

## Brief Reports

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### Coupled-cluster calculation of hyperpolarizabilities and polarizabilities for Be

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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 state of the beryllium atom. The results are based on finite-field energies computed using the coupled-cluster double-excitation model (commonly known as CCD), corrected by fourth-order contributions from single and triple excitations computed with CCD amplitudes. The final values are  $\alpha_1 = 37.30e^2a_0^2E_H^{-1}$ ,  $\alpha_2 = 298.8e^2a_0^4E_H^{-1}$ ,  $B = -2102e^3a_0^4E_H^{-2}$ , and  $\gamma = 3.15 \times 10^4e^4a_0^4E_H^{-3}$ .

#### I. INTRODUCTION

Polarizabilities and hyperpolarizabilities play an important role in studies of electron-atom scattering and various phenomena induced by intermolecular forces. They can be defined in terms of the energy change caused by a static, axially symmetric field  $F_z$ , with gradient  $F_{zz}$ . For a neutral  $S$ -state atom, this energy change is given<sup>1</sup> by

$$\Delta E = -\alpha_1 F_z^2/2 - \alpha_2 F_{zz}^2/8 - B F_z^2 F_{zz}/4 - \gamma F_z^4/24 - \dots,$$

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. Note that our quadrupole polarizability  $\alpha_2$  is precisely the  $\alpha_q$  of Dalgarno,<sup>2</sup> but is twice the  $C$  of Buckingham.<sup>1</sup>

There are no experimental values for any of these properties of the beryllium atom. Many theoretical calculations of the dipole and quadrupole polarizabilities of Be have been made.<sup>3,4</sup> However, there has been only one computation<sup>4</sup> of its hyperpolarizabilities, using a method that accounts for electron correlation. The latter calculation<sup>4</sup> was based on fourth-order Moeller-Plesset perturbation theory (MPPT) relative to a coupled self-consistent-field (SCF) reference. The quasidegeneracy between the  $1s^2 2s^2$  and  $1s^2 2p^2$  configurations leads to rather slow convergence<sup>4-6</sup> of the MPPT series for the hyperpolarizabilities and polarizabilities of Be. Hence an improved calculation is desirable. Coupled-cluster (CC) theory is an infinite-order extension of many-body perturbation

theory that has enough stability to produce reasonable results with a single reference configuration even when quasidegeneracies are present.<sup>7</sup> Computations of the energy of the Be atom<sup>8</sup> and the dipole polarizability of the isoelectronic  $\text{Li}^-$  anion<sup>9</sup> suggest that CC hyperpolarizabilities of Be should be substantially more accurate than the fourth-order MPPT values.

This paper is a report of a calculation based on the coupled-cluster double-excitation model<sup>7</sup> (commonly known as CCD), including corrections for single and triple excitations,<sup>10</sup> of the dipole-dipole-quadrupole and second-dipole hyperpolarizabilities, and the dipole and quadrupole polarizabilities of ground-state Be. Computational details are summarized in Sec. II. The results are presented in Sec. III. Hartree atomic units are used throughout this paper.

#### II. COMPUTATIONAL DETAILS

The polarizabilities and hyperpolarizabilities were computed from energies of the atom, both free and in finite fields produced by point charges as in our earlier work.<sup>4</sup> The only difference was that slightly weaker dipolar fields of 0.0024, 0.0036, 0.0048, and 0.0060  $e^{-1}a_0^{-1}E_h$  were used because they led to greater stability of the second-dipole hyperpolarizability. All requisite energies were computed with GAUSSIAN-86.<sup>11</sup> The one-particle basis sets, composed of (15s12p6d2f) Gaussian-type functions contracted to [9s9p6d2f] basis-set functions, were precisely the sets 2A and 2B used earlier<sup>4</sup> for the dipole and quadrupole properties, respectively.

### III. RESULTS AND DISCUSSION

The polarizabilities are based solely on perturbed energies in order to avoid possible problems<sup>12</sup> associated with violations of the Hellmann-Feynman theorem. Moreover, true correlation effects are obtained because the occupied and virtual orbitals are allowed to relax in the external field so that the coupled Hartree-Fock (CHF) state is the reference state.

The results are presented in Table I. The SCF values for  $\alpha_1$ ,  $\alpha_2$ ,  $B$ , and  $\gamma$  are within 0.02%, 0.90%, 0.12%, and 2.0%, respectively, of the CHF limits.<sup>13</sup> MPPT( $n$ ) denotes the  $n$ th-order MPPT result. SDQ-MPPT(4) is an approximation to MPPT(4) that includes contributions from single ( $S$ ), double ( $D$ ), and quadruple ( $Q$ ) excitations but neglects  $T(4)$ , the fourth-order contribution from triple excitations. DQ-MPPT(4) is a cruder approximation to MPPT(4) that includes contributions from double and quadruple excitations but neglects both  $T(4)$  and  $S(4)$  (the fourth-order contribution from single excitations). Note that the MPPT series converge rather slowly. The MPPT results for  $\gamma$  are slightly different from, and more accurate than, our earlier values.<sup>4</sup>

Comparison to the accurate value<sup>14</sup> of  $\alpha_1 = 37.29e^2a_0^2E_h^{-1}$  shows that the CCD result is significantly better than the MPPT(4) value. The differences between the CCD and DQ-MPPT(4) results show just how important higher-order contributions from double and unlinked quadruple excitations are. Addition of  $D(5)$  and  $D(6)$ , fifth- and sixth-order contributions from double excitations computed by Diercksen *et al.*,<sup>6</sup> to the DQ-MPPT(4) value in Table I leads to  $\alpha_1 \approx 36.81e^2a_0^2E_h^{-1}$  which is 1.1% lower than the CCD value. This shows that higher-order contributions from the unlinked quadruple excitations cannot be neglected.

Next, the CCD values can be corrected for the effects of single and triple excitations. The simplest way<sup>15</sup> to do that is to add  $S(4)$  and  $T(4)$ . A better way is to compute single- and triple-excitation contributions from the MPPT formulas, but with the first-order amplitudes replaced by the converged CCD amplitudes.<sup>10</sup> The latter method, referred to as CCD+ST(CCD), is size consistent and includes fifth-order terms corresponding to the couplings between double excitations and single and triple excitations. It does not, however, allow for any coupling among the single and triple excitations, nor does it permit single or triple excitations to modify the double-excitation amplitudes at higher orders.

Results obtained by both methods are listed in Table I. The contributions from single and triple excitations as

TABLE I. Polarizabilities of beryllium. One atomic unit of  $\alpha_1$ ,  $\alpha_2$ ,  $B$ , and  $\gamma$  equals  $1.648\,778 \times 10^{-41} \text{ C}^2\text{m}^2\text{J}^{-1}$ ,  $4.617\,048 \times 10^{-62} \text{ C}^2\text{m}^4\text{J}^{-1}$ ,  $1.696\,733 \times 10^{-63} \text{ C}^3\text{m}^4\text{J}^{-2}$ , and  $6.235\,378 \times 10^{-65} \text{ C}^4\text{m}^4\text{J}^{-3}$ , respectively.

Method	$\alpha_1$	$\alpha_2$	$B$	$10^{-4}\gamma$
SCF	45.608	339.5	-3339	3.876
MPPT(2)	42.114	313.4	-2838	3.594
MPPT(3)	40.151	301.8	-2524	3.413
DQ-MPPT(4)	38.798	296.2	-2308	3.313
SDQ-MPPT(4)	38.869	297.7	-2337	3.327
MPPT(4)	38.851	297.7	-2337	3.326
$P[2/1]$	36.299	295.4	-2063	3.247
$P[E[2/1]]$	37.327	295.6	-2136	3.229
CCD	37.205	294.5	-2026	3.137
CCD+S(4)	37.276	296.0	-2054	3.151
CCD+ST(4)	37.257	296.0	-2054	3.150
CCD+S(CCD)	37.425	298.9	-2116	3.153
CCD+ST(CCD)	37.298	298.8	-2102	3.148

computed from CDD amplitudes are *larger* in magnitude than their fourth-order counterparts. This is precisely the opposite of what has been found in cases<sup>16-18</sup> where the DQ-MPPT(4) and CCD results are similar. The CCD+ST(CCD) value of  $\alpha_1$  is in perfect agreement with the most accurate value<sup>14</sup> in the literature.<sup>3</sup> The CCD+ST(CCD) values of  $\alpha_2$  and the hyperpolarizabilities are more accurate than our previous results,<sup>4</sup> and should therefore<sup>3,4</sup> be the most accurate ones available. The remaining errors in the CCD+ST(CCD) values are likely to be dominated by the one-particle basis-set errors discussed earlier. The basis set cannot be improved by simply adding more functions because of linear dependency problems; further optimization of the exponents of the  $s$ - and  $p$ -type Gaussians will be necessary.

Table I lists [2/1] Padé approximants,<sup>19</sup> denoted  $P[2/1]$ , to the MPPT series for the polarizabilities. Also listed are different approximations<sup>4</sup> obtained by differentiating  $E[2/1]$  for the field-dependent energy. The latter approximants are satisfyingly close to the CCD+ST(CCD) results and better than the  $P[2/1]$  Padé approximants.

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