

## Quadrupole moments and hyperfine constants of metastable states of $\text{Ca}^+$ , $\text{Sr}^+$ , $\text{Ba}^+$ , $\text{Yb}^+$ , $\text{Hg}^+$ , and $\text{Au}$

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Atomic quadrupole moments and hyperfine constants of the metastable  ${}^2D_{3/2,5/2}$  states of  $\text{Ca}^+$ ,  $\text{Sr}^+$ ,  $\text{Ba}^+$ ,  $\text{Yb}^+$ , and  $\text{Hg}^+$  are calculated by the multiconfiguration Dirac-Hartree-Fock and relativistic configuration-interaction methods. For  $\text{Hg}^+$ , the configuration is  $5d^96s^2$ . For the other ions, the configuration consists of a single  $d$ -electron outside a set of closed shells. Current interest in the quadrupole moments of these states is due to the fact that optical transitions of these ions may be useful as references for frequency standards. Energy shifts of the metastable states due to the interactions of the quadrupole moments with external electric field gradients are among the largest sources of error in these frequency standards. For the quadrupole moments, agreement is obtained to within about 10% with the available measurements. For the hyperfine constants, good agreement is obtained with measurements and with other calculations, except for the  $A$  factors of the  ${}^2D_{5/2}$  states of  $\text{Sr}^+$ ,  $\text{Ba}^+$ , and  $\text{Yb}^+$ , where the correlation effects are so large that they reverse the sign of the constant relative to the Dirac-Hartree-Fock value. As a test of the  $\text{Hg}^+$  calculational methods, quadrupole moments and hyperfine constants are calculated for the  $5d^96s^2$   ${}^2D_{3/2,5/2}$  states in isoelectronic neutral  $\text{Au}$ . This yields a value of the nuclear quadrupole moment  $Q(^{197}\text{Au}) = +0.587(29)$  b.

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### I. INTRODUCTION

The electric quadrupole moment  $\Theta(\gamma, J)$  of an atom in electronic state  $|\gamma J\rangle$  having total electronic angular momentum  $J$  is conventionally defined by the diagonal matrix element in the sublevel with the maximum value of the magnetic quantum number  $M_J$ :

$$\Theta(\gamma, J) = -e \left\langle \gamma J J \left| \sum_{i=1}^N r_i^2 C_0^2(\theta_i, \phi_i) \right| \gamma J J \right\rangle, \quad (1)$$

where  $e$  is the elementary charge,  $r_i$  is the radial coordinate of the  $i$ th electron,  $C_0^2$  is a spherical harmonic,  $\theta_i$  and  $\phi_i$  are the angular coordinates of the  $i$ th electron, and the summation is over all  $N$  electrons.

In comparison with other atomic properties, such as oscillator strengths or hyperfine constants, atomic quadrupole moments have received little theoretical attention, due in part to the lack of experimental data. Only a few atomic quadrupole moments have been measured, and most of the theoretical work appears to have been focused on these cases.

The quadrupole moments of the  $3p$   ${}^2P_{3/2}$  state of  $\text{Al}$ , the  $5p$   ${}^2P_{3/2}$  state of  $\text{In}$ , and the metastable  $np^5(n+1)s$   ${}^3P_2$  states of  $\text{Ne}$ ,  $\text{Ar}$ ,  $\text{Kr}$ , and  $\text{Xe}$  ( $n=2, 3, 4$ , and  $5$ , respectively) were measured by atomic beam radio frequency spectroscopy [1,2]. In these experiments, energy level shifts were observed upon application of an external electric field gradient. The quadrupole moments of the  $4$   ${}^3P$  and  $5$   ${}^3P$  excited states of  $\text{He}$  were determined indirectly from measurements of the anisotropy of the diamagnetic susceptibility [3,4]. Since the quadrupole moment of the ionic core influences the fine-structure of nonpenetrating Rydberg states, it is possible to extract the quadrupole moment of the ion from an analysis of

the Rydberg spectrum of the neutral atom [5]. The quadrupole moments of several atomic ions, including  $\text{C}^+$  [5,6],  $\text{Ne}^+$  [5–9], and  $\text{N}^+$  [5,10], have been determined in this way.

Current interest in the quadrupole moments of the metastable states of certain atomic ions stems from the application of narrow optical transitions to frequency standards [11]. For several ions that might be used for frequency standards, including  $\text{Ca}^+$ ,  $\text{Sr}^+$ ,  $\text{Ba}^+$ ,  $\text{Yb}^+$ , and  $\text{Hg}^+$ , the energy shifts due to the interaction of the quadrupole moments of the metastable states with stray electric field gradients, due, for example, to stray electric charges on ion trap electrodes, are among the largest sources of systematic error. This problem was pointed out by Dehmelt [12]. In practice, it does not affect neutral-atom optical frequency standards to the same extent because of the absence of nearby charged objects. Recently, the quadrupole moments of the  $4d$   ${}^2D_{5/2}$  state of  $\text{Sr}^+$  [13], the  $5d$   ${}^2D_{3/2}$  state of  $\text{Yb}^+$  [14], and the  $5d^96s^2$   ${}^2D_{5/2}$  state of  $\text{Hg}^+$  [15] were determined by observing the changes in the optical transition frequencies as static electric field gradients were applied.

In a first approximation, the metastable  $nd$   ${}^2D_{3/2,5/2}$  states of  $\text{Ca}^+$ ,  $\text{Sr}^+$ ,  $\text{Ba}^+$ , and  $\text{Yb}^+$  ( $n=3, 4, 5$ , and  $5$ , respectively) are described by a single configuration involving one  $d$ -electron outside a set of filled shells or, in the case of  $\text{Hg}^+$  and isoelectronic  $\text{Au}$ , a single  $d$ -vacancy in a set of otherwise filled shells. In this approximation, the quadrupole moment is due entirely to the single  $d$ -electron or  $d$ -vacancy. A single-configuration estimate of the quadrupole moment of the  $5d^96s^2$   ${}^2D_{5/2}$  state of  $\text{Hg}^+$  was published in Ref. [16]. However, electron correlation effects can in some cases lead to large corrections to the single-configuration estimates for the quadrupole moments. For example, the metastable  ${}^3P_2$  states of the rare gases  $\text{Ne}$ ,  $\text{Ar}$ ,  $\text{Kr}$ , and  $\text{Xe}$  are known to have quadrupole moments that deviate strongly from the single-configuration values [2]. For  $\text{Kr}$  and  $\text{Xe}$ , even the signs of the

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quadrupole moments differ from the single-configuration predictions.

Sternheimer obtained good agreement with experiment for the rare gas quadrupole moments with a perturbative model in which the outer  $(n+1)s$  orbital is polarized by the  $np$  vacancy [17,18]. Although Sternheimer's results were in good agreement with experiment, Sundholm and Olsen regarded this agreement as fortuitous, particularly for Xe [19]. For Xe, they showed that the DTQ electron correlation contribution (due to double, triple, and quadruple excitations from the  $5p$  and  $6s$  shells), relativistic corrections, and excitations to virtual  $f$  and  $g$  orbitals all make contributions to the quadrupole moment of about the same magnitude as the total moment. None of these effects are included in Sternheimer's treatment. Sundholm and Olsen applied the multiconfiguration Hartree-Fock (MCHF) method to calculate the quadrupole moments of the rare gas metastable atoms and some other atoms, including Al, In, Be, Ca,  $C^+$ ,  $Ne^+$ , and  $Ar^+$  [19–22]. Agreement with experiment is good for the cases that have been measured. The electric quadrupole moments of the metastable  $^3P_2$  states of Mg, Ca, and Sr have been calculated because of their importance in ultracold collision processes [23–25]. Recently, Sur *et al.* have calculated the quadrupole moment of the  $4d\ ^2D_{5/2}$  state of  $Sr^+$  by the relativistic coupled-cluster method [26].

In this work, I apply the multiconfiguration Dirac-Hartree-Fock (MCDHF) method, i.e., the relativistic generalization of the MCHF method. In the final stages of the calculations, relativistic configuration-interaction (RCI) calculations are carried out, using the orbitals determined by MCDHF. This method of computing the atomic wave function is similar to that used by Bieroń and co-workers to calculate atomic hyperfine constants [27]. MCDHF appears not to have been applied previously to the calculation of atomic quadrupole moments. It has the advantage of taking relativity into account from the start, rather than as a correction applied at the end of the calculation, as is done with the MCHF method [19]. This is especially important for heavy atoms such as  $Yb^+$  and  $Hg^+$ . Some preliminary results have been published [15]. In addition, the magnetic dipole ( $A$ ) and electric quadrupole ( $B$ ) hyperfine constants are calculated and compared with experiment, as an indication of the quality of the wave functions. The calculation for  $Hg^+$  was more complex than for the other ions because of the presence of the open  $d$ -shell. Also, there are few measurements of the hyperfine constants of the  $5d^9 6s^2\ ^2D_{3/2,5/2}$  states. For this reason, equivalent calculations were made for Au, which is isoelectronic to  $Hg^+$ , and for which the  $A$  and  $B$  hyperfine constants have been measured for both fine-structure states [28,29].

## II. METHODS

### A. Single-configuration estimates of the quadrupole moment

In a single-configuration Hartree-Fock (HF) or Dirac-Hartree-Fock (DHF) approximation,  $\Theta(\gamma, J)$  depends only on the mean values of  $r^2$  for the electrons which are not in closed shells. For a configuration consisting of a single  $nd$ -electron outside a set of filled shells, the electric quadrupole

moments for the  $J=3/2$  and  $J=5/2$  states are

$$\Theta(nd, 3/2) = \frac{e}{5} \langle nd_{3/2} | r^2 | nd_{3/2} \rangle, \quad (2a)$$

$$\Theta(nd, 5/2) = \frac{2e}{7} \langle nd_{5/2} | r^2 | nd_{5/2} \rangle. \quad (2b)$$

For a  $nd^9 n' s^2$  configuration as in  $Hg^+$ , Eqs. (2a) and (2b) hold with a change of sign because the electric quadrupole moment is due to a single vacancy in an otherwise filled shell rather than to a single electron. In the nonrelativistic Hartree-Fock approximation,  $\langle nd_j | r^2 | nd_j \rangle$  does not depend on  $j$ . Several estimates of  $\Theta(\gamma, J)$  based on Eqs. (2a) and (2b) have appeared in the literature [13,16,30,31]. The radial matrix elements were estimated from Cowan's Hartree-Fock program [32] or from simple Coulombic wave functions.

### B. Multiconfiguration Dirac-Hartree-Fock method

One method of obtaining an approximation to the relativistic atomic wave function is the MCDHF method [33]. In the MCDHF method an atomic state function  $|\Gamma P J M_J\rangle$  of parity  $P$ , electronic angular momentum  $J$ , and  $z$ -component of electronic angular momentum  $M_J$  is taken to be a linear combination of relativistic configurational state functions (CSFs)  $|\gamma_k P J M_J\rangle$ :

$$|\Gamma P J M_J\rangle = \sum_k c_k |\gamma_k P J M_J\rangle, \quad (3)$$

where each CSF is a linear combination of antisymmetrized product wave functions (Slater determinants) such that the CSF has definite values of  $P$ ,  $J$ , and  $M_J$ . The CSFs differ from one another by the orbitals (single-electron radial functions) that are occupied and in the ways in which the angular momenta of the electrons are coupled together.

In a MCDHF calculation, the atomic Hamiltonian is usually taken to be the Dirac-Coulomb Hamiltonian, which includes the kinetic energy of each electron and the Coulomb interactions of each electron with the nucleus and with the other electrons. Additional terms, such as the Breit interaction, may be included but increase the difficulty of the calculation. Solving the MCDHF equations then determines an approximate eigenfunction of the Dirac-Coulomb Hamiltonian having the form of Eq. (3) by optimizing both the orbitals and the coefficients  $c_k$ .

Once a set of orbitals has been determined by MCDHF using a limited set of CSFs, the atomic state function can be improved by a RCI calculation, in which the Dirac-Coulomb Hamiltonian matrix (with or without the Breit interaction) is diagonalized in a basis consisting of an expanded set of CSFs. The CSFs are generated from the orbitals calculated in the previous steps. The result of an RCI calculation is an atomic state function having the form of Eq. (3), but only the coefficients and not the orbitals are optimized. Given an approximate atomic state function, obtained by either MCDHF or RCI, the atomic quadrupole moment can be calculated by evaluating Eq. (1).

TABLE I. Nuclear spins  $I$  and quadrupole moments  $Q$  used in the calculations of electric quadrupole hyperfine constants  $B$  ( $1 \text{ b} = 10^{-28} \text{ m}^2$ ).

Nucleus	$I$	$Q$ (b)	Reference
$^{43}\text{Ca}$	7/2	-0.0408(8)	[42]
$^{87}\text{Sr}$	9/2	+0.335(20)	[42]
$^{137}\text{Ba}$	3/2	+0.245(4)	[42]
$^{173}\text{Yb}$	5/2	+2.80(4)	[42]
$^{201}\text{Hg}$	3/2	+0.387(6)	[27]
$^{197}\text{Au}$	3/2	+0.547(16)	[42]

### C. Computational details

In the present work, the MCDHF and RCI calculations were carried out with versions of the GRASP (general-purpose relativistic atomic structure program) code [34–36]. Modules from the GRASP92 version, documented in Ref. [36], and the GRASPVU version, available from a website [37], were used.

Successively improved approximations to the atomic state functions were made in three stages. First, the orbitals belonging to the shells that are occupied in the lowest-order approximation were calculated by minimizing an energy functional that weighted the  $^2D_{3/2}$  and  $^2D_{5/2}$  states by their statistical  $(2J+1)$  weights. This is called an extended-optimal-level (EOL) calculation [35]. For example, in the calculation for the  $\text{Ca}^+ 3d \ ^2D_{3/2}$  and  $3d \ ^2D_{5/2}$  states, the  $1s$ ,  $2s$ ,  $2p$ ,  $3s$ ,  $3p$ , and  $3d$  orbitals were optimized. (Here,  $2p$  refers to both the  $2p_{1/2}$  and  $2p_{3/2}$  orbitals, etc.) Orbitals belonging to the same angular momentum were required to be orthogonal. A Fermi model was used for the nuclear charge distribution. The Breit interaction, QED effects, and finite nuclear mass effects were ignored throughout the calculation.

In the second stage of the calculation, several layers of virtual orbitals were successively optimized in a series of MCDHF-EOL calculations. Each layer consisted of a set of orbitals having different angular momenta. All previously calculated orbitals were kept fixed, and only the new orbitals were optimized. Different orbitals of the same angular momentum were required to be orthogonal. A limited set of CSFs was considered. CSFs generated by allowing excitations of valence electrons, with or without single excitations of certain core shells, were included.

In the final stage of the calculation, the set of CSFs was systematically increased by allowing single excitations from lower-lying core shells with or without valence excitations (core-valence correlation) and double or triple excitations from some of the higher-lying core shells (core-core correlation) to unoccupied shells. RCI calculations were then carried out in the expanded basis of CSFs, using the orbitals determined in the previous stage. A practical limit to the number of CSFs in a single RCI calculation was somewhat above 45 000 for a single  $J$ -value. The general method is similar to that used by Bieroń *et al.* for the calculation of hyperfine constants of neutral mercury [27]. At each step of the calculation, the hyperfine constants and atomic quadrupole moments were calculated. The program HFS92 [38] was used to calculate the  $A$  and  $B$  hyperfine constants. I made a minor modification to the  $B$  constant part of HFS92 to enable it to calculate atomic quadrupole moments. In some cases, core-valence contributions to the quadrupole moment and to the hyperfine constants from different core shells were calculated in separate RCI calculations and then combined, making use of the fact that such contributions are approximately additive.

Just before this paper was submitted for publication, the author learned of an error in the GRASP codes, specifically in the library function `tnsrj.f` [39]. The calculations were repeated with the corrected codes. In some cases, the values of the atomic quadrupole moments and the  $B$  factors calculated with the corrected codes differ by as much as a few percent from those calculated with the uncorrected codes. The values of the  $A$  factors are not affected to the same extent.

### D. Nuclear models and moments

For each of the atoms studied,  $\text{Ca}^+$ ,  $\text{Sr}^+$ ,  $\text{Ba}^+$ ,  $\text{Yb}^+$ ,  $\text{Hg}^+$ , and  $\text{Au}$ , a particular isotope was chosen to define the nuclear charge distribution  $\rho(r)$  used for the Dirac-Coulomb Hamiltonian used for the MCDHF and RCI calculations. A Fermi distribution of the form

$$\rho(r) = \frac{\rho_0}{1 + e^{(r-c)/a}} \quad (4)$$

is assumed, with fitted values for the  $a$  and  $c$  parameters [40]. The isotopes chosen for the calculations were  $^{43}\text{Ca}$ ,  $^{87}\text{Sr}$ ,  $^{137}\text{Ba}$ ,  $^{171}\text{Yb}$ ,  $^{199}\text{Hg}$ , and  $^{197}\text{Au}$ . The  $^{171}\text{Yb}$  and  $^{199}\text{Hg}$

TABLE II. Quadrupole moments (in atomic units) and hyperfine constants (in MHz) for  $^{43}\text{Ca}^+ 3d \ ^2D_{3/2,5/2}$  states calculated with different approximations to the atomic state function.

Step	Description	$\Theta_{3/2}$	$A_{3/2}$	$B_{3/2}$	$\Theta_{5/2}$	$A_{5/2}$	$B_{5/2}$
1	DHF	1.461	-39.12	-2.61	2.093	-16.66	-3.70
2	MCDHF (+layer 1)	1.307	-46.69	-1.83	1.872	-8.90	-2.60
3	MCDHF (+layers 1,2)	1.266	-49.83	-2.75	1.815	-7.89	-3.91
4	MCDHF (+layers 1-3)	1.228	-51.47	-2.72	1.759	-6.35	-3.86
5	MCDHF (+layers 1-4)	1.139	-52.51	-2.99	1.633	-6.74	-4.25
6	MCDHF (+layers 1-5)	1.136	-52.60	-2.94	1.629	-6.28	-4.17
7	RCI (step 6+{3s,3p} c-c to layer 1)	1.322	-47.41	-2.93	1.894	-5.16	-4.16
8	RCI (step 6+{3s,3p} c-c to layers 1,2)	1.338	-47.27	-2.94	1.917	-4.84	-4.18

TABLE III. Comparison of calculated and measured hyperfine constants (in MHz) for  $^{43}\text{Ca}^+ 3d^2D_{3/2,5/2}$ . Theoretical  $B$  factors are scaled to the nuclear quadrupole moments listed in Table I.

	Present calc. <sup>a</sup>	Other calc. <sup>b</sup>	Other calc. <sup>c</sup>	Other calc. <sup>d</sup>	Other calc. <sup>e</sup>	Expt. <sup>f</sup>	Expt. <sup>g</sup>
$A_{3/2}$	-47.27	-47.824	-46.70	-49.4	-52	-47.3(0.2)	-48.3(1.6)
$B_{3/2}$	-2.94	-2.777			-2.77	-3.7(1.9)	-0.5(6.0)
$A_{5/2}$	-4.84	-3.552	-3.49	-4.2	-5.2	-3.8(0.6)	
$B_{5/2}$	-4.18	-4.088			-3.97	-3.9(6.0)	

<sup>a</sup>Table II, step 8.

<sup>b</sup>Relativistic many-body perturbation theory [46].

<sup>c</sup>Relativistic coupled-cluster theory [53].

<sup>d</sup>Many-body perturbation theory with relativistic correction [54].

<sup>e</sup>Many-body perturbation theory [55].

<sup>f</sup>Reference [56].

<sup>g</sup>Reference [57].

isotopes were chosen because they are currently used in atomic frequency standards, but since they both have nuclear spin  $I=1/2$ , they provide no information about the electric quadrupole hyperfine structure. For that reason, the hyperfine constants were also calculated for  $^{173}\text{Yb}^+$  ( $I=5/2$ ) and for  $^{201}\text{Hg}^+$  ( $I=3/2$ ). The atomic wave functions calculated for  $^{171}\text{Yb}^+$  and  $^{199}\text{Hg}^+$  were used.

The nuclear magnetic moments are sufficiently well-known that their uncertainties are likely to be much less than the errors in the atomic calculations for  $A$ . The values of the nuclear magnetic moments were taken from the tables of Raghavan [41]. However, nuclear quadrupole moments ( $Q$ ) are less well-known, since they are not measured directly. Nuclear quadrupole moments derived from interaction constants in atoms, molecules, or solids depend on difficult calculations of the electric field gradients at the nucleus. Values derived from muonic x-ray spectra are subject to other systematic errors. For example, some muonic determinations of the nuclear quadrupole moment of  $^{201}\text{Hg}$  differ from each other by more than their combined uncertainties [27]. The  $Q$  values used in these calculations are given in Table I. Most of the values were taken from the compilation of Pyykkö [42]. It is a simple matter to rescale the  $B$  constants if better  $Q$  values become available.

### III. RESULTS

#### A. $\text{Ca}^+$

The results of the calculation for  $^{43}\text{Ca}^+$  are given in Table II. DHF refers to a Dirac-Hartree-Fock EOL calculation. Five layers of virtual orbitals were optimized in a series of MCDHF-EOL calculations. All CSFs having the proper parity and total angular momentum that could be constructed by allowing single and double excitations from the valence  $3d$  and the  $\{2s, 2p, 3s, 3p\}$  core shells, with at most one core excitation, were included. The orbitals in layers 1–5 were  $\{4s, 4p, 4d, 4f, 5g, 6h\}$ ,  $\{5s, 5p, 5d, 5f, 6g\}$ ,  $\{6s, 6p, 6d, 6f\}$ ,  $\{7s, 7p, 7d\}$ , and  $\{8s, 8p, 8d\}$ , respectively. A limited amount of core-core (c-c) correlation was then included by considering the CSFs obtained by allowing double excitations from the  $\{3s, 3p\}$  core shells to layer 1 (step 7) and to layers 1 and 2 (step 8). This set of CSFs was added to the set used in the step 7 MCDF calculation. The atomic state functions were then optimized in RCI calculations. It is of interest to note that the final values of the quadrupole moments and the hyperfine constants are not too different from the DHF values, except for  $A_{5/2}$ , which is smaller in magnitude by a factor of 3.4.

Table III compares the results of the final RCI calculation

TABLE IV. Quadrupole moments (in atomic units) and hyperfine constants (in MHz) for  $^{87}\text{Sr}^+ 4d^2D_{3/2,5/2}$  states calculated with different approximations to the atomic state function.

Step	Description	$\Theta_{3/2}$	$A_{3/2}$	$B_{3/2}$	$\Theta_{5/2}$	$A_{5/2}$	$B_{5/2}$
1	DHF	2.309	-34.23	29.56	3.332	-14.27	40.45
2	MCDHF (+layer 1)	2.083	-45.14	23.47	3.009	0.57	32.34
3	MCDHF (+layers 1,2)	2.021	-47.32	32.66	2.921	-1.01	45.33
4	MCDHF (+layers 1–3)	1.966	-50.96	33.73	2.843	-1.38	46.68
5	MCDHF (+layers 1–4)	1.847	-51.36	35.10	2.674	-2.31	48.63
6	MCDHF (+layers 1–5)	1.844	-51.59	34.76	2.670	-2.07	48.14
7	RCI (step 6+ $\{3s, 3p\}$ c-v)	1.831	-52.20	41.92	2.651	-2.64	58.14
8	RCI (step 6+ $\{3d, 4s, 4p\}$ c-c to layer 1)	2.093	-46.13	34.96	3.028	-2.61	48.38
9	RCI (step 6+ $\{4s, 4p\}$ c-c to layers 1,2)	2.101	-45.14	34.04	3.038	-2.12	47.13
10	RCI (step 8 $\cup$ step 9)	2.117	-45.26	34.30	3.061	-2.37	47.50
11	RCI (step 7 $\cup$ step 8 $\cup$ step 9)	2.107	-45.60	41.04	3.048	-2.77	56.94

TABLE V. Comparison of calculated and measured quadrupole moments (in atomic units) and hyperfine constants (in MHz) for  $^{87}\text{Sr}^+ 4d^2D_{3/2,5/2}$ . Theoretical  $B$  factors are scaled to the nuclear quadrupole moments listed in Table I.

	Present calc. <sup>a</sup>	Other calc. <sup>b</sup>	Other calc. <sup>c</sup>	Other calc. <sup>d</sup>	Expt. <sup>e</sup>	Expt. <sup>f</sup>
$A_{3/2}$	-45.60	-47.356	-47			
$B_{3/2}$	41.04	39.610	38.5			
$\Theta_{5/2}$	3.048			2.94(7)		2.6(3)
$A_{5/2}$	-2.77	2.507	1		2.1743(14)	
$B_{5/2}$	56.94	56.451	56.0		49.11(6)	

<sup>a</sup>Table IV, step 11.

<sup>b</sup>Relativistic many-body perturbation theory [46].

<sup>c</sup>Relativistic coupled-cluster theory [45].

<sup>d</sup>Relativistic coupled-cluster theory [26].

<sup>e</sup>Reference [58].

<sup>f</sup>Reference [13].

with experiment and with other calculations. The agreement of the calculated value for  $A_{3/2}$  with both experiment and with other recent calculations is excellent. For  $A_{5/2}$ , where the corrections to the DHF value are very large, the calculated value disagrees with experiment by about two experimental standard deviations. The calculated  $B_{3/2}$  and  $B_{5/2}$  factors are in agreement with experiment, but the experimental uncertainties are large. They agree well with other calculations.

### B. $\text{Sr}^+$

The results of the calculation for  $^{87}\text{Sr}^+$  are given in Table IV. Similarly to the calculation for  $\text{Ca}^+$ , five layers of virtual orbitals were optimized in a series of MCDHF-EOL calculations. Single and double excitations from the valence  $4d$  and the  $\{3d, 4s, 4p\}$  core shells, with at most one core excitation, were included. The orbitals in layers 1–5 were  $\{5s, 5p, 5d, 4f, 5g, 6h\}$ ,  $\{6s, 6p, 6d, 5f, 6g\}$ ,  $\{7s, 7p, 7d, 6f\}$ ,

$\{8s, 8p, 8d\}$ , and  $\{9s, 9p, 9d\}$ , respectively. Step 7 is an RCI calculation including the CSFs of step 6 and also those involving single excitations from the  $\{3s, 3p\}$  shells. This adds core-valence correlation not already included in the MCDHF calculations. Other RCI calculations including core-core correlation were made, allowing double excitations from the  $\{3d, 4s, 4p\}$  shells to layer 1 (step 8) and allowing double excitations from the  $\{4s, 4p\}$  shells to layers 1 and 2 (step 9), in addition to the step 6 CSFs. Step 10 is an RCI calculation with a set of CSFs that is the union of the sets used for steps 8 and 9. Step 11 uses the union of the sets of CSFs used for steps 7 and 10.

Table V compares the final results with experiment and with other calculations. There are no experimental results for the  $4d^2D_{3/2}$  state. The present results are generally in good agreement with other calculations and with the available experimental data, with the exception of  $A_{5/2}$ . It appears that the correlation correction to  $A_{5/2}$  is so large as to change its sign relative to the DHF value. The difference between the

TABLE VI. Quadrupole moments (in atomic units) and hyperfine constants (in MHz) for  $^{137}\text{Ba}^+ 5d^2D_{3/2,5/2}$  states calculated with different approximations to the atomic state function.

Step	Description	$\Theta_{3/2}$	$A_{3/2}$	$B_{3/2}$	$\Theta_{5/2}$	$A_{5/2}$	$B_{5/2}$
1	DHF	2.589	139.23	35.44	3.788	55.82	45.36
2	MCDHF (+layer 1)	2.284	184.37	24.60	3.354	-20.04	31.98
3	MCDHF (+layers 1,2)	2.202	193.43	35.99	3.239	-10.71	47.79
4	MCDHF (+layers 1–3)	2.110	202.28	35.46	3.116	-9.26	46.82
5	MCDHF (+layers 1–4)	2.094	201.80	36.63	3.088	-6.07	48.72
6	MCDHF (+layers 1–5)	2.073	203.12	36.35	3.051	-7.21	48.01
7	RCI (step 6+ $\{4s, 4p\}$ c-v)	2.061	208.36	46.60	3.034	-4.72	61.87
8	RCI (step 6+ $\{3s, 3p, 3d, 4s, 4p\}$ c-v)	2.058	212.70	49.63	3.029	0.09	65.92
9	RCI (step 6+ $\{5s, 5p\}$ c-c to layer 1)	2.268	185.86	39.33	3.338	-2.10	51.98
10	RCI (step 6+ $\{5s, 5p\}$ c-c to layers 1,2)	2.279	184.05	38.62	3.354	-3.27	51.07
11	RCI (step 6+ $\{4d, 5s, 5p\}$ c-c to layer 1)	2.299	185.90	40.03	3.382	0.05	52.92
12	RCI (step 10 $\cup$ step 11)	2.309	184.31	39.38	3.397	-1.01	52.08
13	RCI (step 7 $\cup$ step 10 $\cup$ step 11)	2.299	188.65	48.29	3.384	4.59	64.11
14	Step 13+ $\{3s, 3p, 3d\}$ c-v	2.297	192.99	51.32	3.379	9.39	68.16

TABLE VII. Comparison of calculated and measured hyperfine constants (in MHz) for  $^{137}\text{Ba}^+ 5d^2D_{3/2,5/2}$ . Theoretical  $B$  factors are scaled to the nuclear quadrupole moments listed in Table I.

	Present calc. <sup>a</sup>	Other calc. <sup>b</sup>	Other calc. <sup>c</sup>	Expt. <sup>d</sup>
$A_{3/2}$	192.99	188.76	215	189.7296(7)
$B_{3/2}$	51.32		47.3	44.5408(17)
$A_{5/2}$	9.39		-18	-12.028(11)
$B_{5/2}$	68.16		63.2	59.533(43)

<sup>a</sup>Table VI, step 14.

<sup>b</sup>Relativistic coupled-cluster theory [59].

<sup>c</sup>Many-body perturbation theory [60].

<sup>d</sup>Reference [60].

present calculation and the experimental value is  $-4.94$  MHz, which is 30% of the total correlation correction, obtained by taking the difference of the DHF value and the experimental value. The fact that three calculations yield a value for  $B_{5/2}$  of approximately 56 MHz, while the experimental value is 49.11(6) MHz, suggests that the  $^{87}\text{Sr}$  nuclear quadrupole might be approximately 0.29 b, rather than 0.335(20) b as listed in Table I. The value in Table I is based on the measured  $B$  factor of the  $5s5p^3P_2$  state of  $^{87}\text{Sr}$ , combined with a semiempirical calculation of the electric field gradient based on the measured magnetic dipole hyperfine interaction constants [43]. A calculated Sternheimer antishielding correction [44] was applied. Some other recent determinations of  $Q$  for  $^{87}\text{Sr}$ , based on the measured  $B$  factor of the  $5p^2P_{3/2}$  state of  $^{87}\text{Sr}^+$  combined with *ab initio* calculations of the electric field gradient, are 0.327(24) b [45] and 0.323(20) b [46]. The present calculation of  $\Theta_{5/2}$  agrees to within 4% with a recent relativistic coupled-cluster calculation. The measured value of  $\Theta_{5/2}$  disagrees with the present calculation by about 1.5 standard deviations of the measurement.

TABLE VIII. Quadrupole moments (in atomic units) and hyperfine constants (in MHz) for  $^{171}\text{Yb}^+$  and  $^{173}\text{Yb}^+ 5d^2D_{3/2,5/2}$  states calculated with different approximations to the atomic state function.

Step	Description	$^{171}\text{Yb}^+$				$^{173}\text{Yb}^+$			
		$\Theta_{3/2}$	$A_{3/2}$	$\Theta_{5/2}$	$A_{5/2}$	$A_{3/2}$	$B_{3/2}$	$A_{5/2}$	$B_{5/2}$
1	DHF	2.343	319.59	3.467	121.39	-88.03	612.0	-33.44	719.5
2	MCDHF (+layer 1)	2.157	383.38	3.204	-82.91	-105.60	474.8	22.84	564.0
3	MCDHF (+layers 1,2)	1.989	404.88	2.989	-82.82	-111.52	649.7	22.81	815.3
4	MCDHF (+layers 1-3)	1.891	437.03	2.847	-87.12	-120.38	686.8	24.00	845.8
5	MCDHF (+layers 1-4)	1.845	430.20	2.780	-83.48	-118.50	687.4	22.99	853.1
6	MCDHF (+layers 1-5)	1.823	435.77	2.743	-83.95	-120.03	694.9	23.12	861.4
7	RCI (step 6+{4s,4p,4d} c-v)	1.805	467.15	2.718	-61.08	-128.67	965.0	16.82	1207.3
8	RCI (step 6+{3s,3p,3d,4s,4p,4d} c-v)	1.804	469.95	2.716	-61.07	-129.45	981.7	16.82	1228.7
9	RCI (step 6+4f c-c to layer 1')	2.036	401.79	3.047	-53.12	-110.67	694.0	14.63	860.5
10	RCI (step 6+{4f,5s,5p} c-c to layer 1')	2.183	384.04	3.256	-26.55	-105.78	748.8	7.31	929.8
11	RCI (step 7 $\cup$ step 10)	2.175	397.68	3.245	-12.59	-109.54	934.7	3.47	1169.0
12	Step 11+{3s,3p,3d} c-v	2.174	400.48	3.244	-12.58	-110.31	951.4	3.47	1190.4

### C. Ba<sup>+</sup>

The results of the calculation for  $^{137}\text{Ba}^+$  are given in Table VI. Five layers of virtual orbitals were optimized in a series of MCDHF-EOL calculations. Single and double excitations from the valence  $5d$  and the  $\{4d,5s,5p\}$  core shells, with at most one core excitation, were included. The orbitals in layers 1-5 were  $\{6s,6p,6d,4f,5g,6h\}$ ,  $\{7s,7p,7d,5f,6g\}$ ,  $\{8s,8p,8d,6f\}$ ,  $\{9s,9p,9d\}$ , and  $\{10s,10p,10d\}$ , respectively. Step 7 is an RCI calculation including the CSFs of step 6 and also those involving single excitations from the  $\{4s,4p\}$  shells (additional core-valence correlation). In step 8, core-valence correlation involving the  $\{3s,3p,3d\}$  shells is added in an RCI calculation. Other RCI calculations including core-core correlation were made, allowing double excitations from the  $\{5s,5p\}$  shells to layer 1 (step 9) and to layers 1 and 2 (step 10), in addition to the step 6 CSFs. In step 11, double excitations from the  $\{4d,5s,5p\}$  shells to layer 1 were allowed, in addition to the step 6 CSFs. Step 12 is an RCI calculation with a set of CSFs that is the union of the sets used for steps 10 and 11. Step 13 is an RCI calculation that uses the union of the sets of CSFs used for steps 7, 10, and 11. In step 14, the  $\{3s,3p,3d\}$  core-valence contribution (taken as the difference between the results of step 8 and step 7) is added to the results of step 13. It was not feasible to include all of the CSFs of step 13 and step 8 in a single RCI calculation.

Table VII compares the final results with experiment and with other calculations. The present results are generally in good agreement with other calculations and with the available experimental data, with the exception of  $A_{5/2}$ . As with  $^{87}\text{Sr}^+$ , the correlation correction to  $A_{5/2}$  is so large as to change its sign relative to the DHF value. The difference between the present calculation and the experimental value is 21.4 MHz, which is 31% of the total correlation correction.

TABLE IX. Comparison of calculated and measured quadrupole moments (in atomic units) and hyperfine constants (in MHz) for  $^{171}\text{Yb}^+ 5d^2 D_{3/2,5/2}$ .

	Present calc. <sup>a</sup>	Expt. <sup>b</sup>	Expt. <sup>c</sup>	Expt. <sup>d</sup>
$\Theta_{3/2}$	2.174		2.08(11)	
$A_{3/2}$	400.48	430(43)		
$A_{5/2}$	-12.58			-63.6(7)

<sup>a</sup>Table VIII, step 12.

<sup>b</sup>Reference [47].

<sup>c</sup>Reference [14].

<sup>d</sup>Reference [61].

#### D. Yb<sup>+</sup>

The results of the calculations for  $^{171}\text{Yb}^+$  and  $^{173}\text{Yb}^+$  are given in Table VIII. The electronic structures of the lowest-energy states of Yb<sup>+</sup> differ from those of Ba<sup>+</sup> in having fully filled  $4f$  shells. Since the  $4f$  electrons are easily excited, correlation effects are expected to be large. Five layers of virtual orbitals were optimized in a series of MCDHF-EOL calculations. Single and double excitations from the valence  $5d$  and the  $\{4f, 5s, 5p\}$  core shells, with at most one core excitation, were included. The orbitals in layers 1–5 were  $\{6s, 6p, 6d, 5f, 5g, 6h\}$ ,  $\{7s, 7p, 7d, 6f, 6g\}$ ,  $\{8s, 8p, 8d, 7f\}$ ,  $\{9s, 9p, 9d\}$ , and  $\{10s, 10p, 10d\}$ , respectively. Step 7 is an RCI calculation including the CSFs of step 6 and also those involving single excitations from the  $\{4s, 4p, 4d\}$  shells. In step 8, core-valence correlation involving the  $\{3s, 3p, 3d\}$  shells is added in an RCI calculation. Step 9 is an RCI calculation allowing double excitations from the  $4f$  shell to layer 1' (layer 1 without  $6h$ ), in addition to the step 6 CSFs. In step 10, double excitations from the  $\{4f, 5s, 5p\}$  shells to layer 1' were allowed, in addition to the step 6 CSFs. Step 11

is an RCI calculation with a set of CSFs that is the union of the sets used for steps 7 and 10. In step 12, the  $\{3s, 3p, 3d\}$  core-valence contribution (taken as the difference between the results of step 8 and step 7) is added to the results of step 11.

Table IX compares the final results for  $^{171}\text{Yb}^+$  with experiment. It appears that there are no relevant experimental results for  $^{173}\text{Yb}^+$  nor any comparable calculations for either isotope. An experimental value for  $A_{3/2}$  of  $^{171}\text{Yb}^+$  has been published, but without an estimate of the uncertainty [47]. The uncertainty listed in Table IX is based on a private communication [48]. The calculated and measured values agree to within this uncertainty. The sign of the calculated value of  $A_{5/2}$  for  $^{171}\text{Yb}^+$  is correct (unlike the cases for Sr<sup>+</sup> and Ba<sup>+</sup>), but its magnitude differs from the calculated value by about a factor of 5. The difference between the present calculation and the experimental value is 51.1 MHz, which is 28% of the total correlation correction. The present calculation of  $\Theta_{3/2}$  agrees with the experimental value to within the experimental uncertainty of 5%.

#### E. Hg<sup>+</sup>

The results of the calculations for  $^{199}\text{Hg}^+$  and  $^{201}\text{Hg}^+$   $5d^9 6s^2 D_{3/2,5/2}$  states are given in Table X. Hg<sup>+</sup> differs from the other ions considered here in having a more complex electronic configuration. This necessitated carefully limiting the CSF expansions to keep the total number of CSFs per  $J$  state below about 45 000. Four layers of virtual orbitals were optimized in a series of MCDHF-EOL calculations. Single and double excitations from the valence  $6s$  and the  $\{5s, 5p, 5d\}$  core shells, with at most one core excitation, were included. The orbitals in layers 1–4 were  $\{7s, 6p, 6d, 5f, 5g, 6h\}$ ,  $\{8s, 7p, 7d, 6f, 6g\}$ ,  $\{9s, 8p, 8d\}$ , and  $\{10s, 9p\}$ , respectively. The change in the  $A$  and  $B$  factors

 TABLE X. Quadrupole moments (in atomic units) and hyperfine constants (in MHz) for  $^{199}\text{Hg}^+$  and  $^{201}\text{Hg}^+ 5d^9 6s^2 D_{3/2,5/2}$  states calculated with different approximations to the atomic state function.

Step	Description	$^{199}\text{Hg}^+$				$^{201}\text{Hg}^+$			
		$\Theta_{3/2}$	$A_{3/2}$	$\Theta_{5/2}$	$A_{5/2}$	$A_{3/2}$	$B_{3/2}$	$A_{5/2}$	$B_{5/2}$
1	DHF	-0.44575	2689.4	-0.68869	991.1	-992.8	-772.2	-365.9	-798.8
2	MCDHF (+layer 1)	-0.33741	2496.7	-0.53697	1087.1	-921.6	-655.5	-401.3	-714.7
3	MCDHF (+layers 1,2)	-0.35076	2507.5	-0.55342	940.2	-925.6	-652.2	-347.1	-722.6
4	MCDHF (+layers 1–3)	-0.34786	2478.6	-0.54965	911.0	-914.9	-662.6	-336.3	-741.3
5	MCDHF (+layers 1–4)	-0.34729	2457.7	-0.54914	900.7	-907.2	-666.4	-332.5	-747.7
6	RCI (step 4+4f c-v)	-0.34726	2447.8	-0.54913	898.4	-903.6	-663.1	-331.6	-742.4
7	RCI (step 4+4d c-v)	-0.34716	2525.2	-0.54898	928.7	-932.2	-682.3	-342.8	-765.2
8	RCI (step 4+4p c-v)	-0.34722	2504.4	-0.54905	922.1	-924.5	-712.0	-340.4	-807.5
9	RCI (step 4+4s c-v)	-0.34739	2452.5	-0.54928	930.6	-905.3	-662.2	-343.5	-740.4
10	RCI (step 4+3d c-v)	-0.34739	2482.8	-0.54929	912.5	-916.5	-664.2	-336.8	-742.8
11	RCI (step 4+ $\{5d, 6s\}$ d c-c)	-0.36528	2506.3	-0.57286	879.3	-925.2	-663.8	-324.6	-746.2
12	RCI (step 4+ $\{5d, 6s\}$ dt c-c)	-0.35470	2441.4	-0.55744	962.1	-901.2	-661.5	-355.1	-742.8
13	RCI (step 12 $\cup$ $\{5s, 5p, 5d\}$ c-c)	-0.36070	2458.5	-0.56627	926.2	-907.5	-666.1	-341.9	-747.4
14	RCI (step 13+ $\{3d, 4spdf\}$ c-v)	-0.35795	2478.3	-0.56374	963.5	-914.8	-737.0	-355.7	-839.4

upon adding layer 4 was on the order of 1%. The change in the quadrupole moments was less than 0.2%. In order to limit the numbers of CSFs, the orbitals of layer 4 were not used in the RCI calculations.

Steps 6–10 are RCI calculations including the CSFs of step 4 and also those involving single excitations from each of the  $4f$ ,  $4d$ ,  $4p$ ,  $4s$ , and  $3d$  core shells individually (additional core-valence correlation). The core-valence contributions to the hyperfine constants are on the order of 1 to 2% per shell for the  $n=4$  shells, but less for the  $3d$  shell. The corresponding contributions to the quadrupole moments are small, less than 0.2% per shell. Step 11 is an RCI calculation allowing double ( $d$ ) excitations from the  $\{5d, 6s\}$  shells to layer 1' ( $\{7s, 6p, 6d, 5f\}$ ), in addition to the step 4 CSFs. In step 12, double and triple ( $dt$ ) excitations from the  $\{5d, 6s\}$  shells to layer 1' were allowed, in addition to the step 4 CSFs. Significant changes in both the hyperfine constants and the quadrupole moments were noted in both step 11 and step 12. Step 13 is an RCI calculation with a set of CSFs that is the union of the set used for step 12 and the set obtained by allowing double excitations from the  $\{5s, 5p, 5d\}$  shells to layer 1'. In step 14, the core-valence contributions from the  $\{3d, 4s, 4p, 4d, 4f\}$  shells calculated in separate RCI calculations (steps 6–10) are added to the results of step 13.

The validity of adding core-valence contributions from separate RCI calculations was verified by comparing the results for pairs of core shells considered together and separately. For example, the  $4s$  core-valence RCI calculation (step 9) changes  $A_{5/2}$  of  $^{199}\text{Hg}^+$  by +19.6 MHz compared to the step 4 MCDHF result. The  $4p$  core-valence RCI calculation (step 8) changes it by +11.1 MHz. An RCI calculation in which the  $4s$  and  $4p$  core-valence contributions were both included resulted in a change of +31.1 MHz, compared to +30.7 MHz for the sum of the  $4s$  and  $4p$  contributions calculated separately. It was not feasible to include all of the core-valence contributions in a single RCI calculation.

Table XI compares the final results for  $^{199}\text{Hg}^+$  and  $^{201}\text{Hg}^+$  with experiment and with other calculations. The present re-

TABLE XI. Comparison of calculated and measured quadrupole moments (in atomic units) and hyperfine constants (in MHz) for  $^{199}\text{Hg}^+$  and  $^{201}\text{Hg}^+ 5d^9 6s^2 {}^2D_{3/2,5/2}$ . Theoretical  $B$  factors are scaled to the nuclear quadrupole moments listed in Table I.

		Present calc. <sup>a</sup>	Other calc. <sup>b</sup>	Expt. <sup>c</sup>	Expt. <sup>d</sup>
$^{199}\text{Hg}^+$	$A_{3/2}$	2478.3	2399		
	$\Theta_{5/2}$	-0.56374			-0.510(18)
	$A_{5/2}$	963.5	1315	986.19(4)	
$^{201}\text{Hg}^+$	$A_{3/2}$	-914.8	-879		
	$B_{3/2}$	-737.0	-674		
	$A_{5/2}$	-355.7	-482		
	$B_{5/2}$	-839.4	-731		

<sup>a</sup>Table X, step 14.

<sup>b</sup>MCDHF [51].

<sup>c</sup>Reference [16].

<sup>d</sup>Reference [15].

sult for  $A_{5/2}$  of  $^{199}\text{Hg}^+$  agrees within 2.4% with the experimental result. No experimental values for the  $B$  factors of  $^{201}\text{Hg}^+$  are available for comparison. Observations of the hyperfine structure by classical optical spectroscopy [49,50] are not precise enough for this purpose. The calculations of Brage *et al.* [51] were carried out by the MCDHF and RCI methods with a set of CSFs more limited than that for the present calculation. The experimental value for  $\Theta_{5/2}$  is 26% smaller in magnitude than the DHF value, so the correlation contribution to the quadrupole moment is greater than for the other ions studied here. The present result for  $\Theta_{5/2}$  disagrees with the experimental value by about 10.5%, which is about three times the experimental uncertainty. The disagreement is about 30% of the total correlation contribution.

## F. Au

The results of the calculations for the  $^{197}\text{Au} 5d^9 6s^2 {}^2D_{3/2,5/2}$  states are given in Table XII. The steps in the

TABLE XII. Quadrupole moments (in atomic units) and hyperfine constants (in MHz) for  $^{197}\text{Au} 5d^9 6s^2 {}^2D_{3/2,5/2}$  states calculated with different approximations to the atomic state function.

Step	Description	$\Theta_{3/2}$	$A_{3/2}$	$B_{3/2}$	$\Theta_{5/2}$	$A_{5/2}$	$B_{5/2}$
1	DHF	-0.52677	217.34	-855.4	-0.82660	79.34	-940.3
2	MCDHF (+layer 1)	-0.40166	196.90	-764.3	-0.65285	91.57	-824.8
3	MCDHF (+layers 1,2)	-0.42674	198.07	-756.7	-0.68586	77.07	-832.4
4	MCDHF (+layers 1-3)	-0.42469	196.81	-771.6	-0.68413	72.44	-859.5
5	MCDHF (+layers 1-4)	-0.42348	195.07	-778.2	-0.68308	71.13	-870.0
6	RCI (step 4+4f c-v)	-0.42353	194.01	-771.7	-0.68316	71.28	-860.2
7	RCI (step 4+4d c-v)	-0.42341	200.50	-795.0	-0.68299	73.80	-887.6
8	RCI (step 4+4p c-v)	-0.42359	199.48	-827.3	-0.68322	73.12	-932.3
9	RCI (step 4+4s c-v)	-0.42364	194.05	-770.8	-0.68333	74.77	-858.0
10	RCI (step 4+3d c-v)	-0.42365	197.13	-772.9	-0.68331	72.53	-860.6
11	RCI (step 4+ $\{5d, 6s\}$ d c-c)	-0.44945	200.65	-774.8	-0.71684	68.32	-868.8
12	RCI (step 4+ $\{5d, 6s\}$ dt c-c)	-0.43511	192.36	-770.2	-0.69560	78.59	-861.6
13	RCI (step 12 $\cup\{5s, 5p, 5d\}$ c-c)	-0.44396	194.85	-777.0	-0.70940	74.50	-868.9
14	RCI (step 13+ $\{3d, 4spdf\}$ c-v)	-0.43831	195.96	-856.9	-0.70473	77.77	-970.2



TABLE XIII. Comparison of calculated and measured hyperfine constants (in MHz) for  $^{197}\text{Au } 5d^9 6s^2 {}^2D_{3/2,5/2}$ . Theoretical  $B$  factors are scaled to the nuclear quadrupole moments listed in Table I.

	Present calc. <sup>a</sup>	Expt. <sup>b</sup>	Expt. <sup>c</sup>
$A_{3/2}$	195.96	199.8425(2)	
$B_{3/2}$	-856.9	-911.0766(5)	
$A_{5/2}$	77.77		80.236(3)
$B_{5/2}$	-970.2		-1049.781(11)

<sup>a</sup>Table XII, step 14.

<sup>b</sup>Reference [29].

<sup>c</sup>Reference [28].

calculation are the same as for  $\text{Hg}^+$  (Table X). Table XIII compares the final results with experiment. The calculated values of  $A_{3/2}$  and  $A_{5/2}$  agree with the experimental values to within 3%. The calculated values of  $B_{3/2}$  and  $B_{5/2}$  differ from experiment by about 8%. However, this comparison depends on the value assumed for the nuclear quadrupole moment  $Q(^{197}\text{Au})$ .

The current status of knowledge of  $Q(^{197}\text{Au})$  has been summarized by Schwerdtfeger *et al.* [52]. The currently accepted value listed by Pyykkö [42] is  $+0.547(16)$  b ( $1 \text{ b} = 10^{-28} \text{ m}^2$ ) and is based on muonic hyperfine measurements. A value of  $+0.594(10)$  b was derived by Blachman *et al.* [29] based on the experimental  $B$  factors of the Au  $5d^9 6s^2 {}^2D_{3/2,5/2}$  states [28,29], i.e., the same states studied in the present work. However, Blachman *et al.* did not calculate the atomic electric field gradients from *ab initio* theory, as in the present work, but inferred them from the experimental  $A$  factors. This method is of uncertain accuracy and does not include the Sternheimer antishielding correction, which is included in the present calculation. Schwerdtfeger *et al.* [52] obtained  $Q(^{197}\text{Au}) = +0.60$  b from measured Mössbauer electric quadrupole splittings in a large number of gold compounds combined with solid-state density-functional calculations. They obtained  $Q(^{197}\text{Au}) = +0.64$  b from the measured electric quadrupole coupling constant in  $(\text{CO})\text{AuF}$  (i.e., the weakly bound complex of a CO molecule and a AuF molecule), together with a relativistic coupled-cluster calculation of the electronic structure of the complex.

Since the muonic and the other determinations of  $Q(^{197}\text{Au})$  appear to be discrepant, it is of interest to derive a value based on the present calculations. These calculations imply values of  $Q(^{197}\text{Au})$  of  $+0.5918$  b and  $+0.5816$  b, based on the experimental values of  $B_{3/2}$  and  $B_{5/2}$ , respectively. These values agree to within about 2%. Assigning an uncertainty to the value of  $Q$  derived in this way is difficult. One way is to make use of the fact that the relative calculational errors for the  $A$  and  $B$  factors are similar, since they both depend to first order on matrix elements of  $1/r^3$  for the  $5d$  electrons. (This method of estimating the relative errors would not hold for cases where there are large cancellations, as for  $A_{5/2}$  in  $\text{Ca}^+$ ,  $\text{Sr}^+$ ,  $\text{Ba}^+$ , and  $\text{Yb}^+$ .) Based on the fact that the calculated values of  $A_{3/2}$  and  $A_{5/2}$  for  $^{197}\text{Au}$  and  $A_{5/2}$  for  $^{199}\text{Hg}^+$  agree with the experimental values to within 3% or

better, 5% is a reasonable estimate for the error in the estimate of  $Q$ . The new estimate, based on the average of the values derived from  $B_{3/2}$  and  $B_{5/2}$  of  $^{197}\text{Au}$ , is  $Q(^{197}\text{Au}) = +0.587(29)$  b. The error bars of the present measurement overlap those of the muonic measurement.

#### IV. CONCLUSIONS

The main object of this study was to calculate the atomic quadrupole moments of the metastable  ${}^2D_{3/2,5/2}$  states of several ions and atoms to an uncertainty better than those of the simple estimates obtained from Hartree-Fock or Dirac-Hartree-Fock calculations [e.g., Eqs. (2a) and (2b)]. This is apparently the first use of MCDHF and RCI methods for this purpose. For  $\text{Ca}^+$ ,  $\text{Ba}^+$ , and  $\text{Au}$ , there are no experimental or other theoretical values for comparison. For  $\Theta_{5/2}$  of  $\text{Sr}^+$ , the experimental determination has an uncertainty of 11.5%, so it does not provide a precise test of the calculation. However, a recent relativistic coupled-cluster calculation [26] agrees with the present calculation to within 4%. An experimental determination of  $\Theta_{3/2}$  of  $\text{Yb}^+$  agrees with the present calculation to within the experimental uncertainty of 5%. The experimental determination of  $\Theta_{5/2}$  for  $\text{Hg}^+$  differs from the present calculation by 10.5%. In summary, the method used in this work appears to be capable of calculating the atomic quadrupole moments to about 5% or better for configurations consisting of a single  $nd$  electron outside a set of closed shells, while the error appears to be about 10% for the more complex  $5d^9 6s^2 {}^2D_{3/2,5/2}$  states.

The second object was to calculate the hyperfine constants of the same states. For most of the cases where there is experimental data, the agreement is within a few percent. For the  $B$  factors, some of the discrepancies may be due to errors in the nuclear quadrupole moments used. The exception to the generally good agreement is for the  $A$  factors of the  ${}^2D_{5/2}$  states of  $\text{Sr}^+$ ,  $\text{Ba}^+$ , and  $\text{Yb}^+$ , where the correlation contributions exceed 100% of the Dirac-Hartree-Fock values, leading to a change in sign of the constants, relative to the DHF values. The present calculations are in error by about 30% of the total correlation contribution. The source of the error is not understood. It may be related to limitations on the form of the CSFs included in the calculations or to the particular strategy used for the optimization of the orbitals. Apparently, many-body perturbation theory or coupled-cluster theory can give better results for the  $A$  factors of these states, although this has not yet been demonstrated for  $\text{Yb}^+$ .

The present methods give good results for the hyperfine constants of the  $5d^9 6s^2 {}^2D_{3/2,5/2}$  states of  $\text{Hg}^+$  and  $\text{Au}$ . The  $A$  factors agree with experiment to about 3%. The  $B$  factors calculated for  $\text{Au}$  disagree by about 8%, but this may be due to an error in the currently accepted value of the nuclear quadrupole moment. The present calculations are the most accurate *ab initio* calculations for the hyperfine constants of these states. Apparently, many-body perturbation theory or coupled-cluster theory has not yet been applied to these systems.

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