Nuclear Quadrupole Moments of Bismuth

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Multiconfiguration Dirac-Fock models have been employed to compute the electric field gradient in the ground state of the neutral bismuth atom. Combined with the experimental electric quadrupole hyperfine interaction constant, one obtains for ^{209}Bi the nuclear quadrupole moment $Q = -516$ (15) mb, which is almost 40% away from the previously accepted standard value [-370 (26) mb], and narrows by over an order of magnitude the long-standing, extremely broad array of various results ranging from -370 to -710 mb. The recent Q values of $^{202-208,210^m-213}$Bi by Pearson *et al.* suffer a consequent change.

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The knowledge of nuclear quadrupole moments, Q, is important in nuclear physics and in atomic, molecular, and solid-state spectroscopy. Yet many Q values remain little known; some recent summaries are given in Refs. [1–4].

A case in point is bismuth (in nature 100% $^{209}_{83}$Bi, $I = \frac{9}{2}$), for which Schüler and Schmidt [5] proposed a Q of -400 mb in 1936 and whose recently quoted Q values still range from -370 to -710 mb. Of these, a "pionic" value of -500 (80) mb [6] was chosen in the compilation [3], while a "muonic" value of -370 (26) mb [1,7] was chosen as the primary standard for a recent study of the Q values of $^{202-208,210^m-213}$Bi by Pearson *et al.* [8]. These authors have performed gas cell laser measurements of the ratios of the atomic quadrupole splittings between different isotopes, and used these ratios to extract quadrupole moments of all isotopes.

It is already commonplace that the most reliable Q values for lighter elements come from measured quadrupole coupling constants, B, in atoms or small molecules, combined with precise *ab initio* calculations of the electric field gradients (EFG) at the nucleus. We present the first accurate relativistic *ab initio* calculation of the EFG for a very heavy element, Bi, which allows an extraction of the nuclear electric quadrupole moment Q of ^{209}Bi from the accurate experimental B of $-305.067(2)$ MHz by Hull and Brink [9].

Theory.—The theory [10,11], implementation [12], and method of calculation [13,14] have been described elsewhere, and we will only briefly state here that the atomic wave functions Ψ, for a particular atomic state Γ,

$$\Psi(\Gamma PJM) = \sum_r^{NCF} c_r \Phi(\gamma_r PJM), \tag{1}$$

are obtained as the self-consistent solutions of Dirac-Fock equations [10] in systematically increased multiconfiguration basis NCF of symmetry-adapted eigenfunctions of J^2, J_z, and parity P. Configuration mixing coefficients c_r are obtained through diagonalization of the Dirac-Coulomb Hamiltonian

$$H_{\mathrm{DC}} = \sum_i c\boldsymbol{\alpha}_i \cdot \boldsymbol{p}_i + (\beta_i - 1)c^2 - Z/r_i + \sum_{i>j} 1/r_{ij}\,. \tag{2}$$

The effect of the Breit interaction has been estimated in independent configuration-interaction calculation, where the matrix elements of the Breit operator in low-frequency limit [15]

$$B_{ij} = -\frac{1}{2r_{ij}}\left[\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j + \frac{(\boldsymbol{\alpha}_i \cdot \boldsymbol{r}_{ij})(\boldsymbol{\alpha}_j \cdot \boldsymbol{r}_{ij})}{r_{ij}^2}\right] \tag{3}$$

were evaluated perturbatively, as described in [16]. The coefficients c_r, together with the one-electron orbital set, provide a numerical representation of the state $\Psi(\Gamma PJM)$ for further calculation of atomic expectation values of magnetic dipole hyperfine constant A and EFG in the $^4S_{3/2}$ ground state of ^{209}Bi. The calculated electric field gradient, together with the experimental value of hyperfine constant B [9], allows one to extract the nuclear electric quadrupole moment Q from equation

$$\mathrm{B}(\Gamma PJM) = \mathrm{EFG}(\Gamma PJM)\ (\mathrm{eQ})/h\,, \tag{4}$$

where $\mathrm{EFG}(\Gamma PJM)$ denotes the electric field gradient, and eQ is the electric quadrupole moment of the nucleus.

Method of calculation.—We employed the method described as systematic expansion of configuration set [13,14], in which configuration state functions of a particular parity and symmetry are generated by substitutions from reference configurations to an active set of orbitals. The active set is systematically increased until the convergence of the observable is obtained. In first-order perturbation theory, only single substitutions contribute to the hyperfine energy operator [17,18], so they usually comprise the dominant part of the hyperfine energy correction. On the other hand, double substitutions dominate energetically over the valence correlation corrections and, consequently, the virtual orbitals obtained in fully correlated variational calculations are optimized predominantly

through the effects of double substitutions on the total energy. In the present paper we adopted a scheme [19], in which the virtual orbital space is optimized for the single substitutions, while the effects of the double substitutions were evaluated later in configuration-interaction calculations.

Monitoring the dependence of an expectation value on the size of the multiconfiguration space allows one to study the convergence of the atomic property and offers a tool to estimate the precision of the final expectation value. Figure 1 shows the value of the quadrupole moment Q of ^{209}Bi, as a function of the size of the multiconfiguration space. The first, highly oscillatory part of the curve represents the values of Q obtained in the single-substitution calculations, where electrons were promoted from the occupied shells $5spd6sp$ to the $4spdfg1h$ virtual orbital space [20]. After they saturated, the series of double-substitution configuration-interaction calculations have been done, in such a manner, that saturation of the expectation value of EFG has been ensured for substitutions arising from $6sp$, and then subsequently from $5spd$ shells. The final, largest calculation has been performed with single substitutions from occupied orbitals $4spdf5spd6sp$ to the virtual space spanned by three layers of virtual shells ($3spdfg1h$), augmented by double substitutions from $6sp$ shells to the virtual space spanned by three layers of virtual shells ($3spdfg1h$), and double substitutions from $5spd6sp$ shells to the virtual space spanned by one layer of virtual shells ($1spdfgh$), which together amount to 20 131 relativistic configurations.

Results.—As a test of the accuracy of the calculations, the expectation value of the magnetic dipole hyperfine constant A has been evaluated at each step of the computations. It is a well known fact that the magnetic dipole constant A is more sensitive to electron correlation effects than electric quadrupole constant B, which is a consequence of spin polarization [21]. However, they both have similar r^{-3} dependence on the radial part of the electronic wave function, which makes them both sensitive to the innermost part of the electronic cloud. Therefore, the relative accuracy of the calculated hyperfine constant A, with respect to the experimental result [9,22], should constitute an upper limit for the relative accuracy of the value of the calculated value of EFG. Figure 2 shows the value of the magnetic dipole hyperfine constant A of ^{209}Bi, as a function of the size of the multiconfiguration space [Eq. (1)]. As in the case of Q, the first, highly oscillatory part of the curve, represents the values of A, obtained in single-substitution calculations. As can be seen from Fig. 2, the calculated value of A has not converged properly, but further calculations would not serve the purpose of the error estimate, due to the fact that several sources of possible systematic error have not been taken care of in the multiconfiguration Dirac-Fock (MCDF) model employed in this study. These include the following: (a) the effect of omitted subset of double substitutions from $5spd6sp$, which we estimate to affect the observables at most by a few percent in the case of A, and much less in the case of EFG; (b) opening of $4spdf$ shells for double substitutions; single substitutions from $4spdf$ gave a 5% increase of A and a 0.1% increase of EFG, so double substitutions would yield much less than that; (c) triple substitutions, which turned out to yield as large a contribution as 2% for EFG in sodium [23] (however, sodium is an alkali, which is notorious for large electron correlation effects).

The Breit interaction yields a -8.27 MHz shift to the Dirac-Coulomb value of $A(\mathrm{DC}) = -424.01$ MHz, which together gives our final Dirac-Coulomb-Breit result $A(\mathrm{DCB}) = -432.28$ MHz, which is 3% away from the experimental result $A = -446.937(1)$ MHz [9]. From these considerations and the above-mentioned accuracy of the calculated value of A, we may conclude that 3% would constitute a conservative estimate of an error of our calculated value of EFG. The calculated Dirac-Coulomb value

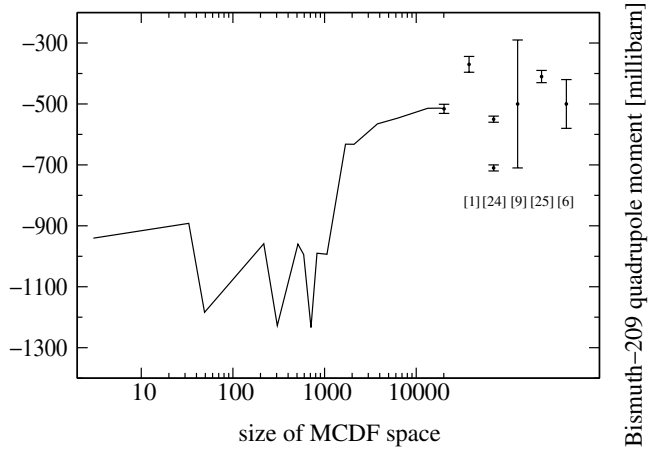

FIG. 1. The ^{209}Bi nuclear quadrupole moment Q as a function of the size of multiconfiguration expansion, compared with some of the most recent determinations; the numbers in square brackets indicate the literature references; see Table I for further details.

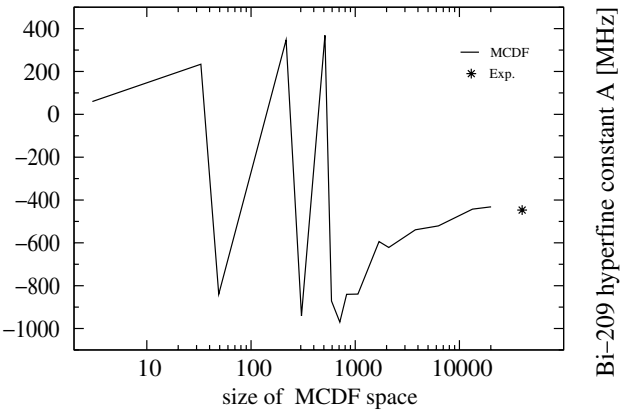

FIG. 2. The ^{209}Bi hyperfine magnetic dipole constant A as a function of the size of multiconfiguration expansion, compared with experimental value.

TABLE I. Proposed values of nuclear electric quadrupole moment Q of ^{209}Bi in reverse chronological order.

Q (mb)	Method	Reference
−516 (15)	Bi atom, MCDF	This work
−370 (26)	"Standard"	Raghavan [1]
−550 (10)	Bi atom[a,b]	Dembczyński *et al.* [24]
−710 (10)	Bi atom[a,c]	Dembczyński *et al.* [24]
−500 (210)	Pionic Bi	Batty *et al.* [25]
−410 (20)	Bi atom[d]	Skovpen [26]
−500 (80)	Pionic Bi	Beetz *et al.* [6]
−400	Bi^+6p7s[e]	Holmgren and Rosén [27]
−400 to −460	Bi atom[f]	Lindgren and Rosén [28]
−370 (30)	Muonic Bi	Lee *et al.* [7]
−460	Bi atom[e]	Rosen [29]
−410 (40)	Opt. spectroscopy	George *et al.* [30]
−385 (40)	Bi atom[a]	Landman and Lurio [31]
−379 (15)	Bi atom[d]	Eisele *et al.* [32]
−370 (40)	Opt. spectroscopy	Dickie *et al.* [33]
−400	Bi, $Bi^{1+,2+}$	Schüler and Schmidt [5]

[a]The $\langle r^{-3}\rangle$ integrals deduced from magnetic hfs.
[b]Using b^{02}.
[c]Using b^{11}.
[d]Dirac $\langle r^{-3}\rangle$ integrals in a model potential.
[e]Optical data, Dirac-Slater $\langle r^{-3}\rangle$ integrals.
[f]Dirac-Fock and Dirac-Slater $\langle r^{-3}\rangle$ integrals.

of $Q(\mathrm{DC}) = -505.69$ mb, together with a correction arising from the Breit interaction (−10.32 mb), yields the final $Q = -516$ (15) mb, as extracted from experimental value $B = -305.067(2)$ MHz [9] and from the calculated electric field gradient.

Table I presents the electric quadrupole moment Q of the ^{209}Bi isotope, compared to values from the literature. Our result appears to be outside the error bars of nearly all of them, with the exception of two pionic determinations. However, the accuracy of the pionic values is much worse than ours.

TABLE II. Nuclear electric quadrupole moments for various Bi isotopes deduced from experimental values of hyperfine structure constants $B(^4S_{3/2})$ of reference isotope 209 and of other isotopes, and from calculated electric field gradient.

Isotope	I^π	Q (mb)
202	(5^+)	−1001 (86)
202	(6^+)	−1214 (92)
203	$9/2^-$	−929 (73)
204	6^+	−677 (204)
205	$9/2^-$	−814 (29)
206	6^+	−538 (37)
207	$9/2^-$	−759 (23)
208	5^+	−704 (79)
209	$9/2^-$	−516 (15)
210	(1^-)	190.1 (5.6)
210^m	9^-	−655 (70)
212	(1^-)	135 (381)
213	$9/2^-$	−830 (49)

We have performed a thorough evaluation of electron correlation effects, including deep core polarization, and saturation of (very large) multiconfigurational Dirac-Fock space for the $6p^3\,^4S_{3/2}$ ground state of bismuth. We propose a new value of −516 (15) mb for the electric quadrupole moment of the ^{209}Bi isotope. Noting the large variation in recent literature, the two main candidates being −370 (26) mb [1,7] or −500 (80) mb [6], this is an important benchmark. The resultant values of the quadrupole moments of the other Bi isotopes are given in Table II (the bracketed spin assignments in Table II are explained in Ref. [8]). These were deduced from the experimental hyperfine structure constant $B(^4S_{3/2})$ of Hull and Brink [9] for isotope 209, from the hyperfine structure constants $B(^4S_{3/2})$ for the other isotopes taken from the Table I of Pearson *et al.* (Ref. [8]), and from the nuclear quadrupole moment of isotope 209 evaluated in the present work.

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