Electric quadrupole moments of metastable states of Ca+, Sr+, and Ba+

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The electric quadrupole moments of the metastable $nd_{3/2}$ and $nd_{5/2}$ states of Ca+, Sr+, and Ba+ are calculated using the relativistic all-order method including all single, double, and partial triple excitations of the Dirac-Hartree-Fock wave function to provide recommended values for the cases where no experimental data are available. The contributions of all nonlinear single and double terms are also calculated for the case of Ca+ for comparison of our approach with results of the coupled-cluster method with singles, doubles, and perturbative triples. Third-order many-body perturbation theory is used to evaluate the contributions of high partial waves and the Breit interaction. The remaining omitted correlation corrections are estimated as well. An extensive study of the uncertainty of our calculations is carried out to establish the accuracy of our recommended values as 0.5–1 % depending on the particular ion. A comprehensive comparison of our results with other theoretical values and experimental results is carried out. Our result for the quadrupole moment of the $3d_{5/2}$ state of the Ca+ ion, $1.849(17)ea_0^2$, is in agreement with the most precise recent measurement $1.83(1)ea_0^2$ by Roos *et al.* [Nature (London) **443**, 316 (2006)].

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I. INTRODUCTION

Frequency standards based on optical transitions of trapped ions have the potential to reach a systematic fractional uncertainty on the order of 10^{-18} [1]. The ability to develop more precise optical frequency standards will open ways to improve global positioning system measurements and tracking of deep-space probes and perform more accurate measurements of physical constants and tests of fundamental physics such as searches for nonlinearity of quantum mechanics, gravitational waves, etc. Some of the promising candidates for such ultrahigh-precision frequency standards with trapped ions are ^{27}Al+ [2,3], ^{199}Hg+ [4,5], ^{171}Yb+ [6,7], ^{87}Sr+ [8,9], ^{43}Ca+ [10], ^{115}In+ [11], and ^{137}Ba+. One of the largest sources of systematic errors in such frequency standards with monovalent ions is due to interaction of the quadrupole moments of metastable states with stray electric field gradients [12,13]. The electric quadrupole moments of the metastable states are hard to calculate accurately even for the simplest monovalent systems owing to the large correlation corrections (over 30% for Ca+). The relativistic configuration-interaction (RCI) method with a multiconfiguration Dirac-Fock orbital basis was used by Itano [14] to calculate relevant quadrupole moments in Ca+, Sr+, Ba+, Yb+, Hg+, and Au. The RCI results agreed with available measurement within 10%. The relativistic coupled-cluster calculations of quadrupole moments of metastable nd states were carried out by Sur *et al.* [15] for Ca+, Sr+, and Ba+ and by Sahoo [16] for Ba+. These calculations yielded results 5%

and 13% higher than the recent measurements of Ca+ [17] and Sr+ [18] quadrupole moments, respectively. Mitroy and Zhang [19,20] calculated the quadrupole moments of the $3d_{5/2}$ state in Ca+ and the $4d_{5/2}$ state in Sr+ by diagonalizing a semiempirical Hamiltonian in a large-dimension single-electron basis. Their values are in good agreement with the experiment. However, they noted that their particular definition of the polarization potential may lead to a possible problem with the accuracy of properties of these nd states calculated using this method [19,20]. Large differences between theoretical calculations and experimental values, especially the 5% discrepancy between the recent precise measurement of the $3d_{5/2}$ state quadrupole moment of Ca+ by Roos *et al.* [17] and values of coupled-cluster calculations with singles, doubles, and partial triples [CCSD(T)] from [15], and the consequent need for comprehensive analysis of the theoretical uncertainties have in part motivated this work.

In this paper, we present relativistic all-order calculations of the electric quadrupole moments of the $nd_{3/2}$ and $nd_{5/2}$ states of Ca+, Sr+, and Ba+ ions. The relativistic all-order method is one of the most accurate methods used for the calculation of atomic properties of monovalent systems (see Ref. [21] for a review and references therein). The lifetimes of the $3d$ levels in Ca+ calculated in this approach and estimated to be accurate to 1% were found to be in agreement with the high-precision experiment [22]. The calculation of the nd quadrupole moments is very similar to the calculation of the nd lifetimes, so similar accuracy is expected. The long lifetimes of the metastable nd states of these ions also make these systems well suited for the study of quantum-information processing and quantum simulation [23,24].

The atomic properties of Ba+ are also of particular interest owing to the prospects for studying parity nonconservation with a single trapped ion [25]. Progress on related spectros-

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copy with a single Ba$^+$ ion is reported in [26,27], and precision measurements of light shifts in a single trapped Ba$^+$ ion have been reported in [28].

Another motivation for this work is the opportunity to evaluate the importance of the nonlinear terms as well as triple and higher excitations in the coupled-cluster approach. It has been indicated in Refs. [29,30] that nonlinear terms may be relatively large and significantly cancel with triple and higher-excitation terms that are not included in the CCSD(T) calculations of Ref. [15] or all-order single, double, and partial triple (SDpT) approach [21]. In this work, we include all nonlinear terms at the single-double (SD) level and evaluate triple and higher-excitation corrections beyond CCSD(T) or SDpT treatments for Ca$^+$. Our calculations demonstrate significant cancellation between these terms. Our results in part explain the discrepancy of previous high-precision calculations with the Ca$^+$ experiment and represent the most complete calculation to date to our knowledge. We also present a detailed analysis of the uncertainty of our calculations.

II. METHOD

The electric quadrupole moment $\Theta(\gamma J)$ of an atom in electronic state $|\gamma J\rangle$ is defined as the diagonal matrix element of the $q=0$ component of the electric quadrupole operator Q in a spherical basis

$$\Theta(\gamma J) = \langle \Psi(\gamma J M_J)|Q_0|\Psi(\gamma J M_J)\rangle, \qquad (1)$$

with the magnetic quantum number M_J taken to be equal to its maximum value, $M_J = J$ [14]. Applying the Wigner-Eckart theorem and using the analytical expression for the relevant 3-j coefficient [31] allows us to express the quadrupole moment via the reduced matrix element of the quadrupole operator as

$$\Theta(\gamma J) = \frac{(2J)!}{\sqrt{(2J-2)!(2J+3)!}}\langle \Psi(\gamma J)\|Q\|\Psi(\gamma J)\rangle, \qquad (2)$$

where the electric quadrupole operator Q is represented in second quantization as a one-body operator

$$Q = \sum_{ij} q_{ij}a_i^\dagger a_j. \qquad (3)$$

Here, $a_i^\dagger$ and a_i are the creation and annihilation operators.

In the coupled-cluster method, the exact many-body wave function $\Psi(\gamma J)$ is represented in the form [32]

$$|\Psi\rangle = \exp(S)|\Psi^{(0)}\rangle, \qquad (4)$$

where $|\Psi^{(0)}\rangle$ is the lowest-order wave function. We have omitted the indices (γJ) in this equation and formulas below for convenience. The operator S for an N-electron atom consists of "cluster" contributions from one-electron, two-electron, $\cdots$, N-electron excitations of the lowest-order wave function $|\Psi^{(0)}\rangle$:

$$S = S_1 + S_2 + \cdots + S_N. \qquad (5)$$

The expansion of the exponential in Eq. (4) in terms of the n-body excitations S_n gives

$$|\Psi\rangle = \left(1 + S_1 + S_2 + \frac{1}{2}S_1^2 + S_1 S_2 + \frac{1}{2}S_2^2 + \cdots\right)|\Psi^{(0)}\rangle. \quad (6)$$

In the linearized coupled-cluster method, only linear terms are considered, and the wave function takes the form

$$|\Psi\rangle = (1 + S_1 + S_2 + S_3 + \cdots + S_N)|\Psi^{(0)}\rangle. \qquad (7)$$

We note that the contributions from the nonlinear terms are expected to be relatively small, but the computational complexity and time increases significantly with their addition in the present approach [33]. The relativistic all-order single-double method is the linearized coupled-cluster method restricted to single and double excitations only, with the wave function given by

$$\begin{aligned}
|\Psi_{SD}\rangle &= (1 + S_1 + S_2)|\Psi^{(0)}\rangle \\
&= \left(1 + \sum_{ma} \rho_{ma}a_m^\dagger a_a + \sum_{m \neq v} \rho_{mv}a_m^\dagger a_v \right. \\
&\quad \left. + \frac{1}{2}\sum_{mnab} \rho_{mnab}a_m^\dagger a_n^\dagger a_b a_a + \sum_{mna} \rho_{mnva}a_m^\dagger a_n^\dagger a_a a_v\right)|\Psi^{(0)}\rangle,
\end{aligned}$$

$$(8)$$

where we take frozen-core Dirac-Hartree-Fock (DHF) wave function to be the lowest-order wave function $|\Psi^{(0)}\rangle$. The indices m and n designate excited states while indices a and b designate core states; the index v labels the valence electron. The equations for the single-excitation coefficients ρ_{ma}, ρ_{mv}, double-excitation coefficients ρ_{mnab}, ρ_{mnva}, and the corresponding correlation core and valence energies δE_{core}, δE_v are solved iteratively in a finite basis set. The finite basis set used in our calculations consists of single-particle orbitals which are linear combinations of B splines [34] constrained to a spherical cavity.

The all-order SDpT method is an extension of the SD method in which the valence part of the linear triple-excitation term S_3 is added to the wave function:

$$|\Psi_{SDpT}\rangle = |\Psi_{SD}\rangle + \frac{1}{6}\sum_{mnrab} \rho_{mnrvab}a_m^\dagger a_n^\dagger a_r^\dagger a_b a_a a_v|\Psi^{(0)}\rangle,$$

$$(9)$$

where $|\Psi_{SD}\rangle$ is given by Eq. (8). The dominant part of S_3 is treated perturbatively, i.e., its effect on the valence energies δE_v and single-excitation coefficients ρ_{mv} is calculated, but the equations for the triple-excitation coefficients ρ_{mnrvab} are not iterated. A detailed description of the SD and SDpT methods is given in Refs. [21,35,36].

We carry out both SD and SDpT calculations in this work to establish the size of the triple corrections in the perturbative approach. The CCSD(T) method used in calculation of the quadrupole moments in Refs. [15,16] also includes the triple excitations perturbatively even though the particular terms that are considered somewhat differ.

In this work, we also carry out the all-order calculation that includes all nonlinear terms that arise from single- and double-excitation terms S_1 and S_2 for the case of Ca$^+$. There are only six of such terms that can contribute to the equations for single- and double-excitation coefficients, and the complete coupled-cluster single-double wave function is then written as

$$
\begin{aligned}
|\Psi_{\text{CCSD}}\rangle &= \exp(S_1 + S_2)|\Psi^{(0)}\rangle \\
&= |\Psi_{\text{SD}}\rangle + \left(\frac{1}{2}S_1^2 + S_1 S_2 + \frac{1}{2}S_2^2 + \frac{1}{6}S_1^3 + \frac{1}{2}S_1^2 S_2 \right. \\
&\quad \left. + \frac{1}{24}S_1^4 \right)|\Psi^{(0)}\rangle,
\end{aligned}
\tag{10}
$$

where $|\Psi_{\text{SD}}\rangle$ is given by Eq. (8). The complete formulas for the CCSD equations are given in Ref. [33]. Our approach allows us to explicitly calculate the contribution of the nonlinear terms to the quadrupole moments as the difference of the results obtained in the CCSD and SD approaches.

The matrix element of any one-body operator Z in the all-order method is obtained as

$$
Z_{vw} = \frac{\langle \Psi_v|Z|\Psi_w \rangle}{\sqrt{\langle \Psi_v|\Psi_v \rangle \langle \Psi_w|\Psi_w \rangle}}.
\tag{11}
$$

For nonscalar operators, this expression becomes

$$
Z_{vw} = \frac{Z_{\text{val}}}{\sqrt{(1+N_v)(1+N_w)}},
\tag{12}
$$

where the expression for the numerator of Eq. (12) derived with the $|\Psi_{\text{SD}}\rangle$ wave function consists of the sum of the DHF matrix element z_{wv} and 20 other terms $Z^{(k)}$, $k=a,\dots,t$. These terms and the normalization terms N_v are linear or quadratic functions of the excitation coefficients ρ_{ma}, ρ_{mv}, ρ_{mnab}, and ρ_{mnva}. The complete expression for the matrix elements can be found in [37]. The same expression [Eq. (12)] for the matrix elements is used in all calculations in this work.

We carry out three different *ab initio* calculations of the quadrupole matrix elements. In the first one, all excitation coefficients are obtained in the SD approach [Eq. (8)], in the second one they are obtained in the SDpT approach [Eq. (9)], and in the third one (carried out for Ca$^+$) the excitation coefficients are obtained in the CCSD approach [Eq. (10)]. We refer to these results as SD, SDpT, and CCSD values in the text and tables below.

While the numerator of Eq. (12) contains 20 correlation terms, only one term is overwhelmingly dominant for the quadrupole moments considered in this work, contributing over 90% of the total correlation correction. Following the notation of Ref. [37], this is the term $Z^{(c)}$ that is equal in the case of the diagonal quadrupole matrix element to

$$
Z^{(c)} = 2\sum_m q_{vm}\rho_{mv},
\tag{13}
$$

where the sum over m ranges over all excited basis set states. The lowest-order DHF matrix elements q_{ij} of the quadrupole operator are given by

$$
q_{ij} = \langle i\|C^{(2)}\|j\rangle \int_0^\infty r^2[g_i(r)g_j(r) + f_i(r)f_j(r)]dr,
\tag{14}
$$

where $C^{(2)}$ is the normalized spherical harmonic of rank 2 and g_i, f_i are large and small components of the Dirac wave function, respectively. The ρ_{mv} are single-valence excitation coefficients calculated in either SD [Eq. (8)], SDpT [Eq. (9)], or CCSD [Eq. (10)] approximations as described above. Therefore, evaluation of the omitted higher-order corrections to ρ_{mv} provides an estimate of the dominant part of the missing contributions in each approximation. These excitation coefficients are closely related to the correlation energy δE_v. If we introduce the self-energy operator (also referred to as the correlation potential in some works) Σ_{mv} as

$$
\Sigma_{mv} = (\epsilon_v - \epsilon_m + \delta E_v)\rho_{mv},
\tag{15}
$$

where ϵ_i is the DHF energy of the state i, then the correlation energy will correspond to the diagonal term Σ_{vv}. Therefore, the omitted correlation correction can be estimated by adjusting the single-excitation coefficients ρ_{mv} to the experimentally well-known value of the valence correlation energy, and then recalculating the matrix elements using Eq. (12) with the modified coefficients [35]

$$
\rho'_{mv} = \rho_{mv}\frac{\delta E_v^{\text{expt}}}{\delta E_v^{\text{theory}}}.
\tag{16}
$$

δE_v^{expt} is defined as the experimental energy [38] minus the lowest-order DHF energy ϵ_v. The theoretical correlation energy is somewhat different in the SD, SDpT, and CCSD approaches. Therefore, this scaling procedure has to be conducted separately for each of these three calculations with $\delta E_v^{\text{theory}}$ taken to be δE_v^{SD}, δE_v^{SDpT}, and δE_v^{CCSD}, respectively. We refer to the results of these calculations as SD$_{\text{sc}}$, SDpT$_{\text{sc}}$, and CCSD$_{\text{sc}}$ values.

Before discussing the final results of our calculations, we describe the calculation of two other corrections that need to be accounted for in the *ab initio* SD, SDpT, and CCSD calculations. Any sum over the excited states in the calculation of either the excitation coefficients or matrix elements using Eq. (12) involve a sum over the principal quantum number, calculated essentially exactly, and the sum over the partial waves, which needs to be truncated after some value l_{max} [see the sum over m in Eq. (13) for an example]. In all of our all-order calculations, we chose $l_{\text{max}}=6$. We find that the contributions from higher partial waves are small but significant and should not be omitted at the present level of accuracy. The size of the contribution of the higher partial waves may also shed some light on the disagreement of some previous calculations with experiment.

To evaluate this contribution, we first carried out a third-order many-body perturbation theory (MBPT) calculation with the same basis set and l_{max} as the all-order calculations, and then performed the same calculation with larger basis set and larger l_{max}. A detailed description of the third-order MBPT method is given in Ref. [39].

The results of the third-order calculation with increasing values of l_{max} for the quadrupole moments of Ca$^+$ are given in Table I. While the total contribution of the $l=7,8$ partial

TABLE I. Contributions of high partial waves and Breit interaction to the electric quadrupole moments of Ca$^+$ calculated using third-order many-body perturbation theory; l_{max} is the highest number of partial waves included in the particular calculation. All values are given in atomic units.

State	l_{max}				$l = 7, \ldots, 12$	Breit
	6	8	10	12		
$3d_{3/2}$	1.134	1.127	1.124	1.123	−0.011	−0.001
$3d_{5/2}$	1.628	1.617	1.614	1.612	−0.015	−0.003

waves is rather substantial, 0.6%, contributions of even higher partial waves are small. We truncated the sum after $l=12$, with the expected uncertainty of this truncation being well below our final accuracy. The difference between the MBPT calculations with $l_{max}=6$ and 12 is taken to be the correction for the contribution of higher partial waves and is added to the *ab initio* all-order results.

We have also evaluated the total contribution of the $l=5,6$ partial waves to establish its size, and found it to be 3%. Moreover, the inclusion of a larger number of partial waves *reduces* the values of the quadruple moments since the term $Z^{(c)}$ contributes with a sign opposite to that of the lowest-order value. The inclusion of a larger number of partial waves increases the absolute value of the correlation correction leading to lower total final values. Therefore, omitting the contributions of higher partial waves or exclusion of such orbitals from the basis set in other calculations may result in an overestimation of the quadrupole moments by a few percent.

We also investigated the effect of the Breit interaction, which arises due to exchange of a virtual photon between atomic electrons and can be written as

$$B_{ij} = -\frac{1}{r_{ij}}\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j + \frac{1}{2r_{ij}}[\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j - (\boldsymbol{\alpha}_i \cdot \hat{\mathbf{r}}_{ij})(\boldsymbol{\alpha}_j \cdot \hat{\mathbf{r}}_{ij})], \quad (17)$$

where $\boldsymbol{\alpha}_i$ are the Dirac matrices. This correction includes instantaneous magnetic interaction between Dirac currents (the first term) and the retardation correction to the electric interaction (the second term). In order to calculate the Breit correction to the quadrupole matrix elements, we modify the generation of the B-spline basis set to intrinsically include the Breit interaction on the same footing as the Coulomb interaction, and repeat the third-order calculation with the modified basis set. The difference between the new values and the original third-order calculation is taken to be the correction due to Breit interaction. This contribution is listed in the last column of Table I. In second quantization, the Breit interaction operator in a normal form is separated into a one-body and a two-body part [40]. The two-body Breit contribution is omitted in our approach. The total Breit corrections are small and are below the estimated uncertainty of our theoretical values. Therefore, the possible uncertainty introduced by the omission of the two-body Breit correction is negligible. In fact, we find that most of the Breit correction arises at the DHF level.

III. RESULTS AND DISCUSSION

The results of our calculations of the quadrupole moments of the metastable $nd_{3/2}$ and $nd_{5/2}$ states of Ca$^+$, Sr$^+$, and Ba$^+$ ions are summarized in Table II, where we list the lowest-order DHF, third-order MBPT, all-order SD and SDpT *ab initio*, and corresponding all-order scaled values calculated as described in Sec. II. In the case of Ca$^+$, we also list the results of our CCSD and scaled CCSD calculations. The *ab initio* values contain the corrections for the higher partial wave contributions and Breit interaction. These corrections do not need to be included into the scaled results as that will lead to double counting of these effects. We take the scaled SD numbers as the final values based on the comparisons of similar calculations in alkali-metal atoms with experiment (see Refs. [41–45] and references therein).

We take the maximum difference between the final values and the SDpT *ab initio*, SDpT scaled (SDpT$_{sc}$), and CCSD scaled (CCSD$_{sc}$) values to be the uncertainty of the dominant contribution. We assume that any remaining uncertainty does not exceed the uncertainty of the dominant term and take it to be equal to the uncertainty in the dominant term evaluated as described above. The two uncertainties are added in quadrature to obtain the final estimate of the uncertainty of our values.

TABLE II. Electric quadrupole moments of Ca$^+$, Sr$^+$, and Ba$^+$ calculated using different approximations: Dirac-Hartree-Fock (DHF), third-order many-body perturbation theory (MBPT), single-double all-order method (SD), and single-double all-order method including partial triple-excitation contributions (SDpT); the label "sc" indicates the corresponding scaled values. The results of the full single-double couple-cluster calculation for Ca$^+$ are listed in the column labeled CCSD; the corresponding scaled values are listed in the column CCSD$_{sc}$. All values are given in atomic units.

Ion	State	DHF	MBPT	SD	SDpT	SD$_{sc}$	SDpT$_{sc}$	CCSD	CCSD$_{sc}$	Final
Ca$^+$	$3d_{3/2}$	1.712	1.122	1.245	1.282	1.289	1.281	1.271	1.292	1.289(11)
	$3d_{5/2}$	2.451	1.610	1.785	1.837	1.849	1.836	1.822	1.851	1.849(17)
Sr$^+$	$4d_{3/2}$	2.469	1.876	1.987	2.021	2.029	2.020			2.029(12)
	$4d_{5/2}$	3.559	2.721	2.876	2.922	2.935	2.923			2.935(17)
Ba$^+$	$5d_{3/2}$	2.732	2.086	2.217	2.260	2.256	2.248			2.256(11)
	$5d_{5/2}$	3.994	3.087	3.263	3.323	3.319	3.308			3.319(15)

TABLE III. Comparison of the present results for electric quadrupole moments in Ca^+, Sr^+, and Ba^+ with other calculations and experiments. All values are in atomic units.

Ion	State	Present	Ref. [14]	Ref. [15]	Other	Expt.
Ca^+	$3d_{3/2}$	1.289(11)	1.338	1.338		
	$3d_{5/2}$	1.849(17)	1.917	1.916	1.819[a]	1.83(1)[b]
Sr^+	$4d_{3/2}$	2.029(12)	2.107	2.12		
	$4d_{5/2}$	2.935(17)	3.048	2.94(7)	2.840[c]	2.6(3)[d]
Ba^+	$5d_{3/2}$	2.256(11)	2.297	2.309	2.315[e]	
	$5d_{5/2}$	3.319(15)	3.379	3.382	3.382[e]	

[a]Reference [19].
[b]Reference [17].
[c]Reference [20].
[d]Reference [18].
[e]Reference [16], CCSD(T).

We make several conclusions from our results (all the percentages are given for Ca^+, but the general trends are the same for all ions considered in this work).

(1) The triple contributions included in the perturbative approach contribute about 3% and *increase* the values of the quadrupole moments.

(2) The nonlinear terms contribute about 2% and also *increase* the values of the quadrupole moments.

(3) While the SD, SDpT, and CCSD results vary by a few percent, the addition of the estimated omitted correlation correction carried out according to Eq. (16), brings all these results to very close agreement providing additional validation of this procedure.

(4) The linearized SD_{sc} and complete coupled-cluster $CCSD_{sc}$ scaled results are nearly exactly the same, with the differences being well below our estimated uncertainty. Therefore, we found it unnecessary to carry out CCSD calculations for Sr^+ and Ba^+.

(5) We confirm that nonlinear terms strongly cancel with the triple- and higher-excitation contributions not included in the perturbative approach. As a result, the CCSD(T) method used in Refs. [15,16] that includes both nonlinear terms and triple excitations in the perturbative approach only is expected to yield results a few percent higher than the experimental values.

In Table III, we compare our final values with other calculations and available experimental results. We note that our calculation is the most complete one at the present time. The J-independent moments, i.e., the values with the all angular factors divided out, can be obtained by multiplying our results in Table III by 5 and 7/2 for the $nd_{3/2}$ and $nd_{5/2}$ states, respectively, according to Eq. (1).

Our values are systematically lower than the results of relativistic configuration-interaction calculation carried out with a multiconfiguration Dirac-Fock orbital basis by Itano [14]. As we noted above, high partial waves ($l > 4$) contribute significantly (about 4%) to the quadrupole moments and reduce the values. Therefore, the restriction of the excitations to mostly low-l orbitals in Ref. [14] is expected to lead to higher values in RCI calculations. The relativistic coupled-cluster CCSD(T) results by Sur *et al.* [15] for Ca^+, Sr^+, and

Ba^+ and by Sahoo [16] for Ba^+ are also systematically lower than our values, with the exception of the $4d_{5/2}$ Sr^+ quadrupole moment, which is in agreement with our value. It is unclear why this one value compares differently. Since this particular value was the focus of the work [15], perhaps it was treated differently from the other cases. As we noted above, we expect the CCSD(T) results of Refs. [15,16] to be a few percent too high owing to the cancellation of the nonlinear terms and higher-excitation terms not included in CCSD(T) approach. Another possible issue is the treatment of the high partial wave contributions. While the tests of various basis sets were conducted in Ref. [15], it is not stated how high partial waves were considered. We note that the implementation of the coupled-cluster method in Refs. [15,16] is significantly different from ours and is more closely related to the quantum chemistry calculations.

The results of Mitroy and Zhang [19,20] calculated by diagonalizing a semiempirical Hamiltonian in a large-dimension single-electron basis are in good agreement with experiment. Our analysis of the correlation correction is consistent with such results. We demonstrated in Sec. II that the dominant part of the correlation correction to quadrupole matrix elements comes from the term containing essentially the correlation potential Σ_{vm} that is closely related to the correlation energy. Since the cutoff function in the semiempirical potential used in Refs. [19,20] is adjusted to reproduce experimental binding energies, it appears to be a good representation for this application.

Our result for the $3d_{5/2}$ Ca^+ quadrupole moment, $1.849(17)ea_0^2$, agrees within the quoted uncertainties with the recent high-precision measurement $1.83(1)ea_0^2$ reported by Roos *et al.* in Ref. [17] that was carried out using a decoherence-free subspace with specially designed entangled states of trapped ions. We also verify (by varying the nuclear parameter) that our value is not dependent on the particular isotope within our accuracy. Our result for the Sr^+ $4d_{5/2}$ quadrupole moment $2.935(17)ea_0^2$ is in good agreement (just outside the upper 1σ bound) with experimental value $2.6(3)ea_0^2$ by Barwood *et al.* [18] measured with a single laser-cooled ion confined in an end cap trap with variable dc quadrupole potential.

IV. CONCLUSION

In summary, we performed a relativistic coupled-cluster calculation of the electric quadrupole moments for the $nd_{3/2}$ and $nd_{5/2}$ states of Ca^+, Sr^+, and Ba^+ ions. Our analysis of various contributions in part explains the discrepancy of previous high-precision theory with experiment. We also present detailed evaluation of the uncertainty of our results and provide recommended values for the cases where no precision experiments are available. Our result for the quadrupole moment of the $3d_{5/2}$ state of the Ca^+ ion, $1.849(17)ea_0^2$, is in agreement with the recent measurement $1.83(1)ea_0^2$ by Roos *et al.* [17].

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