

Electric Quadrupole Moments of the D States of Alkaline-Earth-Metal Ions

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The electric quadrupole moment for the $4d^2D_{5/2}$ state of $^{88}\text{Sr}^+$; one of the most important candidates for an optical clock, has been calculated using the relativistic coupled-cluster theory. This is the first application of this theory to determine atomic electric quadrupole moments. The result of the calculation is presented and the important many-body contributions are highlighted. The calculated electric quadrupole moment is $(2.94 \pm 0.07)ea_0^2$, where a_0 is the Bohr radius and e the electronic charge while the measured value is $(2.6 \pm 0.3)ea_0^2$. This is so far the most accurate determination of the electric quadrupole moment for the above mentioned state. We have also calculated the electric quadrupole moments for the metastable $4d^2D_{3/2}$ state of $^{88}\text{Sr}^+$ and for the $3d^2D_{3/2,5/2}$ and $5d^2D_{3/2,5/2}$ states of $^{43}\text{Ca}^+$ and $^{138}\text{Ba}^+$, respectively.

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The current frequency standard is based on the ground state hyperfine transition in ^{133}Cs which is in the microwave regime and has an uncertainty of one part in 10^{15} [1]. However, demands from several areas of science and technology have led to a worldwide search [2] for even more accurate clocks in the optical regime. Some of the prominent candidates that belong to this category are $^{199}\text{Hg}^+$ [3], $^{88}\text{Sr}^+$ [4,5], $^{171}\text{Yb}^+$ [6], $^{43}\text{Ca}^+$ [7], $^{138}\text{Ba}^+$, etc. A series of measurements of the electric quadrupole moments have been performed on the metastable D states of most of these ions fairly recently [8–11] in connection with the investigations for accurate optical frequency standards. These measurements provide an excellent opportunity for new tests of relativistic atomic many-body theories. The hyperfine structure constants and the electric quadrupole moments are sensitive to the regions near and far from the nucleus, respectively, but they both are influenced by electron correlation. Therefore, the knowledge that one would acquire from calculations of atomic electric quadrupole moments is complementary to that acquired from hyperfine interactions. However, calculations of atomic electric quadrupole moments have received relatively little attention so far. The most rigorous calculation to date has been performed by Itano [12] by using the relativistic configuration interaction (RCI) method with a multiconfiguration Dirac-Fock—extended optimized level (MCDF-EOL) orbital basis. In this Letter, we use the relativistic coupled-cluster (RCC) theory to calculate the electric quadrupole moments of $^{88}\text{Sr}^+$, $^{43}\text{Ca}^+$, and $^{138}\text{Ba}^+$. This is the first application of this theory to calculate atomic electric quadrupole moments. We place special emphasis on our Sr^+ calculation as this ion is one of the leading candidates in the search for an optical frequency standard [3–7].

The RCC theory is equivalent to all-order relativistic many-body perturbation theory. The details of the applica-

tion of this theory have been discussed earlier in the literature [13–15]. Here we shall only give a brief outline. Treating the N -electron closed shell Dirac-Fock state $|\Phi\rangle$ as the reference state, the exact wave function in RCC theory can be expressed as

$$|\Psi\rangle = \exp(T)|\Phi\rangle, \quad (1)$$

where T is the core electron excitation operator. In the coupled-cluster singles and doubles (CCSD) approximation, T can be expressed as the sum of one- and two-body excitation operators, i.e., $T = T_1 + T_2$, and can be written in the second quantized form as

$$T = T_1 + T_2 = \sum_{ap} a_p^\dagger a_a t_a^p + \frac{1}{4} \sum_{abpq} a_p^\dagger a_q^\dagger a_b a_a t_{ab}^{pq}, \quad (2)$$

where t_a^p and t_{ab}^{pq} are the amplitudes of the singles and double excitation operators, respectively. For a single valence system we define the reference state as,

$$|\Phi_v^{N+1}\rangle \equiv a_v^\dagger |\Phi\rangle \quad (3)$$

with the particle creation operator a_v^\dagger . The wave function corresponding to this state can be written as

$$|\Psi_v^{N+1}\rangle = \exp(T)\{(1 + S_v)\}|\Phi_v^{N+1}\rangle. \quad (4)$$

Here,

$$S_v = S_{1v} + S_{2v} = \sum_{v \neq p} a_p^\dagger a_v s_v^p + \frac{1}{2} \sum_{bpq} a_p^\dagger a_q^\dagger a_b a_v s_{vb}^{pq} \quad (5)$$

corresponds to the excitation operator in the valence sector and v stands for valence orbital; s_v^p and s_{vb}^{pq} are the amplitudes of single and doubles excitations, respectively. Details concerning the evaluation of the closed and open shell amplitudes have been discussed earlier [16]. Triple

excitations are included in our open shell RCC amplitude calculations in an approximate way [CCSD(T)] [17,18].

The expectation value of any operator O with respect to the state $|\Psi^{N+1}\rangle$ is given by

$$\begin{aligned} \langle O \rangle &= \frac{\langle \Psi^{N+1} | O | \Psi^{N+1} \rangle}{\langle \Psi^{N+1} | \Psi^{N+1} \rangle} \\ &= \frac{\langle \Phi^{N+1} | \{1 + S^\dagger\} \bar{O} \{1 + S\} | \Phi^{N+1} \rangle}{\langle \Phi^{N+1} | \{1 + S^\dagger\} \exp(T^\dagger) \exp(T) \{1 + S\} | \Phi^{N+1} \rangle}, \end{aligned} \quad (6)$$

where $\bar{O} = \exp(T^\dagger) O \exp(T)$.

The first few terms in the above expectation value can be identified as \bar{O} , $\bar{O}S_1$, $\bar{O}S_2$, $S_1^\dagger \bar{O}S_1$, etc.; are referred to as dressed Dirac-Fock (DDF), dressed pair correlation (DPC) [Fig. 1(a)] and dressed core polarization (DCP) [Fig. 1(b)], respectively. We use the term “dressed” because the operator O includes the effects of the core excitation operator T . Among the above, we can identify few other terms which play crucial role in determining the correlation effects. One of those terms is $S_1^\dagger \bar{O}S_1 + \text{c.c.}$ [Fig. 1(c)] which is called as dressed higher order pair correlation (DHOPC) since it directly involves the correlation between a pair of electrons. In Table II individual contributions from these diagrams are listed.

The orbitals used in the present work are expanded in terms of a finite basis set comprising of Gaussian type orbitals using a two parameter Fermi nuclear distribution [19]. The interaction of the atomic quadrupole moment with the external electric-field gradient is analogous to the interaction of a nuclear quadrupole moment with the electric fields generated by the atomic electrons inside the nucleus. In the presence of the electric field, this gives rise to an energy shift by coupling with the gradient of the electric field. Thus the treatment of the electric quadrupole moment is analogous to the nuclear counterpart. The quadrupole moment Θ of an atomic state $|\Psi(\gamma, J, M)\rangle$ is defined as the diagonal matrix element of the quadrupole operator with the maximum value M_J , given by

$$\Theta = \langle \Psi(\gamma J J) | \Theta_{zz} | \Psi(\gamma J J) \rangle. \quad (7)$$

Here, γ is an additional quantum number which distinguishes the initial and final states. The electric quadrupole operator in terms of the electronic coordinates is given by

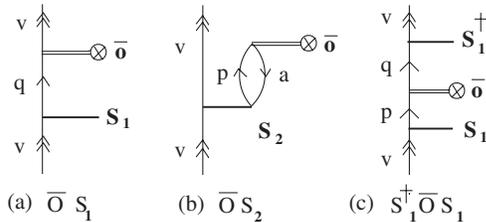


FIG. 1. The diagrams (a) and (c) are subsets of DPC diagrams. Diagram (b) is one of the direct DCP diagram.

$$\Theta_{zz} = -\frac{e}{2} \sum_j (3z_j^2 - r_j^2),$$

where the sum is over all the electrons and z is the coordinate of the j th electron. To calculate the quantity we express the quadrupole operator in its single particle form as

$$\Theta_m^{(2)} = \sum_m q_m^{(2)} \quad (8)$$

and the single particle reduced matrix element is expressed as [20]

$$\langle j_f || q_m^{(2)} || j_i \rangle = \langle j_f || C_m^{(2)} || j_i \rangle \int dr r^2 (P_{\kappa_f} P_{\kappa_i} + Q_{\kappa_f} Q_{\kappa_i}). \quad (9)$$

In Eq. (9), the subscripts f and i correspond to the final and initial states, respectively; P and Q are the radial part of the large and small components of the single particle Dirac-Fock wave functions, respectively, j_i is the total angular momentum for the i th electron. The angular factor is given in by

$$\begin{aligned} \langle j_f || C_m^{(k)} || j_i \rangle &= (-1)^{(j_f+1/2)} \sqrt{(2j_f+1)} \sqrt{(2j_i+1)} \\ &\times \begin{pmatrix} j_f & 2 & j_i \\ -1/2 & 0 & 1/2 \end{pmatrix} \pi(l, k, l'), \end{aligned} \quad (10)$$

where

$$\pi(l, k, l') = \begin{cases} 1 & \text{if } l+k+l' \text{ even} \\ 0 & \text{otherwise;} \end{cases}$$

l and k being the orbital angular momentum and the rank, respectively.

Finally using the Wigner-Eckart theorem we define the electric quadrupole moment in terms of the reduced matrix elements as

$$\langle j_f | \Theta_m^{(2)} | j_i \rangle = (-1)^{j_f-m_f} \begin{pmatrix} j_f & 2 & j_i \\ -m_f & 0 & m_f \end{pmatrix} \langle j_f || \Theta^{(2)} || j_i \rangle. \quad (11)$$

We focus on the clock transition $5s^2 S_{1/2} - 4d^2 D_{5/2}$ in $^{88}\text{Sr}^+$ shown in Fig. 2. The electric quadrupole shift in the energy levels arises due to the interaction of atomic electric quadrupole moment (EQM) with the external electric-field gradient. The electric quadrupole moment in the state $4d^2 D_{5/2}$ was measured experimentally by Barwood *et al.* at the National Physical Laboratory, UK [8]. Since the ground state $5s^2 S_{1/2}$ does not possess any electric quadrupole moment, the contribution to the quadrupole shift for the clock frequency comes only from the $4d^2 D_{5/2}$ state.

In Table I we have presented the details of the basis functions used in this calculation and in Table II contributions from different many-body terms. The value of Θ in the $4d^2 D_{5/2}$ state measured experimentally is

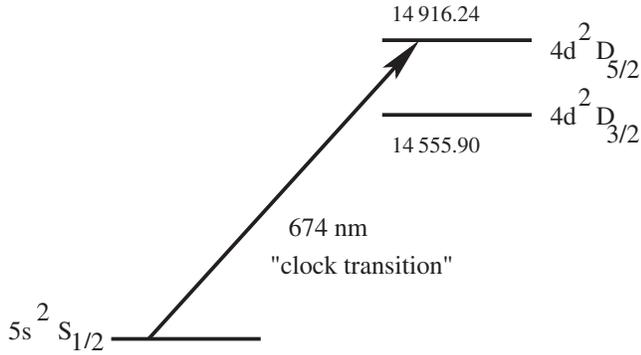


FIG. 2. Diagram indicating the clock transition in $^{88}\text{Sr}^+$. Excitation energies of the $4d^2D_{3/2}$ and $4d^2D_{5/2}$ levels are given in cm^{-1} .

$(2.6 \pm 0.3)ea_0^2$ [8], where e is the electronic charge and a_0 is the Bohr radius. Our calculated value for the $4d^2D_{5/2}$ stretched state is $(2.94 \pm 0.07)ea_0^2$. To test the convergence of our calculation we have performed more than five calculations with different basis sets of increasing dimensions and by extrapolating the results to an infinite basis set. We have estimated the error incurred in our present work, by taking the difference between our RCC calculations with singles, doubles as well as the most important triple excitations [CCSD(T)] and only single and double excitations (CCSD). We have also estimated the effect of Breit interaction which turns out to be 0.3% and lies between the error of our calculation. A nonrelativistic Hartree-Fock determination resulted in $\Theta = 3.03ea_0^2$ [8]. A subsequent calculation based on RCI with MCDF-EOL orbital basis yielded $\Theta = 3.02ea_0^2$ [10]. In that calculation, correlation effects arising from a subset of the terms S_1 , T_1 for single excitations and S_2 and T_2 for double excitations were considered, where S_1 and S_2 are the cluster operators representing single excitations from the valence $4d$ orbital to a virtual orbital and double excitations from the valence $4d$ and the core $\{4s, 4p, 3d\}$ orbitals, with at most one excitation from the core, respectively. In our calculation, in addition to these effects, the effects arising from the nonlinear terms like T_2^2 , T_1T_2 , etc., have been included. In the framework of CCSD theory, the single and double excitations have been treated to all orders in electron correlation including excitations from the entire core.

TABLE I. Number of basis functions used to generate the even-tempered Dirac-Fock orbitals and the corresponding value of α_0 and β used for Sr^+ .

	$s_{1/2}$	$p_{1/2}$	$p_{3/2}$	$d_{3/2}$	$d_{5/2}$	$f_{5/2}$	$f_{7/2}$	$g_{7/2}$	$g_{9/2}$
Number of basis	38	35	35	30	30	25	25	20	20
$\alpha_0(\times 10^{-5})$	525	525	525	425	425	427	427	425	425
β	2.33	2.33	2.33	2.13	2.13	2.13	2.13	1.98	1.98
Active holes	4	3	3	1	1	0	0	0	0
Active particles	10	10	10	11	11	8	8	6	6

TABLE II. Contributions of the electric quadrupole moment for the $4d^2D_{5/2}$ state of $^{88}\text{Sr}^+$ in atomic units from different many-body effects in the CCSD(T) calculation. The terms like DDF, DCP, DPC, DHOPC are explained in the text. The remaining terms in Eq. (6) are referred to as "others." The number given in the column "Triples" corresponds to the contribution from approximate perturbative triple excitations.

DDF	DPC	DCP	DHOPC	Others	Triples	Total
3.4963	-0.4306	-0.0642	0.0353	-0.0944	-0.07	2.94

This amounts to a more rigorous treatment of electron correlation in comparison to the previous calculation performed using the RCI method. We have also determined the EQM for the metastable $4d^2D_{3/2}$ state of $^{88}\text{Sr}^+$. The value we obtained is $2.12ea_0^2$, whereas Itano's calculation yields the value $2.107ea_0^2$ [12].

It is clear from Table II that the DDF contribution is the largest. The leading correlation contribution comes from the DPC effects and the DCP effects are an order of magnitude smaller. This can be understood from the DPC diagram [Fig. 1(a)] which has a valence electron in the $4d_{5/2}$ state. Hence the dominant contribution to the electric quadrupole moment arises from the overlap between virtual $d_{5/2}$ orbitals and the valence, owing to the fact that S_1 is an operator of rank 0 and the electric quadrupole matrix elements for the valence $4d_{5/2}$ and the diffuse virtual $d_{5/2}$ orbitals are substantial. On the other hand, in the DCP diagram [Fig. 1(b)], the matrix element of the same operator could also involve the less diffuse s or p orbitals. Hence, for a property like the electric quadrupole moment, whose magnitude depends on the square of the radial distance from the nucleus, this trend seems reasonable, whereas for properties like hyperfine interaction which is sensitive to the near nuclear region, the trend is just the opposite for the d states [15]. As expected, the contribution of the DHOPC effect, i.e., $S_1^\dagger \bar{O} S_1$ [Fig. 1(c)] is relatively important as it involves an electric quadrupole matrix element between the valence $4d_{5/2}$ and a virtual $d_{5/2}$ orbital. Unlike many other properties, particularly the hyperfine interactions, an all-order determination of this diagram is essential for obtaining an accurate value of the electric quadrupole moment. One of the strengths of RCC

TABLE III. Electric quadrupole moments (in ea_0^2) for the metastable ${}^2D_{3/2,5/2}$ states of ${}^{43}\text{Ca}^+$ and ${}^{138}\text{Ba}^+$.

States	${}^{43}\text{Ca}^+$		${}^{138}\text{Ba}^+$	
	$3d\ {}^2D_{3/2}$	$3d\ {}^2D_{5/2}$	$5d\ {}^2D_{3/2}$	$5d\ {}^2D_{5/2}$
Present work	1.338	1.916	2.309	3.382
Others [12]	1.338	1.917	2.297	3.379

theory is that it can evaluate such diagrams to all orders in the residual Coulomb interaction.

We have also calculated the EQMs of the metastable ${}^2D_{3/2,5/2}$ states of ${}^{43}\text{Ca}^+$ and ${}^{138}\text{Ba}^+$ and they are given in Table III. We have also estimated the error for these calculations similar to ${}^{88}\text{Sr}^+$ and they vary from 0.5% to 1.8%. Our coupled-cluster calculations of EQMs for the metastable D states of these two ions agree well with the other calculations [12]. We find that the correlation effects are similar to ${}^{88}\text{Sr}^+$. Our analyses reveal that for both the ${}^2D_{3/2}$ and ${}^2D_{5/2}$ states the largest contribution is at the DDF level, followed by DPC and DCP, respectively. The latter two are opposite in sign. More specifically, the Dirac-Fock values overestimate the EQMs and that is the reason why the correlation effects are so important in these cases. This is demonstrated in the case of the ${}^{88}\text{Sr}^+$ $4d^2D_{5/2}$ state in Table II.

In conclusion, we have performed an *ab initio* calculation of the electric quadrupole moment for the $4d\ {}^2D_{5/2}$ state of ${}^{88}\text{Sr}^+$ to an accuracy of less than 2.5% using the RCC theory. In addition we have also determined the EQM of $4d\ {}^2D_{3/2}$ state of the same ion and the EQMs of the metastable ${}^2D_{3/2,5/2}$ states of ${}^{43}\text{Ca}^+$ and ${}^{138}\text{Ba}^+$. Evaluation of the correlation effects to all orders as well as the inclusion of the dominant triple excitations in our calculation were crucial in achieving this accuracy. This is the first application of RCC theory to determine the electric quadrupole moment of atomic systems. Our RCC

calculation of the EQM for the $4d\ {}^2D_{5/2}$ state in ${}^{88}\text{Sr}^+$ is the most accurate determination of this property to date. It also highlights the potential of the RCC theory to determine the atomic properties at large distances from the nucleus with unprecedented accuracy.

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