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Finite-element multiconfiguration Hartree-Fock calculations of the atomic quadrupole moments of excited states of Be, Al, In, Ne, Ar, Kr, and Xe

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The atomic quadrupole moments Q_{zz} of Be($2s2p;{}^3P_2$), Al($3p;{}^2P_{3/2}$), In($5p;{}^2P_{3/2}$), Ne($2p^5 3s\,{}^3P_2$), Ar($3p^5 4s;{}^3P_2$), Kr($4p^5 5s;{}^3P_2$), and Xe($5p^5 6s;{}^3P_2$) have been calculated using a finite-element multiconfiguration Hartree-Fock method. The obtained Q_{zz}(Be) of 2.265 a.u. agrees with previously calculated values. The calculated Q_{zz}(Al) and Q_{zz}(In) of 2.579 and 3.165 a.u. are in good agreement with the experimental values of 2.53(15) a.u. and 2.94(10) a.u. A large *s-d* polarization contribution to the Q_{zz} of the rare gases is found in the present calculations. The correlation contributions from double (D), triple (T), and quadruple (Q) excitations to the Q_{zz} of the rare gases alternate; the total DTQ correlation contribution is negligibly small for Ne, Ar, and Kr, while the DTQ correlation contribution to the Q_{zz}(Xe) is 25% of the final Q_{zz}. The final values are Q_{zz}(Ne)$=-0.0506$ a.u., Q_{zz}(Ar)$=-0.0553$ a.u., Q_{zz}(Kr)$=+0.0601$ a.u., and Q_{zz}(Xe)$=+0.4505$ a.u., as compared to the experimental values of $-0.048(5)$ a.u., $-0.042(4)$ a.u., $+0.046(5)$ a.u., and $+0.30(3)$ a.u. for Ne, Ar, Kr, and Xe, respectively.

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I. INTRODUCTION

A direct measurement of atomic quadrupole moments was reported in 1967 by Angel, Sandars, and Woodgate [1] who measured the quadrupole moment of the ${}^2P_{3/2}$ state of aluminum using atomic beam resonance apparatus. Using the same apparatus, Sandars and Stewart [2] measured the quadrupole moment of the ${}^2P_{3/2}$ state of indium, and the quadrupole moments of the $np^5(n+1)s\;{}^3P_2$ excited states of the rare-gas atoms neon, argon, krypton, and xenon. Miller and Freund [3,4] have measured the quadrupole moment of the $1s4p$ and $1s5p\;{}^3P$ excited states of helium using atomic alignment experiments based on the diamagnetic polarizability anisotropy. To our knowledge there are no other measurements of atomic quadrupole moments.

An experimental apparatus similar to that used for obtaining the quadrupole moments for the excited states of the rare-gas atoms has also been used by Player and Sandars [5] on the $5p^5 6s\;{}^3P_2$ state of xenon in the search for an electronic dipole moment.

Theoretical estimates for the quadrupole moments of aluminum [1], indium, neon, argon, krypton, and xenon [2] have been obtained using Hartree-Fock and Hartree-Fock-Slater wave functions. The quadrupole shielding factors were determined by comparing calculated quadrupole moments with experimental ones [2]. For aluminum and indium the quadrupole moments obtained in the Hartree-Fock approximation are in reasonable agreement with the measured ones. However, for the rare-gas states the Hartree-Fock and Hartree-Fock-Slater approximations did not provide quadrupole moments in agreement with the experimental ones. In the work of Sandars and Stewart [2] this discrepancy was discussed and they concluded that the excitation of the $(n+1)s$ electron into a *d* shell gives rise to significantly modified quadrupole moments of the rare-gas atoms. This polarization is not taken into account in a Hartree-Fock or in a Hartree-Fock-Slater calculation. Sen [6] calculated the quadrupole shielding factors for aluminum and indium using Sternheimer's perturbation approach [7] and obtained a good agreement with experiment. The quadrupole shielding factors for the rare-gas states were calculated by Sternheimer [8,9]. A very good agreement with experimental values was obtained.

Sinanoğlu and Beck [10] and McCavert [11] have calculated the quadrupole moment of the $2s2p\;{}^3P_2$ state of beryllium using Hartree-Fock and the "nonclosed shell many electron theory" (NCMET) methods. Recently Ceraulo and Berry [12] calculated, using unrestricted Hartree-Fock (UHF), configuration-interaction (CI), and rotor-vibrator (RV) approaches, the quadrupole moments of the lowest *nsnp* excited states of the alkaline-earth atoms beryllium, magnesium, calcium, strontium, and barium. They also calculated the quadrupole moments of the singly excited $1s4p$ and $1s5p\;{}^3P$ states of helium. The discrepancy between the calculated quadrupole moments and those measured by Miller and Freund [3,4] for the excited states of helium was about 30%. For beryllium, the discrepancies between the quadrupole moments calculated by Ceraulo and Berry [12] and those calculated by Sinanoğlu and Beck [10] and by McCavert [11] were up to 16%.

The purpose of this work is to study the quadrupole moments of Be($2s2p;{}^3P_2$), Al($2p;{}^2P_{3/2}$), In($5p;{}^2P_{3/2}$), and of the $np^5(n+1)s;{}^3P_2$ ($n=2$–5 for Ne to Xe) excited states of the rare-gas atoms using the finite-element multiconfiguration Hartree-Fock (MCHF) program

LUCAS [13–18]. The atomic quadrupole moment of Ca($3d4s$;^1D) [13] and the electric field gradient at the nucleus (efg) of Ne($2p^53s$;$^3P_2$) [14] have previously been studied using the present finite-element (FE) MCHF approach. The efg combined with the nuclear quadrupole coupling constant yielded the nuclear quadrupole moment of the ^{21}Ne nucleus [14]. The efg operator has the same angular part as the quadrupole-moment operator but the radial integrals are mainly determined by the inner part of the atom.

II. METHODS

The finite-element multiconfiguration Hartree-Fock method used in this work has previously been discussed [15–18]. To facilitate the selection of the configurations, the MCHF method is based on the restricted active space (RAS) [19,20] method which is an adaptation of the complete active space (CAS) method [21]. The active orbital space consists of three subspaces, the RAS I, the RAS II, and the RAS III spaces. In a RAS calculation a lower limit is given for the number of electrons in RAS I, and an upper limit is given for the number of electrons in RAS III, while there is no restriction on the number of electrons in RAS II. The following notations are used for the RAS calculations: inactive orbitals // the orbitals of RAS I {minimum number of electrons in RAS I } / the orbitals of RAS II / the orbitals of RAS III (maximum number of electrons in RAS III). When a hyphen appears in the notation it means that all the orbitals to the left are frozen while those to the right are fully optimized. If it is not otherwise quoted, the frozen shells are always taken from the previous calculation of the table.

For an LS-coupled wave function, the atomic quadrupole moment is usually characterized by the $M_L = L$ component of the wave function [1] and evaluated from

$$Q_{zz} = -\sum_{i,j} \sqrt{(4\pi/5)} \langle Y_{l(i)}^{m(i)} | Y_2^0 | Y_{l(j)}^{m(j)} \rangle \langle \phi_i | r^2 | \phi_j \rangle \Gamma_{ij} \ . \tag{2.1}$$

In Eq. (2.1), Y_l^m are the spherical harmonics, ϕ_i is the radial part of the orbital i, and Γ_{ij} are the elements of the one-electron density matrix. The relativistic effects are estimated using a quasirelativistic configuration-interaction (QRCI) approach where the Darwin and the mass-velocity integrals are added to the one-electron integrals, and a nonrelativistic CI is performed with the modified integrals.

III. RESULTS AND DISCUSSION

A. Be

The quadrupole moment of Be($2s2p$;$^3P_2$), Q_{zz}(Be), was obtained by performing CAS calculations with systematically increased size of the active space. Calculations with the $1s$ shell inactive yielded a two-electron limit of 2.2996 a.u. for Q_{zz}(Be). The four-electron limit of Q_{zz}(Be) obtained in a $6s5p4d3f$ CAS calculation (Be-9) became 2.2652 a.u. (see Table I). A comparison between the Be-8 and Be-10 CAS calculations shows that the contributions to Q_{zz}(be) from g shells are very small. The changes of Q_{zz}(Be) due to relativistic effects are also small, as expected. In Table II the present quadrupole moments of Be are compared to values from the literature.

TABLE I. The quadrupole moment Q_{zz} and the total energy E_T of Be($2s2p$;$^3P_2$) as a function of the active space (in a.u.).

Active space[a]	Label	Q_{zz}	E_T[b]
$1s//1s/1p(1)$	Be-1	2.0478	−14.511 502
$1s//2s2p$	Be-2	2.0669	−14.513 065
$1s//2s2p1d$	Be-3	2.3062	−14.518 265
$1s//3s3p2d1f$	Be-4	2.3002	−14.518 632
$1s//4s4p3d2f1g$	Be-5	2.2996	−14.518 694
$3s2p1d$	Be-6	2.2435	−14.553 679
$4s3p2d1f$	Be-7	2.2276	−14.560 524
$5s4p3d2f$	Be-8	2.2559	−14.564 109
$6s5p4d3f$	Be-9	2.2652	−14.565 581
$5s4p3d2f1g$	Be-10	2.2558	−14.564 298
$5s4p3d2f1g$-[c]	Be-11	2.2557	−14.566 817
$1s//5s5p4d3f$-[d]	Be-12	2.2909	−14.518 541

[a] For notation see text.

[b] The number of grid points is 201 and the practical infinity is set to 100 a.u. Fourth-order element functions are used.

[c] Quasirelativistic calculation. See text.

[d] Two-electron CI in the shells of the Be-9 calculation.

The present two-electron value for Q_{zz}(Be) is very close to the NCMET results calculated by Sinanoğlu and Beck [10], and to those calculated by McCavert [11]. Sinanoğlu and Beck [10] found a negligibly small contribution (0.05%) from $1s$. However, according to the present calculations the $1s$ polarization contribution to Q_{zz}(Be) is significantly larger (1.0–1.5 %). A core-correlation contribution to Q_{zz}(Be) of −0.034 a.u. is obtained by comparing the Q_{zz} of the Be-9 and the Be-5 calculations, while the core-correlation contribution becomes −0.026 a.u. when it is estimated as the difference

TABLE II. The quadrupole moment Q_{zz} of Be($2s2p$;$^3P_2$) as compared to literature values (in a.u.).

Method	Value	Ref.[a]
Hartree-Fock	2.048	PW
Two-electron limit	2.300	PW
Core-correlation correction	−0.026	PW
Four-electron limit	2.265	PW
Relativistic correction	−0.0001	PW
Extrapolated value[b]	2.274	PW
Hartree-Fock	2.045	[10]
NCMET[c]	2.296	[10]
NCMET[c]	2.306	[11]
Unrestricted Hartree-Fock	1.833	[12]
Configuration-interaction	2.140	[12]
Rotor-vibrator	1.919	[12]

[a] PW denotes present work.

[b] Obtained by adding the core-correlation correction to the two-electron limit.

[c] A "nonclosed shell many-electron theory" calculation.

between the Q_{zz} of a two-electron CI calculation (Be-12) and the Q_{zz} of the Be-9 calculation. The Be-12 CI calculation is performed in the shells of the Be-9 calculation.

The configuration-interaction, the unrestricted Hartree-Fock, and the rotor-vibrator calculations by Ceraulo and Berry [12] yielded values for Q_{zz}(Be) which are 19%, 5.5%, and 15% smaller than the present four-electron limit, respectively. Although Ceraulo and Berry consider the results of the rotor-vibrator method to be sound, it does not seem to be a very accurate method.

B. Al and In

The valence limits for Q_{zz}(Al) and Q_{zz}(In) are obtained by performing valence (three electron) CAS calculations with systematically enlarged active spaces. The largest valence calculations (Al-4 and In-4) yielded a Q_{zz}(Al) of 2.5995 a.u. and a Q_{zz}(In) of 3.1720 a.u. (see Tables III and IV).

The relativistic correction to Q_{zz}(Al) obtained from the QRCI calculation is 0.0004 a.u. For In, the corresponding relativistic correction became −0.021 a.u. These relativistic corrections significantly differ from the ones obtained by comparing Hartree-Fock and Dirac-Fock (DF) calculations. The $\langle r^2\rangle_{\text{rel}}/\langle r^2\rangle_{\text{nonrel}}$ ratio of 1.002 69 for the $3p_{3/2}$ shell of Al yields a relativistic correction of 0.007 a.u. [22], and for In, the $\langle r^2\rangle_{\text{rel}}/\langle r^2\rangle_{\text{nonrel}}$ of 1.017 93 for the $5p_{3/2}$ shell yields a relativistic correction of 0.056 a.u. [22]. The Al($3p;{}^2P_{3/2}$) and the In($5p;{}^2P_{3/2}$) states have one dominating configuration and are therefore well described in the HF (DF) model. The relativistic corrections of Table V are the ones deduced from the $\langle r^2\rangle$ ratios.

The core-correlation and the polarization contributions to Q_{zz}(Al) of −0.028 a.u. were estimated by comparing the result of the valence CAS calculation (Al-6) with that of the $2s//1s2p/2s2p2d\text{-}1s1p1d(2)$ RAS calculation (Al-9). The contributions from most of the triple, quadruple, and higher excitations are not considered in the Al-9 RAS calculation. These contributions are estimated as the difference between the Q_{zz}(Al) of the Al-7 and Al-8 calculations. The core-correlation correction in Table V is estimated as Q_{zz}(Al-9)−Q_{zz}(Al-6)+Q_{zz}(Al-7)−Q_{zz}(Al-8). The 1*s* and 2*s* shells are uncorrelated in all Al calculations and therefore do not contribute to the final Q_{zz}(Al). The contribution to Q_{zz}(Al) from the contracted 1*s* and 2*s* is expected to be very small.

TABLE III. The quadrupole moment Q_{zz} and the total energy E_T of Al($3p;{}^2P_{3/2}$) as a function of the active space (in a.u.).

Active space[a]	Label	Q_{zz}	E_T[b]
$3s1p//1p$	Al-1	2.8012	−241.876 710
$2s1p//2s2p1d$	Al-2	2.5256	−241.930 931
$2s1p//3s3p2d1f$	Al-3	2.5917	−241.934 195
$2s1p//4s4p3d2f1g$	Al-4	2.5995	−241.934 839
$2s1p//4s4p3d2f1g$-[c]	Al-5	2.5999	−242.369 851
$2s1p//3s3p2d$	Al-6	2.5767	−241.932 375
$2s1p//4s4p3d$	Al-7	2.5835	−241.932 554
$2s1p//1s1p/3s3p3d$-(2)	Al-8	2.5808	−241.932 199
$2s//1s2p/2s2p2d\text{-}1s1p1d(2)$[d]	Al-9	2.5456	−242.107 318

[a] For notation see text.

[b] See footnote b of Table I.

[c] Quasirelativistic calculation. See text.

[d] The frozen shells are taken from the Al-6 calculation.

Valence correlation effects reduce the size of Q_{zz}(Al) by 7.2% and core correlation and polarization reduce it further by about 1% of the Hartree-Fock value. The final Q_{zz}(Al) is in an excellent agreement with the experimental result [1]. The uncertainty in the calculated value is estimated to be less than 1% as compared to the experimental error of 6% [1]. The Al and In results are compared to literature values in Table V.

For In, valence correlation reduces Q_{zz}(In) with only 4.7% as compared to 7.2% for Al. The core-valence correlation contribution of −0.063 a.u. to Q_{zz}(In) was estimated as the difference between the Q_{zz} of the In-10 RAS calculation and the Q_{zz} of the In-11 valence CI calculation and correcting for a core-valence correlation *f*-shell contribution of −0.010 a.u. estimated as Q_{zz}(In-12)−Q_{zz}(In-8)−Q_{zz}(In-13)+Q_{zz}(In-9) (see Table IV). In the core-valence RAS calculations (In-7, In-8, In-10, and In-12), only single excitations are allowed from the 4*d* shell to the shells of the RAS III space, and only the core-valence *spd* shells of the RAS III space are optimized. The 4*d* polarization contribution to Q_{zz}(In) became only 2% of the HF value. The final calculated value for Q_{zz}(In) of 3.165 a.u. is 4−11 % larger than the experimental result of 2.94(10) a.u. [2]. The main reason for the discrepancy is probably the neglect of the core-core (4*d*) correlation in the MCHF calculations.

C. Ne, Ar, Kr, and Xe

The computational procedure for the MCHF determination of the quadrupole moments of the excited states of the rare-gas atoms is slightly different from that of the Be, Al, and In calculations. The $(n+1)s$ shell is diffuse ($\langle r\rangle_{3s,\text{Ne}}$=4.39 a.u., $\langle r\rangle_{4s,\text{Ar}}$=5.43 a.u., $\langle r\rangle_{3s,\text{Kr}}$=5.78 a.u., and $\langle r\rangle_{4s,\text{Xe}}$=6.45 a.u.) and soft. The $(n+1)s$ shell is polarized by the hole in the *np* shell [2]. The first step in the computational procedure is to design the orbitals that give the *s*-*d* polarization of the $(n+1)s$ shell.

In order to design polarization shells, polarization and core-valence correlation calculations (pol+CV) were performed. In the pol+CV calculations, the HF shells were frozen, and single excitations from the *nsnp* shells in RAS I to the shells of RAS II were included. All RAS II shells but the HF $(n+1)s$ shell were optimized. In the HF reference the *np* shell contains five electrons, and in a pol+CV calculation there must be at least four electrons in the *np* shell or alternatively, with *ns* correlated, at least six electrons in the *nsnp* shells. Obviously, there are one or two electrons in RAS II. All configurations which have RAS II singly occupied are polarization configurations, while those with two electrons in RAS II are core-valence correlation configurations.

The pol+CV *spd* limit for the Q_{zz}'s of Ne, Ar, Kr, and Xe were obtained by systematically augmenting the RAS II space with *s*, *p*, and *d* shells (Ne-2 to Ne-8 of Table VI,

TABLE IV. The quadrupole moment Q_{zz} and the total energy E_T of In($5p;{}^2P_{3/2}$) as a function of the active space (in a.u.).

Active space[a]	Label	Q_{zz}	E_T[b]
5s3p2d//1p	In-1	3.3294	−5740.169 221
4s3p2d//2s2p1d	In-2	3.0924	−5740.213 529
4s3p2d//3s3p2d1f	In-3	3.1615	−5740.216 646
4s3p2d//4s4p3d2f1g	In-4	3.1720	−5740.217 424
4s3p2d//4s4p3d2f1g-[c]	In-5	3.1507	−5870.695 171
4s3p2d//3s3p2d	In-6	3.1474	−5740.214 744
4s3p1d//1d{9}/3s3p2d-1s1p1d	In-7	3.0934	−5740.237 918
4s3p1d//1d{9}/2s2p1d/-1s1p1d(2)[d]	In-8	3.0683	−5740.236 124
4s3p2d//2s2p1d/1s1p1d-(2)[e]	In-9	3.1111	−5740.214 409
4s3p1d//1d{9}/2s2p1d/-2s2p2d(2)[d]	In-10	3.0741	−5740.238 099
4s3p2d//2s2p1d/2s2p2d-(2)[e]	In-11	3.1276	−5740.214 737
4s3p1d//1d{9}/2s2p1d/-1s1p1d1f(2)[d]	In-12	3.0586	−5740.283 919
4s3p2d//2s2p1d/1s1p1d1f-(2)[e]	In-13	3.1109	−5740.214 833

[a] For notation see text.

[b] The number of grid points is 401 and the practical infinity is set to 1000 a.u. Fourth-order element functions are used.

[c] Quasirelativistic calculation. See text.

[d] The frozen shells are from the In-2 calculation.

[e] Valence CI in the shells of the previous calculation in the table.

Ar-2 to Ar-7 of Table VII, Kr-2 to Kr-7 of Table VIII, and Xe-2 to Xe-7 of Table IX). The core-polarization contribution to the Q_{zz}'s (from 1*s*, 2*s*1*p*, 3*s*2*p*1*d*, and 4*s*3*p*2*d* for Ne to Xe) is small and neglected. The *f*- and *g*-shell contributions to Q_{zz} were estimated by adding optimized *f* and *g* shells to the RAS II space and comparing this Q_{zz} with that of the corresponding *spd* calculation. The shells of the *spd* calculation (Ne-8, Ar-7, Kr-7, and Xe-5) were frozen. For Ne, also the *f* shells were frozen in the *g*-shell calculation.

The effect of double and triple excitations from the *ns*, *np*, and $(n+1)s$ orbitals on Q_{zz} was estimated by performing multireference CI (MRCI) calculations in the shells of the pol+CV RAS calculations. The change in Q_{zz} due to quadruple excitations was estimated by comparing MR SDT and MR SDTQ CI calculations with the *ns* shell doubly occupied in all configurations.

The polarization calculations (Ne-21, Ar-20, Kr-19, and Xe-20) were performed as follows. The HF shells were frozen. The *np* shell was set in RAS II and the $(n+1)s$ shell in RAS III. The RAS III space was augmented by one *d* shell which was optimized. There is only one electron in RAS III. The most important excitation of the polarization calculations is the $(n+1)s$ to *d* excitation mimicking the *s*-*d* polarization.

The HF values for Q_{zz} of the rare gases are close to the Hartree-Fock-Slater (HFS) ones [2], while they significantly differ from the experimental results. The *spd* limits of −0.0500, −0.0740, +0.0376, and ±0.5064 a.u. for the Q_{zz}'s of Ne, Ar, Kr, and Xe, respectively, obtained in the pol+CV calculations are reminiscent of the experimental values. (See Table X). In the *spd*-limit calculations, the first set of *spd* shells hardly affects the Q_{zz}. For Ne, Ar, and Kr, the third and fourth sets of *spd* shells significantly reduce them. These *spd* shells are also very unimportant for the energies. The lowering in the total energy due to the addition of the third and fourth sets of *spd* shells is −0.0759, −0.782, and −0.890 mH

TABLE V. The quadrupole moment Q_{zz} of the ${}^2P_{3/2}$ states of Al and In as compared to literature values (in a.u.).

Method	Al	In	Ref.
Hartree-Fock	2.801	3.329	PW
MCHF valence limit	2.600	3.172	PW
Core-valence correlation correction		−0.063	PW
Core-correlation correction[a]	−0.028		PW
Relativistic correction	0.007	0.056	PW
Final value	2.579	3.165	PW
Hartree-Fock	2.801	3.329	[23]
Hartree-Fock	2.8	3.32	[1,2]
Experiment	2.53(15)	2.94(10)	[1,2]

[a] Includes both core-core and core-valence correlation corrections.

for Ne, Ar, and Kr, respectively. For Xe, the second and third sets of *spd* shells change the Q_{zz} by 1.6005 a.u., yet their contribution to the total energy is only 5.109 mH.

The *f*-shell contributions, estimated as Ne-12 − Ne-8, Ar-11 − Ar-7, Kr-9 − Kr-7, and Xe-10 − Xe-5, are all positive, and they are larger for the heavier rare gases. For Xe, the *f*-shell contribution is about 30% of the final Q_{zz}.

The *g*-shell contributions are estimated as the Q_{zz} differences Ne-13 − Ne-12, Ar-12 − Ar-8, Kr-10 − Kr-8, and Xe-12 − Xe-9. For Ne and Ar, the *g*-shell contributions are very small and negative, for Kr it is +0.0043 a.u. and for Xe +0.0700 a.u., i.e., about half of the *f*-shell contribution.

The *s*-*d* polarization is not obtained in the HF model, and the relativistic contributions to Q_{zz} cannot be reliably estimated from DF (HF) calculations. The relativistic corrections to Q_{zz}(Ne) (Ne-14 − Ne-8) and to Q_{zz}(Ar) (Ar-13 − Ar-7) are negligibly small. The relativistic corrections are all negative and become as expected, in absolute value, larger with increasing nuclear charge. For Xe, the relativistic correction (Xe-13 − Xe-7) is −0.1612 a.u. or 36% of the final Q_{zz}(Xe), and for Kr (Kr-11 − Kr-7) it is about one order of magnitude smaller than for Xe. The quasirelativistic method (QRCI) used in this work which is based on relativistic perturbation expansions does not consider spin-orbit splittings. The QRCI method becomes less reliable for heavier systems. However, for Kr and Xe the discrepancy between the nonrelativistic and the experimental Q_{zz} values is reduced by the relativistic corrections. For the ground state of Xe, the difference in $\langle r^2 \rangle$ of $5p_{1/2}$ and $5p_{3/2}$ is 0.6 a.u. [22]. The spin-orbit effects which are not considered in the QRCI calculations may be responsible for a large fraction of the discrepancy between the final Q_{zz}(Xe) and the experimental value.

A comparison of the Q_{zz} obtained in the pol+CV RAS calculations and those of the MRSD CI calculations in the same shells show that the *s*-*d* polarization of the $(n+1)s$ is lost in the MRSD CI calculation. The Q_{zz}'s contained in the MRSDT CI calculations are very close to the pol+CV values. The triple excitations introduce polarization of the doubly excited configurations. The quadruple excitations contribute one to two orders of magnitude less than double and triple excitations. Quadruple excitations are also found to be more important for the heavier rare gases. The total correlation contribution to Q_{zz} from *D*, *T*, and *Q* are −0.0019, −0.0007, and −0.0005 a.u. for Ne, Ar, and Kr, respectively. Note that we use here the notation *D*, *T*, and *Q* to indicate the number of excitations from RAS I. For Xe, the total *DTQ* correlation contribution is −0.1087 a.u., which is about 25% of the final Q_{xx}(Xe). For Xe, a larger radial overlap between the $(n+1)s$ orbital and the *nsnp* semicore orbitals makes higher-order excitation effects more important.

TABLE VI. The quadrupole moment Q_{zz} and the total energy E_T of Ne($2p^5 3s;{}^3P_2$) as a function of the active space (in a.u.).

Active space[a]	Label	Q_{zz}	E_T[b]
2*s*//1*p*1*s*	Ne-1	−0.1984	−127.992 315
1*s*//1*s*1*p*{6}/1*s*-1*s*1*p*1*d*	Ne-2	−0.2120	−128.023 386
1*s*//1*s*1*p*{6}/1*s*-2*s*2*p*2*d*	Ne-3	−0.1931	−128.025 905
1*s*//1*s*1*p*{6}/1*s*-3*s*3*p*3*d*	Ne-4	−0.1043	−128.026 531
1*s*//1*s*1*p*{6}/1*s*-4*s*4*p*4*d*	Ne-5	−0.0579	−128.026 664
1*s*//1*s*1*p*{6}/1*s*-5*s*5*p*5*d*	Ne-6	−0.0553	−128.026 720
1*s*//1*s*1*p*{6}/1*s*-6*s*6*p*6*d*	Ne-7	−0.0516	−128.026 737
1*s*//1*s*1*p*{6}/1*s*-7*s*7*p*7*d*	Ne-8	−0.0500	−128.026 743
1*s*//1*s*1*p*{6}/8*s*7*p*7*d*-1*f*	Ne-9	−0.0460	−128.031 178
1*s*//1*s*1*p*{6}/8*s*7*p*7*d*-2*f*	Ne-10	−0.0476	−128.031 406
1*s*//1*s*1*p*{6}/8*s*7*p*7*d*-3*f*	Ne-11	−0.0477	−128.031 449
1*s*//1*s*1*p*{6}/8*s*7*p*7*d*-4*f*	Ne-12	−0.0477	−128.031 461
1*s*//1*s*1*p*{6}/8*s*7*p*7*d*4*f*-1g	Ne-13	−0.0481	−128.031 521
1*s*//1*s*1*p*{6}/8*s*7*p*7*d*-[c]	Ne-14	−0.0505	−128.165 229
1*s*//2*s*1*p*/3*s*3*p*3*d*-(2)[d]	Ne-15	−0.1478	−128.187 460
1*s*//2*s*1*p*/4*s*4*p*4*d*-(2)[e]	Ne-16	−0.1331	−128.195 604
1*s*//2*s*1*p*/3*s*3*p*3*d*-(3)[d]	Ne-17	−0.1075	−128.190 810
1*s*//2*s*1*p*/4*s*4*p*4*d*-(3)[e]	Ne-18	−0.0596	−128.199 227
2*s*//1*s*1*p*/3*s*3*p*3*d*-(3)[d]	Ne-19	−0.1176	−128.118 670
2*s*//1*s*1*p*/3*s*3*p*3*d*-(4)[d]	Ne-20	−0.1178	−128.119 688
2*s*//1*p*/1*s*-1*d*(1)[f]	Ne-21	−0.0335	−127.992 602

[a] For notation see text.

[b] The number of grid points is 201 and the practical infinity is set to 100 a.u. Fourth-order element functions are used.

[c] Quasirelativistic CI in the shells of the Ne-8 calculation.

[d] CI in the shells of the Ne-4 calculation.

[e] CI in the shells of the Ne-5 calculation.

[f] Polarization calculation.

TABLE VII. The quadrupole moment Q_{zz} and the total energy E_T of Ar($3p^5 4s;{}^3P_2$) as a function of the active space (in a.u.).

Active space[a]	Label	Q_{zz}	E_T[b]
3s1p//1p1s	Ar-1	−0.5800	−526.416 746
2s1p//1s1p{6}/1s-1s1p1d	Ar-2	−0.5973	−526.454 638
2s1p//1s1p{6}/1s-2s2p2d	Ar-3	−0.4730	−526.458 198
2s1p//1s1p{6}/1s-3s3p3d	Ar-4	−0.1384	−526.458 848
2s1p//1s1p{6}/1s-4s4p4d	Ar-5	−0.0787	−526.458 980
2s1p//1s1p{6}/1s-5s5p5d	Ar-6	−0.0740	−526.459 012
2s1p//1s1p{6}/1s-6s6p6d	Ar-7	−0.0740	−526.459 024
2s1p//1s1p{6}/7s6p6d-1f	Ar-8	−0.0511	−528.466 371
2s1p//1s1p{6}/7s6p6d-2f	Ar-9	−0.0570	−526.466 787
2s1p//1s1p{6}/7s6p6d-3f	Ar-10	−0.0552	−526.466 848
2s1p//1s1p{6}/7s6p6d-4f	Ar-11	−0.0540	−526.466 860
2s1p//1s1p{6}/7s6p6d-1f1g	Ar-12	−0.0512	−526.466 418
2s1p//1s1p{6}/7s6p6d-[c]	Ar-13	−0.0746	−528.262 049
2s1p//2s1p/3s3p3d-(2)[d]	Ar-14	−0.3719	−526.585 598
2s1p//2s1p/4s4p4d-(2)[e]	Ar-15	−0.3600	−526.588 696
2s1p//2s1p/3s3p3d-(3)[d]	Ar-16	−0.1338	−526.591 437
2s1p//2s1p/4s4p4d-(3)[e]	Ar-17	−0.0712	−526.594 847
3s1p//1s1p/3s3p3d-(3)[d]	Ar-18	−0.1304	−526.533 506
3s1p//1s1p/3s3p3d-(4)[d]	Ar-19	−0.1386	−526.536 331
3s1p//1p/1s-1d(1)[f]	Ar-20	+0.0907	−526.417 590

[a] For notation see text.

[b] The number of grid points is 301 and the practical infinity is set to 100 a.u. Fourth-order element functions are used.

[c] Quasirelativistic CI in the shells of the Ar-7 calculation.

[d] CI in the shells of the Ar-4 calculation.

[e] CI in the shells of the Ar-5 calculation.

[f] Polarization calculation.

TABLE VIII. The quadrupole moment Q_{zz} and the total energy E_T of Kr($4p^5 5s;{}^3P_2$) as a function of the active space (in a.u.).

Active space[a]	Label	Q_{zz}	E_T[b]
4s2p1d//1p/1s(1)	Kr-1	−0.7952	−2751.701 567
3s2p1d//1s1p{6}/1s-1s1p1d	Kr-2	−0.8105	−2751.734 276
3s2p1d//1s1p{6}/1s-2s2p2d	Kr-3	−0.5086	−2751.738 187
3s2p1d//1s1p{6}/1s-3s3p3d	Kr-4	−0.0213	−2751.738 958
3s2p1d//1s1p{6}/1s-4s4p4d	Kr-5	+0.0292	−2751.739 077
3s2p1d//1s1p{6}/1s-5s5p5d	Kr-6	+0.0353	−2751.739 105
3s2p1d//1s1p{6}/1s-6s6p6d	Kr-7	+0.0376	−2751.739 113
3s2p1d//1s1p{6}/7s6p6d-1f	Kr-8	+0.0759	−2751.747 078
3s2p1d//1s1p{6}/7s6p6d-2f	Kr-9	+0.0724	−2751.747 567
3s2p1d//1s1p{6}/7s6p6d-1f1g	Kr-10	+0.0802	−2751.747 145
3s2p1d//1s1p{6}/7s6p6d-[c]	Kr-11	+0.0205	−2786.877 527
3s2p1d//2s1p/3s3p3d-(2)[d]	Kr-13	−0.4422	−2751.837 573
3s2p1d//2s1p/4s4p4d-(2)[e]	Kr-14	−0.4409	−2751.840 043
3s2p1d//2s1p/3s3p3d-(3)[d]	Kr-15	−0.0118	−2751.842 276
4s2p1d//1s1p/3s3p3d-(3)[d]	Kr-16	−0.0128	−2751.795 609
4s2p1d//1s1p/4s4p4d-(3)[e]	Kr-17	+0.0430	−2751.796 849
4s2p1d//1s1p/3s3p3d-(4)[d]	Kr-18	−0.0271	−2751.797 721
4s2p1d//1p/1s-1d(1)[f]	Kr-19	+0.3031	−2751.702 880

[a] For notation see text.

[b] The number of grid points is 401 and the practical infinity is set to 1000 a.u. Fourth-order element functions are used.

[c] Quasirelativistic CI in the shells of the Kr-7 calculation.

[d] CI in the shells of the Kr-4 calculation.

[e] CI in the shells of the Kr-5 calculation.

[f] Polarization calculation.

TABLE IX. The quadrupole moment Q_{zz} and the total energy E_T of Xe($4p^5 5s;{}^3P_2$) as a function of the active space (in a.u.).

Active space[a]	Label	Q_{zz}	E_T[b]
5s3p2d//1p1s	Xe-1	−1.1377	−7231.829 651
4s3p2d//1s1p{6}/1s-1s1p1d	Xe-2	−1.1439	−7231.859 552
4s3p2d//1s1p{6}/1s-2s2p2d	Xe-3	−0.1413	−7231.863 800
4s3p2d//1s1p{6}/1s-3s3p3d	Xe-4	+0.4566	−7231.864 661
4s3p2d//1s1p{6}/1s-4s4p4d	Xe-5	+0.4981	−7231.864 767
4s3p2d//1s1p{6}/1s-5s5p5d	Xe-6	+0.5041	−7231.864 790
4s3p2d//1s1p{6}/1s-6s6p6d	Xe-7	+0.5064	−7231.864 797
4s3p2d//1s1p{6}/5s4p4d-1f	Xe-8	+0.5926	−7231.874 116
4s3p2d//1s1p{6}/5s4p4d-2f	Xe-9	+0.6331	−7231.874 701
4s3p2d//1s1p{6}/5s4p4d-3f	Xe-10	+0.6421	−7231.874 773
4s3p2d//1s1p{6}/5s4p4d-1f1g	Xe-11	+0.6526	−7231.874 231
4s3p2d//1s1p{6}/5s4p4d-2f2g	Xe-12	+0.7031	−7231.875 031
4s3p2d//1s1p{6}/7s6p6d-[c]	Xe-13	+0.3452	−7429.144 546
4s3p2d//2s1p/3s3p3d-(2)[d]	Xe-14	−0.5306	−7231.944 360
4s3p2d//2s1p/4s4p4d-(2)[e]	Xe-15	−0.5413	−7231.946 243
4s3p2d//2s1p/3s3p3d-(3)[d]	Xe-16	+0.4324	−7231.949 170
5s3p2d//1s1p/3s3p3d-(3)[d]	Xe-17	+0.4543	−7231.910 686
5s3p2d//1s1p/4s4p4d-(3)[e]	Xe-18	+0.5033	−7231.911 610
5s3p2d//1s1p/3s3p3d-(4)[d]	Xe-19	+0.4113	−7231.912 706
5s3p2d//1p/1s-1d[f]	Xe-20	+1.0962	−7231.831 784

[a] For notation see text.

[b] The number of grid points is 601 and the practical infinity is set to 1000 a.u. Sixth-order element functions are used.

[c] Quasirelativistic CI in the shells of the Xe-7 calculation.

[d] CI in the shells of the Xe-4 calculation.

[e] CI in the shells of the Xe-5 calculation.

[f] Polarization calculation.

The *D* corrections given in Table X are estimated as the Q_{zz} differences Ne-16−Ne-5, Ar-15−Ar-5, Kr-14−Kr-5, and Xe-15−Xe-5. The *T* corrections of Table X are analogously obtained as Ne-18−Ne-16, Ar-17−Ar-15, Kr-17−Kr-16+Kr-15−Kr-14, and Xe-18−Xe-17+Xe-16−Xe-15, while the *Q* correction is simply the differences Ne-20−Ne-19, Ar-19−Ar-18, Kr-18−Kr-16, and Xe-19−Xe-17. The final Q_{zz}'s of Table X are obtained by adding the corrections to the MCHF CV *spd*-limit values in Table X.

Multireference single and double (MRSD) RAS calculations with the *ns*, *np*, and $(n+1)s$ shells ($n=2$–5 for Ne to Xe) in RAS II, and with at most two electrons in the orbitals of RAS III are not capable of reproducing

TABLE X. The quadrupole moment Q_{zz} of the rare-gas atoms in $np^5(n+1)s\ {}^3P_2$ state as compared to literature values (in a.u.).

Method[a]	Ne	Ar	Kr	Xe	Ref.
HF	−0.1984	−0.5800	−0.7952	−1.1377	PW
MCHF CV *spd* limit	−0.0500	−0.0740	+0.0376	+0.5064	PW
f contribution	+0.0023	+0.0200	+0.0348	+0.1440	PW
g contribution	−0.0004	−0.0001	+0.0043	+0.0700	PW
D correction	−0.0752	−0.2813	−0.4701	−1.0394	PW
T correction	+0.0735	+0.2888	+0.4849	+1.0227	PW
Q correction	−0.0002	−0.0082	−0.0143	−0.0920	PW
Relativistic correction	−0.0005	−0.0006	−0.0171	−0.1612	PW
Final value	−0.0506	−0.0553	+0.0601	+0.4505	PW
Polarization calc.	−0.0335	+0.0907	+0.3031	+1.0962	PW
HFS	−0.234	−0.613	−0.822	−1.15	[2]
Sternheimer	−0.0428	+0.0098	+0.0962	+0.380	[8]
Sternheimer	−0.0447	−0.0049	+0.0649	+0.303	[9]
Experiment	−0.048(5)	−0.042(4)	+0.046(5)	+0.30(3)	[2]

[a] For details, see the text.

the *s-d* polarization. In the MRSD RAS calculations, the inactive shells and the shells in RAS II were frozen HF shells, while the shells in RAS III were optimized.

The *s-d* polarization contribution was separately estimated by performing the polarization calculations Ne-21, Ar-20, Kr-19, and Xe-20. The Q_{zz} obtained in the polarization calculations are qualitatively correct but the *s-d* polarization effect is exaggerated. The CV correlation contributions estimated as the difference between the Q_{zz} of the polarization and the Q_{zz} obtained in the pol+CV calculations become -0.02, -0.17, -0.27, and -0.58 a.u. for Ne to Xe, respectively.

For Xe, the *DTQ* correlation and relativistic corrections, and the contributions from higher angular momentum functions (*f* and *g* functions) are of the same magnitude as the experimental Q_{zz}. These effects are not taken into account in Sternheimer's perturbation potential method for estimating the quadrupole polarization effects [7–9]. This shows that the agreement between the experimental Q_{zz} and the Q_{zz} calculated by Sternheimer using his perturbation method [8,9] is fortuitous.

The electric field gradient at the nucleus which was calculated previously for Ne using the same MCHF program [18] is not very sensitive to the *s-d* polarization. The efg operator weights the inner region of the atom, and the major contributions to the efg come from the hole in the *np* shell and from an *s-d* polarization of the inner *ns* shell. The *s-d* polarization of the outer $(n+1)s$ shell hardly contributes to the efg.

IV. CONCLUSION

The Q_{zz} of the $2s2p\ ^3P_2$ excited state of Be, the $^2P_{3/2}$ states of Al and In, and the $np(n+1)s\ ^3P_2$ excited states of Ne, Ar, Kr, and Xe have been determined using a finite-element multiconfiguration Hartree-Fock method. The values obtained for Q_{zz}(Be), Q_{zz}(Ne), Q_{zz}(Al), and Q_{zz}(In) were in good agreement with previous calculated and experimental results. See Tables II, V, and X. The final Q_{zz}(Ar) and Q_{zz}(Kr) are in absolute value only 0.013 and 0.014 a.u. larger than the experimental results. For Q_{zz}(Xe), the discrepancy between calculated and experimental quadrupole moments is 0.15 a.u. A large *s-d* polarization contribution to the Q_{zz} of the rare gases is found in the present calculations. For Ne, Ar, and Kr, contributions from doubles, triples, and quadruples to Q_{zz} alternate but the sum is negligibly small, while for Q_{zz}(Xe) they also alternate but the net contribution to Q_{zz}(Xe) is 0.1 a.u. Contributions from *f* shells are significant for Q_{zz}(Ar), Q_{zz}(Kr), and Q_{zz}(Xe). For Q_{zz}(Xe), the *g*-shell contribution is half of the *f*-shell contribution, and may not be neglected in an accurate determination of Q_{zz}(Xe). It is also shown that core-valence correlation contributions to the Q_{zz} of the rare gases are very important, and a simple polarization model in a limited basis is not able to yield accurate quadrupole moments. Hence the agreement between the experimental Q_{zz} of the rare gases and the ones obtained by Sternheimer using his perturbation potential method [7–9] must be considered fortuitous.

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