jaccarino, 1954 [15][b]	335(20)
King and Jaccarino, 1954 [15][c]	308(18)
Gordy, 1948 [69]	240, 280

[a] Value quoted in her Summary.
[b] $\langle r^{-3}\rangle$ from magnetic hfs.
[c] $\langle r^{-3}\rangle$ from spin-orbit splitting.

TABLE IX. Comparison of present nuclear electric quadrupole moments Q (in mb) of the $^{127}_{53}\mathrm{I}$ isotope with literature values.

	Q
MCDF+ΔFCI correction, this work	−717.1
MCHF + relativistic corrections, this work	−711.1
HI and DI molecules, this work	−705(7)
Final value, this work	−710(10)
van Lenthe and Baerends, 2000 [6]	−690(30)
Haas and Petrilli, 2000 (molecular) [5]	−689(15)
Haas and Petrilli, 2000 (atomic reanalysis) [5]	−711.3
Kellö and Sadlej, 1996 [4]	−651
Kellö and Sadlej, 1990 [3]	−718
Fuller, 1976 [67][a]	−790
Korol'kov and Makhanek, 1962 [68]	−640
Stroke, 1959 [70]	−789
Gordy, 1948 [69]	−590, −750
Murakawa, 1939 [71]	−460

[a] Value quoted in her Summary.

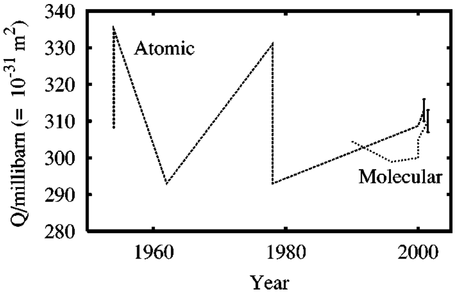

FIG. 1. Reported values for the nuclear quadrupole moment of ${}^{79}_{35}\mathrm{Br}$ as a function of time.

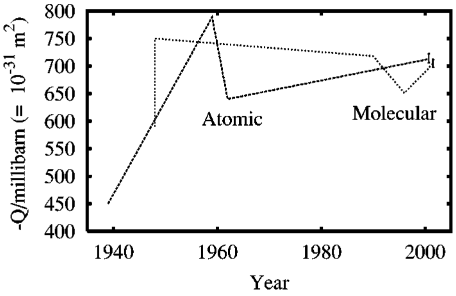

FIG. 2. Reported values for the nuclear quadrupole moment of ${}^{127}_{53}\mathrm{I}$ as a function of time.

Haas and Petrilli [5] performed a reanalysis of the previous atomic data. The reanalyzed Q value for bromine of 308.7 mb is remarkably close to ours, which can be explained by small and canceling effects of double substitutions. In the case of iodine, the double substitutions are not entirely negligible, so the arguments of Haas and Petrilli are not completely correct. Since the overall contribution of doubles is quite small (about 2%), the reanalyzed atomic value stays close to our final result.

Figures 1 and 2 present the historical evolution of "atomic" and "molecular" determinations of nuclear quadrupole moments of bromine and iodine, showing fairly good convergence, although the most recent "atomic" Q values (present MCDF and MCHF results, and "reanalysis" by Haas and Petrilli [5]) tend to cluster around 310 mb for bromine, while "molecular" results, obtained by Haas and Petrilli [5], Kellö and Sadlej [4], and by van Lenthe and Baerends [6] lie around 300 mb.

${}^{127}\mathrm{I}$ has a 58 keV $I=\frac{7}{2}$ Mössbauer state. The ratio between the excited-state and ground-state quadrupole moments has been measured as $Q^*/Q=0.896(2)$ [74]. The new primary value $Q=-710(10)$ mb thus gives $Q[{}^{127}\mathrm{I}(58\ \mathrm{keV}, I=\frac{7}{2})]=-636(9)$ mb The long-lived ${}^{129}\mathrm{I}(I=\frac{7}{2}, 1.6\times 10^7\ \mathrm{y})$ has a ratio $Q({}^{129}\mathrm{I})/Q({}^{127}\mathrm{I})=0.701\,213(15)$ [75], yielding a $Q({}^{129}\mathrm{I})$ of $-498(7)$ mb. The same isotope has a 28 keV $I=\frac{5}{2}$ Mössbauer state. The ratio $Q({}^{129}\mathrm{I}^*)/Q({}^{129}\mathrm{I})$ has been measured as 1.2385(11) [76], yielding $Q({}^{129}\mathrm{I}^*)=-616(9)$ mb.

As a final comment, nuclear theory is only able to bracket $Q({}^{127}\mathrm{I})$ to the interval $-0.74<Q({}^{127}\mathrm{I})<-0.47$ b [77].

V. CONCLUSIONS

Relativistic and nonrelativistic calculations of the electric field gradients for the ground states of bromine and iodine atoms have been performed at the multiconfiguration self-consistent-field level. The calculated EFGs together with experimental values of the hyperfine constants B yield the nuclear quadrupole moments $Q({}^{79}_{35}\mathrm{Br})$ of 313(3) mb, $Q({}^{81}_{35}\mathrm{Br})$ of 261.5(2.5) mb, and $Q({}^{127}_{53}\mathrm{I})$ of $-710(10)$ mb, which we propose as new "standard" values. These values are supported by the molecular DK CCSD(T) ones on HBr, HI, and DI. The present values are already incorporated in the "Year 2001" set of nuclear quadrupole moments [17].

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