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# Finite-field many-body-perturbation-theory calculation of the static hyperpolarizabilities and polarizabilities of Mg, $Al^+$, and Ca

Edet F. Archibong and Ajit J. Thakkar
*Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 6E2*

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The dipole-dipole-quadrupole ($B$) and second dipole ($\gamma$) hyperpolarizabilities and the dipole ($\alpha_1$) and quadrupole ($\alpha_2$) polarizabilities are calculated for the ground states of the magnesium and calcium atoms and the aluminum cation. The results are based on finite-field fourth-order many-body perturbation theory using a finite-field self-consistent-field wave function as the zeroth-order wave function. Our fourth-order results are $\alpha_1=71.7e^2a_0^2E_H^{-1}$, $\alpha_2=809e^2a_0^4E_H^{-1}$, $B=(-7.75\times 10^3)e^3a_0^4E_H^{-2}$, and $\gamma=(1.02\times 10^5)e^4a_0^4E_H^{-3}$ for Mg; $\alpha_1=24.2e^2a_0^2E_H^{-1}$, $\alpha_2=124e^2a_0^4E_H^{-1}$, $B=-642e^3a_0^4E_H^{-2}$, and $\gamma=(2.37\times 10^3)e^4a_0^4E_H^{-3}$ for $Al^+$; and $\alpha_1=157e^2a_0^2E_H^{-1}$, $\alpha_2=(3.02\times 10^3)e^2a_0^4E_H^{-1}$, $B=(-3.29\times 10^4)e^3a_0^4E_H^{-2}$, and $\gamma=(3.83\times 10^5)e^4a_0^4E_H^{-3}$ for Ca.

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## I. INTRODUCTION

Polarizabilities and hyperpolarizabilities are very useful quantities in many areas of atomic and molecular physics [1–3]. For example, they are important in studies of intermolecular forces [4] and related phenomena [5], nonlinear optics [6,7], and low-energy electron scattering off molecules [8]. Despite their importance, reliable values of these properties are known only for a few elements mainly from the alkali-metal, alkaline-earth, and rare-gas groups of the Periodic Table. Even within these groups there are many gaps in our knowledge. For example, the only one of these properties that has been measured for Mg, $Al^+$, or Ca is the dipole polarizability of the calcium atom [9]. Although a few semiempirical estimates [10–12] and many theoretical calculations [13–26] have been made for these three species, only the dipole and quadrupole polarizabilities of Mg and the dipole polarizability of Ca have been established reliably in this manner.

The purpose of this paper is to report a finite-field, fourth-order many-body perturbation theory calculation of the dipole and quadrupole polarizabilities, and the dipole-dipole-quadrupole ($B$) and second dipole ($\gamma$) hyperpolarizabilities of ground-state Mg, $Al^+$, and Ca. The $B$ hyperpolarizability is important in a proper description of the long-range electron-atom interaction, and is needed to estimate the leading coefficients in the long-range multipole moments of dimers [27]. This paper complements our recent work [27–29] on the group II species Be, $Li^-$, and $B^+$. The computational methodology is summarized in Sec. II, and the results are presented, analyzed, and compared with previous work in Sec. III. Hartree atomic units are used throughout this paper.

## II. COMPUTATIONAL METHOD

### A. Finite-field polarizabilities

The change in energy of a neutral, $S$-state atom upon introduction of a static, axially symmetric field $F_z$, with gradient $F_{zz}$, is given [2] by

$$\Delta E=-\alpha_1F_z^2/2-\alpha_2F_{zz}^2/8-BF_z^2F_{zz}/4 -\gamma F_z^4/24-\cdots , \tag{1}$$

in which $\alpha_1$ and $\alpha_2$ are the dipole and quadrupole polarizabilities, respectively, and $B$ and $\gamma$ are the dipole-dipole-quadrupole and second dipole hyperpolarizabilities, respectively. $\alpha_2$ is precisely the $\alpha_q$ of Dalgarno [1], but is twice the $C$ of Buckingham [2].

In the finite-field method [25,30–32], the polarizabilities are obtained from combinations of energies of the atom perturbed by different fields. If the field is homogeneous, then Eq. (1) can be written as

$$\Delta E_d(F_z)=-\alpha_1F_z^2/2-\gamma F_z^4/4!-\gamma_4F_z^6/6! -\gamma_6F_z^8/8!-\cdots , \tag{2}$$

in which $\gamma_4,\gamma_6,\ldots$ are the fourth, sixth, and higher dipole hyperpolarizabilities. Thus, given the energies of an atom perturbed by two or more different homogeneous fields, $\alpha_1$ and $\gamma$ can be obtained from truncations of Eq. (2). In this work five terms were retained in Eq. (2).

In a purely quadrupolar field, Eq. (1) reduces to

$$\Delta E_q(F_{zz})=-\alpha_2F_{zz}^2/8-\Gamma_1F_{zz}^3-\Gamma_2F_{zz}^4-\cdots , \tag{3}$$

in which $\Gamma_1,\Gamma_2,\ldots$ are the first, second, and higher quadrupole hyperpolarizabilities. The odd terms in Eq. (3) can be eliminated as follows:

$$\Delta E_q(F_{zz})+\Delta E_q(-F_{zz})=-\alpha_2F_{zz}^2/4-2\Gamma_2F_{zz}^4 -\cdots . \tag{4}$$

$\alpha_2$ was obtained from Eq. (4) with two terms retained on the right-hand side. Finally, let $\Delta E_{dq}(F_z,F_{zz})$ be the energy change in the presence of both a homogeneous field and a quadrupolar field. Equation (1) shows that the expansion of this quantity contains all powers of $F_{zz}$, all even powers of $F_z$, and all corresponding cross terms. All terms involving even powers of $F_{zz}$ *and* all pure dipolar terms can be eliminated by forming the difference $\Delta E_{dq}(F_z,F_{zz})-\Delta E_{dq}(F_z,-F_{zz})$. It is then easy to eliminate all pure quadrupolar terms as well to find

$$\Delta E_{dq}(F_z,F_{zz})-\Delta E_{dq}(F_z,-F_{zz})-\Delta E_q(F_{zz})+\Delta E_q(-F_{zz})=-BF_z^2F_{zz}/2-\sigma_{23}F_z^2F_{zz}^3-\sigma_{41}F_z^4F_{zz}-\cdots\ , \tag{5}$$

in which $\sigma_{23},\sigma_{41},\ldots$ are higher mixed hyperpolarizabilities. In this work, the field strength and gradient were both weak, and $B$ was obtained from Eq. (5) with only the leading term retained on the right-hand side.

Violations of the Hellmann-Feynman theorem by approximate wave functions do not affect the accuracy of electric properties calculated solely from perturbed energies [25,31–33]. This is not true for electric properties obtained from perturbed multipole moments. Hence, our final results are based on perturbed energies only. However, a useful check is provided by electric properties obtained from perturbed multipole moments at the self-consistent-field (SCF) level for which the Hellmann-Feynman theorem is satisfied. The relevant equations are summarized below.

In the presence of a homogeneous field, the induced dipole ($\mu$) and quadrupole ($\theta$) moments of an $S$-state atom are given by

$$\mu(F_z)=\alpha_1F_z+\gamma F_z^3/3!+\gamma_4F_z^5/5!+\gamma_6F_z^7/7!+\cdots \tag{6}$$

and

$$\theta(F_z)=BF_z^2/2+2\sigma_{41}F_z^4+2\sigma_{61}F_z^6+2\sigma_{81}F_z^8+\cdots\ . \tag{7}$$

$\alpha_1$ and $\gamma$ are obtained from Eq. (6) in a manner analogous to that used to obtain these quantities from Eq. (2), and $B$ is obtained similarly from Eq. (7). In a pure quadrupolar field, the induced quadrupole moment of an $S$-state atom is given by

$$\theta(F_{zz})=\alpha_2F_{zz}/2+6\Gamma_1F_{zz}^2+8\Gamma_2F_{zz}^3+10\Gamma_3F_{zz}^4+\cdots\ . \tag{8}$$

$\alpha_2$ is obtained from Eq.(7) in a manner similar to that used to obtain it from Eq. (3). $B$ can also be obtained, in a manner analogous to that used to obtain it from Eq. (5), from the induced dipole moment in the presence of both a homogeneous field and a quadrupolar field:

$$\begin{aligned}\mu(F_z,F_{zz})-\mu(F_z,-F_{zz})&=BF_zF_{zz}+2\sigma_{23}F_zF_{zz}^3\\&\quad+4\sigma_{41}F_z^3F_{zz}-\cdots\ .\end{aligned} \tag{9}$$

### B. Field-dependent energies

If field-dependent SCF energies are used, then the finite-field method is equivalent to the coupled Hartree-Fock (CHF) procedure and to the static limit of the random-phase approximation [34,35]. A CHF calculation is useful for many purposes but cannot yield high-accuracy results because of the neglect of true correlation effects. The latter can be accounted for if the field-dependent energies are calculated by a method that allows for electron correlation and starts with the field-dependent SCF wave function as the reference function [35,36]. Early finite-field calculations with correlated energies include the polarizability calculations of Werner and Meyer [37], and the hyperpolarizability calculations of Bartlett and Purvis [38]. Hinchliffe [31], Urban *et al.*, and Dykstra [25] provide useful reviews of many finite-field calculations made since then.

In this work the field-dependent correlated energy calculations are based on the Moeller-Plesset (MP) variant of many-body perturbation theory which has been reviewed thoroughly [32,39,40]. A hierarchy of successively more complete MP energies, and therefore also properties computed from them, can be written as

$$E_{\mathrm{MP2}}=E_{\mathrm{SCF}}+E_{D2}\ , \tag{10}$$

$$E_{\mathrm{MP3}}=E_{\mathrm{MP2}}+E_{D3}\ , \tag{11}$$

$$E_{SDQ\text{-}\mathrm{MP4}}=E_{\mathrm{MP3}}+E_{S4}+E_{D4}+E_{\mathrm{QR4}}\ , \tag{12}$$

$$E_{\mathrm{MP4}}=E_{SDQ\text{-}\mathrm{MP4}}+E_{T4}\ , \tag{13}$$

where the numeral indicates order, $S$, $D$, and $T$, respectively, stand for contributions from single, double, and triple substitutions with respect to the zeroth-order function, and QR denotes the contribution from disconnected quadruple substitutions plus the renormalization term.

### C. Basis sets

The selection of a good one-particle basis set is essential to the success of any polarizability calculation

TABLE I. [$14s11p6d3f$] basis set for Mg. Five-component $d$- and seven-component $f$-GTF were used. Exponents are given in parentheses and are preceded by contraction coefficients only if the latter are different from 1. All quantities are in atomic units.

$$\begin{aligned}(7s)/[1s]={}&0.000\,124(1\,708\,066)+0.000\,957(255\,748.6)+0.004\,971(58\,200.05)+0.020\,964(16\,485.12)+0.076\,231(5378.248)\\&+0.246\,878(1941.664)+0.722\,262(757.2925)+13s(314.0328,136.806,61.985\,69,28.976\,43,13.805\,15,6.464\,312,2.994\,069,\\&\qquad 1.364\,919,0.616\,381,0.147\,513,0.066\,715,0.029\,514,0.013\,057)\\+(5p)/[1p]={}&0.001\,146(2263.106)+0.010\,160(536.0126)+0.056\,960(174.0500)+0.236\,257(66.347\,42)+0.769\,500(27.859\,82)\\&+10p(12.500\,59,5.846\,649,2.772\,711,1.313\,476,0.612\,521,0.254\,030,0.096,0.048,0.024,0.012)\\&+6d(1.7,0.425,0.318,0.106\,25,0.0615,0.0243)+3f(0.12,0.080,0.053)\end{aligned}$$

TABLE II. [14$s$11$p$6$d$3$f$] basis set for $Al^+$. Five-component $d$- and seven-component $f$-GTF were used. Exponents are given in parentheses and are preceded by contraction coefficients only if the latter are different from 1. All quantities are in atomic units.

$$\begin{aligned}
(6s)/[1s] ={}& 0.000\,423(2\,203\,790)+0.002\,857(329\,944.1)+0.015\,133(75\,081.71)+0.064\,024(21\,266.41)+0.232\,816(6938.077)\\
&+0.754\,748(2504.811)+13s(976.9710,405.1890,176.6066,80.119\,46,37.552\,62,18.022\,59,8.667\,077,\\
&\quad 3.961\,705,1.828\,544,0.841\,712,0.242\,606,0.109\,717,0.047\,076)\\
+(4p)/[1p] ={}& 0.003\,936(3116.242)+0.034\,650(737.9542)+0.196\,234(239.6734)+0.828\,440(91.499\,85)\\
&+10p(38.542\,44,17.365\,17,8.182\,553,3.930\,197,1.897\,362,0.911\,690,0.411\,189,0.175\,864,0.073\,941,0.030\,777)\\
&+6d(13.8,4.6,1.53,0.3,0.13,0.056)+3f(5.8,1.2,0.25)
\end{aligned}$$

[25,31,32]. An extreme example of the sensitivity of hyperpolarizabilities to the basis set is provided by our work on lithium [41].

The basis set for Mg was constructed by starting with Partridge's (19$s$11$p$) set [42] of Gaussian-type function (GTF), and contracting it to [13$s$7$p$]. Then, we added a diffuse $s$-GTF with an exponent forming a geometric sequence with the exponents of the two most diffuse $s$-GTF in the substrate. Next, a set of four even-tempered $p$-GTF with exponents chosen to maximize the SCF $\alpha_1$ was added. Then, we added six $d$-GTF—three with exponents chosen to maximize $\alpha_2$ at the SCF level, and three to maximize the MP2 corrections to $\alpha_1$ and the field-free energy. Finally, three $f$-GTF chosen to maximize the MP2 corrections to $\alpha_2$ and the field-free energy were added. The resulting [14$s$11$p$6$d$3$f$] basis set, detailed in Table I, contains 98 contracted GTF.

The basis set for $Al^+$ was constructed by contracting Partridge's (19$s$14$p$) set [42] for neutral Al to [14$s$11$p$], and adding six $d$-GTF and three $f$-GTF in the manner described above for Mg. The details are given in Table II.

The basis set for Ca was constructed by starting with the (23$s$15$p$) set of Partridge [43] and contracting it to [13$s$7$p$]. Then, we added two diffuse $s$-GTF with exponents forming a geometric sequence with those of the two most diffuse $s$-GTF in the substrate. Next, three even-tempered $p$-GTF chosen to maximize $\alpha_1$ at the SCF level were added. We then added three even-tempered $d$-GTF to maximize $\alpha_1$ and four $d$-GTF to maximize $\alpha_2$ at the SCF level. To our surprise, a very tight $d$-GTF turned out to be necessary for the latter purpose. One $f$-GTF was added to maximize $\alpha_2$ at the MP2 level, and another one to minimize the field-free second-order energy correction. Finally, a third $f$-GTF whose exponent was the geometric mean of the other two was added. The resulting [15$s$10$p$7$d$3$f$] basis set contains 101 contracted GTF, and is listed in Table III.

### D. Computational details

The occupancies of the lowest orbital in Mg and $Al^+$ and the five lowest orbitals in Ca were kept frozen during the MP calculations which were performed with the GAUSSIAN 86 system [44].

Homogeneous fields were introduced as conventional finite fields but, as in our previous work [27–29], quasi-quadrupolar fields were generated by four point charges of $-32Q$, $Q$, $Q$, and $-32Q$ placed symmetrically about the atomic origin at the $z$ coordinates $-2R$, $-R$, $R$, and $2R$, respectively; with this arrangement,

TABLE III. [15$s$10$p$7$d$3$f$] basis set for Ca. Five-component $d$- and seven-component $f$-GTF were used. Exponents are given in parentheses and are preceded by contraction coefficients only if the latter are different from 1. All quantities are in atomic units.

$$\begin{aligned}
(8s)/[1s] ={}& 0.000\,035(12\,583\,230)+0.000\,318(1\,884\,722)+0.001\,696(429\,114.2)+0.007\,173(121\,605.6)+0.026\,114(39\,688.79)\\
&+0.085\,268(14\,332.73)+0.254\,249(5591.768)+0.698\,294(2320.138)\\
+(4s)/[1s] ={}& 0.116\,772(1012.582)+0.262\,672(460.9642)+0.501\,510(217.4029)+0.297\,741(26.522\,67)\\
&+13s(105.6677,52.638\,32,12.538\,96,6.285\,493,3.166\,764,1.432\,853,0.694\,955,0.326\,331,0.083\,411,0.041\,602,0.019\,838,\\
&\quad 0.009\,460,0.004\,511)\\
+(6p)/[1p] ={}& 0.000\,301(13\,644.11)+0.002\,672(3229.337)+0.015\,516(1049.011)+0.069\,024(401.5885)+0.248\,563(170.5179)\\
&+0.738\,050(77.743\,94)\\
+(4p)/[1p] ={}& 0.155\,887(37.350\,84)+0.285\,156(18.573\,81)+0.377\,212(9.428\,930)+0.300\,628(4.867\,379)\\
&+8p(2.505\,317,1.260\,803,0.621\,035,0.298\,662,0.122\,830,0.045,0.020,0.008\,889)\\
&+7d(9.80,2.5,1.0,0.40,0.095,0.0296,0.013)+3f(1.4,0.277,0.055)
\end{aligned}$$

$F_z, F_{zzz}, F_{zzzzz}, \ldots$ all vanish as does $F_{zzzz}$, and $|F_{zz}|=12Q/R^3$.

The values of the field strengths and gradients were chosen just large enough to produce numerically significant changes in the energies; note that stronger fields are required when small correlation corrections are to be computed than would be necessary if only SCF values were required. Enough terms were retained in the expansions to ensure that the polarizabilities computed from the perturbed SCF energies agreed with those computed from the perturbed SCF multipole moments, and to ensure stable values of the correlated properties of interest.

TABLE V. Correlation corrections to and correlated values of the electric properties of $Al^+$. All quantities are in atomic units. Conversion factors to SI units are given in the caption to Table IV.

| Method | $\alpha_1$ | $\gamma$ | $\alpha_2$ | $B$ |
|---|---|---|---|---|
| SCF | 26.444 | 2942 | 130.4 | −808.7 |
| *D*2 | −2.240 | −348 | −9.2 | 146.5 |
| *D*3 | −0.021 | −146 | 1.1 | 22.0 |
| *DQ*4 | 0.070 | −83 | 1.1 | 3.8 |
| *S*4 | 0.056 | 2 | 0.6 | −9.5 |
| *T*4 | −0.103 | 1 | −0.3 | 4.3 |
| MP2 | 24.204 | 2594 | 121.2 | −662.3 |
| MP3 | 24.183 | 2448 | 122.2 | −640.3 |
| *SDQ*-MP4 | 24.308 | 2367 | 123.9 | −646.0 |
| MP4 | 24.206 | 2368 | 123.5 | −641.7 |
| *P*[2/1] | 24.194 | 2274 | 116.9 | −641.6 |

## III. RESULTS AND DISCUSSION

### A. Quality of basis sets

Our SCF energies of Mg and Ca respectively, were $-199.614\,611E_H$ and $-676.753\,098E_H$; these are $0.025\times10^{-3}E_H$ and $5.1\times10^{-3}E_H$ above the respective numerical Hartree-Fock limits [45]. Our SCF dipole polarizabilities $\alpha_1$ (see Tables IV and V) are essentially identical to the numerical CHF limits [19] of $\alpha_1/e^2a_0^2E_H^{-1}=81.60$, 26.44, and 185.5 for Mg, $Al^+$, and Ca, respectively. Our SCF quadrupole polarizabilities $\alpha_2$ are within 0.2% of the numerical CHF limits [19] of $\alpha_2/e^2a_0^4E_H^{-1}=928.7$, 130.3, and 3604 for Mg, $Al^+$, and Ca, respectively. The very close agreement between our SCF polarizabilities and the CHF limits is an indication of the good quality of our basis sets.

The CHF limits of the $B$ and $\gamma$ hyperpolarizabilities are unknown; in fact, the only prior coupled SCF calculation of these quantities for Mg, $Al^+$, and Ca that we are aware of is the value of $B=-1.25\times10^4e^3a_0^4E_H^{-2}$ obtained by Dykstra [25] for Mg with a $(16s11p7d)/[10s8p7d]$ basis set. However, his value is likely to be less accurate than ours judging by the lack of $f$-GTF in his basis set and by the 3.8% discrepancy between his $\alpha_2$ value of $964.5e^2a_0^4E_H^{-1}$ and the CHF limit. There are uncoupled SCF values of $B/e^3a_0^4E_H^{-2}=-2.09\times10^4$, $-1730$, and $-1.25\times10^5$ for Mg, $Al^+$, and Ca, respectively [14]; however, our SCF results show that these values are too large by a factor of roughly 2. Similarly, the uncoupled SCF values of $\gamma/e^4a_0^4E_H^{-3}=2.19\times10^5$, 5242, and $1.66\times10^6$ for Mg, $Al^+$, and Ca, respectively [13], are too large as well.

### B. Effects of electron correlation

The correlated values of the electric properties of Mg, $Al^+$, and Ca are listed in Tables IV and V. These tables also list [2/1] Padé approximants [46] to the property series; the $P([2/1])$ approximants [27,28] obtained by differentiating [2/1] Padé approximants to the field-dependent energy could not be calculated reliably because of the lack of sufficient significant figures in the order-by-order corrections to the various properties.

The many-body perturbation series are rapidly convergent in all cases except those of $B$ for Ca, and $\alpha_2$ for $Al^+$. The discrepancies among the *SDQ*-MP4, MP4, and $P[2/1]$ values give an indication of the residual errors

TABLE IV. Correlation corrections to and correlated values of the electric properties of Mg and Ca. All quantities are in atomic units. Atomic units of $\alpha_1$ and $\gamma$ are $\simeq 1.648\,778\times10^{-41}$ $C^2m^2J^{-1}$ and $6.235\,378\times10^{-65}$ $C^4m^4J^{-3}$, respectively. Atomic units of $\alpha_2$ and $B\simeq 4.617\,048\times10^{-62}$ $C^2m^4J^{-1}$ and $1.696\,733\times10^{-63}$ $C^3m^4J^{-2}$, respectively.

| | $\alpha_1$ | | $10^{-5}\gamma$ | | $\alpha_2$ | | $10^{-3}B$ | |
|---|---|---|---|---|---|---|---|---|
| Method | Mg | Ca | Mg | Ca | Mg | Ca | Mg | Ca |
| SCF | 81.585 | 185.45 | 1.491 | 7.974 | 927.7 | 3598 | −10.75 | −51.00 |
| *D*2 | −9.301 | −41.11 | −0.372 | −3.526 | −121.2 | −812 | 2.569 | 22.89 |
| *D*3 | −0.623 | 7.73 | −0.087 | −0.653 | −6.8 | 130 | 0.469 | −0.93 |
| *DQ*4 | 0.085 | 5.55 | −0.033 | −0.380 | 5.0 | 84 | 0.110 | −1.71 |
| *S*4 | 0.263 | 2.83 | 0.024 | 0.559 | 8.0 | 91 | −0.189 | −3.47 |
| *T*4 | −0.314 | −3.82 | −0.004 | −0.142 | −3.5 | −74 | 0.044 | 1.38 |
| MP2 | 72.285 | 144.35 | 1.119 | 4.448 | 806.5 | 2786 | −8.180 | −28.12 |
| MP3 | 71.661 | 152.07 | 1.032 | 3.795 | 799.7 | 2916 | −7.711 | −29.05 |
| *SDQ*-MP4 | 72.009 | 160.45 | 1.024 | 3.973 | 812.8 | 3090 | −7.790 | −34.23 |
| MP4 | 71.695 | 156.64 | 1.020 | 3.831 | 809.3 | 3016 | −7.746 | −32.85 |
| *P*[2/1] | 71.693 | 163.25 | 1.018 | 3.829 | 803.7 | 3346 | −7.743 | −27.81 |

due to truncation of the MP series. Note that the computationally expensive triples contributions cannot be neglected because they are of the same order of magnitude as the other fourth-order contributions.

Correlation effects reduce the magnitudes of each of the electric properties. The effects increase in the order $\mathrm{Al}^+$, Mg, and Ca for a given property, and, for a given species, the effects are greater for the hyperpolarizabilities than for the polarizabilities. More specifically, the magnitudes of the MP4 values of $\alpha_1$, $\alpha_2$, $B$, and $\gamma$, respectively, are smaller than their SCF counterparts by 12%, 13%, 28% and 32% for Mg, by 8.5%, 5.3%, 21%, and 20% for $\mathrm{Al}^+$, and by 16%, 16%, 36%, and 52% for Ca.

### C. Correlated polarizabilities

Table VI contains a summary of various correlated calculations, experimental values, and semiempirical estimates of the dipole and quadrupole polarizabilities of magnesium and calcium; $\mathrm{Al}^+$ is not included in the table because there are no such values for $\mathrm{Al}^+$ in the literature. The results of Muller, Flesch, and Meyer [22] show clearly that including only valence correlation leads to values that are too large. We verified this at the MP2 level, and all the correlated calculations reported in this work include correlation of the $L$ and $M$ shells in Mg and $\mathrm{Al}^+$, and the $M$ and $N$ shells in Ca.

First consider the dipole polarizability for Mg. Except for the old $R$-matrix calculation of Robb [16], all theoretical results that include core-valence correlation lie between 70.3 and $72.2 e^2a_0^2E_H^{-1}$. The most accurate of these values are probably the multireference (MR) configuration interaction (CI) value [26] of $71.2 e^2a_0^2E_H^{-1}$ which appeared after the calculations described in this paper had been completed, and our MP4, or $P[2/1]$, result of $71.7 e^2a_0^2E_H^{-1}$. All these theoretical predictions are on the low side of the semiempirical estimates obtained by sum-

TABLE VI. Comparison of correlated and experimental polarizabilities of Mg and Ca. All quantities are in atomic units; see caption to Table IV for conversion factors to SI units.

| | Mg | | Ca | |
|---|---|---|---|---|
| Method[a] | $\alpha_1$ | $\alpha_2$ | $\alpha_1$ | $\alpha_2$ |
| $R$-matrix CI[b] | 75.4 | 1001 | | |
| PNO-CEPA[c] | 71.32 | | 153.9 | |
| Natural states pseudo-potential[d] | 70.5 | 828.0 | 153.7 | 2717 |
| Variation-perturbation valence CI[e] | 73.52 | 845.1 | | |
| Variation-perturbation valence CI[f] | | | 168.6 | 3180 |
| Valence CI[g] | 74.26 | | 175.5 | |
| Valence CI+core polarization[g] | 70.74 | | 156.0 | |
| Valence CI+core polarization[h] | 70.7 | | 157 | |
| Variation-perturbation CI[i] | | | 171.7 | |
| Valence CI+core polarization[j] | 72.2 | 781.0 | | |
| CI[j] | 70.3 | 767.8 | | |
| Multireference CI[k] | 71.2 | 785.1 | | |
| MP4[l] | 71.70 | 809.3 | 156.6 | 3016 |
| $P[2/1]$[m] | 71.69 | 803.7 | 163.3 | 3346 |
| Oscillator strength sums[n] | 75±3 | | | |
| Oscillator strength sums[o] | 75.5 | | 153.9 | |
| Oscillator strength sums[p] | 72.50 | | 155.9 | |
| Experiment[q] | | | 168.7±16.9 | |

[a] All calculations take core-valence correlation into account unless explicitly specified otherwise. CI denotes configuration interaction.

[b] Reference [16].

[c] Pseudonatural orbital coupled electron pair approximation; Ref. [17].

[d] Reference [18].

[e] Reference [20].

[f] Reference [21].

[g] Reference [22].

[h] Reference [23].

[i] Reference [24].

[j] Reference [26].

[k] Reference [26]; includes an approximate correction for quadruple substitutions.

[l] Fourth-order finite-field many-body perturbation theory; this work.

[m] Padé approximant to finite-field many-body perturbation series; this work.

[n] Reference [10].

[o] Reference [11].

[p] Reference [12].

[q] Reference [9].

ming over a mixture of experimental and theoretical oscillator strengths [10–12]. At first sight, this is a bit surprising because these semiempirical estimates would be lower bounds if the oscillator strengths used were sufficiently accurate. However, most of the oscillator strengths used have uncertainties of 3–5 %, and hence the estimates cannot be considered true lower bounds.

Next consider the dipole polarizability for Ca. Except for the calculation of Glass [24], all the theoretical calculations that include core-valence correlation lie between 153.7 and $157e^2a_0^2E_H^{-1}$, and are in good agreement with the oscillator strength sum estimates bearing in mind that the latter need not be lower bounds given the uncertainties in the oscillator strengths. We believe that Glass's variation perturbation result is too high probably because of the difficulty, inherent to that method, of achieving a balanced description of the field-free and perturbed wave functions. All the theoretical values are within the 10% error bars of the experimental measurement of Miller and Bederson [9] although all the calculated values except that of Glass [24] are on the low side of the experimental range. The true $\alpha_1$ for Ca is likely to be a little higher than our MP4 value of $157e^2a_0^2E_H^{-1}$ given that both the *SDQ*-MP4 and $P[2/1]$ values are higher than it.

Consider the quadrupole polarizabilities next. There are hardly any truly reliable values in the literature. The results of Maeder and Kutzelnigg [18] are based on a pseudopotential, and Magnasco and co-workers [20,21] did not include core-valence correlation. Robb's *R*-matrix calculation [16] for Mg included a small amount of core-valence correlation but is nevertheless too high. The true value of $\alpha_2$ for Mg is likely to be between the MR CI value [26] of $785e^2a_0^4E_H^{-1}$ and our MP4 result of $809e^2a_0^4E_H^{-1}$. The true value of $\alpha_2$ for calcium is probably closer to our *SDQ*-MP4 value of $3.09\times10^3e^2a_0^4E_H^{-1}$ than to our MP4 value of $3.02\times10^3e^2a_0^4E_H^{-1}$.

### D. Correlated hyperpolarizabilities

There has been virtually no previous work on correlated hyperpolarizabilities for Mg, $Al^+$, and Ca. There are no experimental results, and the only previous theoretical work attempting to go beyond the uncoupled SCF level is the model potential calculation of Manakov, Ovsyannikov, and Rapoport [15] who obtained $\gamma=1.7\times10^5e^4a_0^4E_H^{-3}$ for Mg which is much too large. Our MP4 values are the best available; an optimistic guess is that they are accurate to within 10%.

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