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# Electric dipole hyperpolarizability and quadrupole polarizability of methane from finite-field coupled cluster and fourth-order many-body perturbation theory calculations

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## Abstract

We rely on a finite-field approach to calculate the static dipole ( $\alpha$ ) and quadrupole ( $C$ ) polarizability and the first ( $\beta$ ) and second ( $\gamma$ ) dipole hyperpolarizability of methane. Our best, CCSD(T) values for  $\alpha$ ,  $\beta$  and the mean value of  $\gamma$  and  $C$ , obtained at  $R_e = 2.052 a_0$  with a (11s7p4d2f/6s2p1d)[6s4p4d2f/4s2p1d] basis set, are  $\alpha = 16.39 e^2 a_0^3 E_h^{-1}$ ,  $\beta = -8.31 e^3 a_0^3 E_h^{-2}$ ,  $\bar{\gamma} = 2312 e^4 a_0^4 E_h^{-3}$  and  $C = 60.45 e^2 a_0^4 E_h^{-1}$ . The derivatives of  $\alpha$ ,  $\beta$  and  $\gamma$  (symmetric stretch) at  $R_e$  were calculated at the SDQ-MP4 level of theory with a (11s7p4d1f/6s2p1d)[6s4p4d1f/4s2p1d] basis set:  $(d\alpha/dR)_e = 15.7 e^2 a_0 E_h^{-1}$ ,  $(d\beta/dR)_e = -25.3 e^3 a_0^2 E_h^{-2}$  and  $(d\bar{\gamma}/dR)_e = 37.4 \times 10^2 e^4 a_0^3 E_h^{-3}$ .

## 1. Introduction

With the notable exception of a SD-CI calculation of the first dipole hyperpolarizability  $\beta$  by Amos [1], theoretical predictions of the electric hyperpolarizability of methane have relied exclusively on SCF or equivalent treatments [2–4]. An experimental value of  $\beta$ , deduced by Maker, exists but its accuracy has been questioned [5]. The second hyperpolarizability  $\gamma$  has also been studied experimentally [6–8].

In this paper we report a study of basis set and electron correlation effects for all the independent components of the dipole polarizability ( $\alpha_{\alpha\beta}$ ), first hyperpolarizability ( $\beta_{\alpha\beta\gamma}$ ), second dipole hyperpolarizability ( $\gamma_{\alpha\beta\gamma\delta}$ ) and the quadrupole polarizability ( $C_{\alpha\beta,\gamma\delta}$ ) tensor. We rely on finite-field CCSD, single and double excitation coupled cluster theory and its extension CCSD(T) which includes an estimate of connected triple excitations obtained via a perturba-

tional treatment and fourth-order many-body perturbation theory (MP4) quantum-chemical calculations to deduce these quantities from the energy of the molecule perturbed by weak, static electric fields. The use of high-quality, zeroth-order wavefunctions in electron correlation correction calculations for molecular polarizabilities largely determines the quality of the theoretical predictions. We base our investigation on the calculation at the self-consistent field (SCF) level of all electric multipole moment and electric polarizability tensors, up to the fourth rank, of methane. Our aim is to obtain reliable values for the static limit of  $\beta_{\alpha\beta\gamma}$ ,  $\gamma_{\alpha\beta\gamma\delta}$  and  $C_{\alpha\beta,\gamma\delta}$ . The hyperpolarizabilities  $\beta$  and  $\gamma$  are of central importance to the interpretation of many non-linear optical processes [9]. The quadrupole polarizability  $C_{\alpha\beta,\gamma\delta}$  is also of importance, due to its relevance to intermolecular interaction studies [10].

Atomic units are used throughout this paper. Conversion factors to SI units are listed in the Appendix.

## 2. Theory

The energy of an uncharged molecule in a weak, static general electric field can be written in terms of the electric multipole moment and polarizability tensors as [10,11]

$$\begin{aligned}
 E^p = & E^0 - \mu_\alpha F_\alpha - \frac{1}{3} \Theta_{\alpha\beta} F_\alpha F_\beta - \frac{1}{15} \Omega_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma \\
 & - \frac{1}{105} \Phi_{\alpha\beta\gamma\delta} F_\alpha F_\beta F_\gamma F_\delta + \dots - \frac{1}{2} \alpha_{\alpha\beta} F_\alpha F_\beta \\
 & - \frac{1}{3} A_{\alpha,\beta\gamma} F_\alpha F_\beta F_\gamma - \frac{1}{6} C_{\alpha\beta,\gamma\delta} F_\alpha F_\beta F_\gamma F_\delta \\
 & - \frac{1}{15} E_{\alpha,\beta\gamma\delta} F_\alpha F_\beta F_\gamma F_\delta + \dots - \frac{1}{6} \beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma \\
 & - \frac{1}{6} B_{\alpha\beta,\gamma\delta} F_\alpha F_\beta F_\gamma F_\delta + \dots \\
 & - \frac{1}{24} \gamma_{\alpha\beta\gamma\delta} F_\alpha F_\beta F_\gamma F_\delta + \dots, \quad (1)
 \end{aligned}$$

where  $E^0$  is the energy of the unperturbed system and  $F_\alpha, F_{\alpha\beta}$ , etc., are the electric field, field gradient, etc., at the chosen origin. A repeated greek subscript implies summation over all Cartesian coordinates  $x, y$  and  $z$ .

Adopting the standard orientation for  $\text{CH}_4$  (the C carbon at the origin (0, 0, 0) and the CH bonds on the directions defined by the origin and the points (1, 1, 1), (1, -1, -1), (-1, 1, -1) and (-1, -1, 1) the tensors with non-vanishing components are specified by  $\Omega, \Phi, \alpha, \beta(\beta_{xyz}), \gamma_{zzzz}, \gamma_{xxxx}, A(A_{x,yz}), C_{zz,zz}, C_{xz,xz}, E(E_{z,zz}), B_{zz,zz}$  and  $B_{xz,xz}$ . We drop the subscript in all cases where there is only one independent component. A more detailed discussion of this choice may be found elsewhere [10,12]. In addition to the above components, we calculate mean values for  $\gamma_{\alpha\beta\gamma\delta}$  and  $C_{\alpha\beta,\gamma\delta}$ , defined as  $\bar{\gamma} = \frac{3}{5}(\gamma_{zzzz} + 2\gamma_{xxxx})$  and  $\bar{C} = \frac{3}{5}(C_{zz,zz} + 2C_{xz,xz})$  [10].

The finite-field approach to the MP calculation of the dipole properties  $\alpha, \beta, \gamma_{\alpha\beta\gamma\delta}$  and the quadrupole polarizability has been presented in some detail in previous work [13,14]. We repeat here only the definition of the various orders of MP used in this work,

$$\text{MP2} = \text{SCF} + \text{D2},$$

$$\text{MP3} = \text{MP2} + \text{D3},$$

$$\text{DQ-MP4} = \text{MP3} + \text{D4} + \text{Q4} + \text{R4} = \text{MP3} + \text{DQR4},$$

$$\text{SDQ-MP4} = \text{DQ-MP4} + \text{S4},$$

$$\text{MP4} = \text{SDQ-MP4} + \text{T4}. \quad (2)$$

A presentation of single and double excitation coupled cluster theory CCSD and CCSD(T) may be found elsewhere [15,16].

## 3. Computational details

Relying on previous experience on hyperpolarizability calculations [13,17,18] we adopted for C/H a flexible substrate of (9s5p/4s) primitive Gaussian functions contracted to [4s2p/2s] [19]. The substrate was augmented to [6s4p/4s] by diffuse functions with exponents  $n_s = 0.047362, 0.014632$  and  $n_p = 0.036542, 0.011652$  for C and  $n_s = 0.048273, 0.013121$  for H. Polarization functions were added and their exponents were chosen to minimize the energy  $E^0$  (one tight d-GTF on C and one tight p-GTF on H) or to maximize the mean quadrupole polarizability and dipole polarizability (d-GTF and f-GTF on C, p-GTF and d-GTF on H), much in the lines followed in previous endeavours on  $\text{F}_2$  [17],  $\text{NH}_3$  [20,21] or  $\text{CS}_2$  [22]. The three smaller basis sets M1, M2 and M3 are constructed as:

$$\text{M1: } [6s4p/4s] + \text{C}(n_d = 0.79568, 0.154069,$$

$$n_f = 0.0932) + \text{H}(n_p = 1.07741, 0.1542, n_d = 0.113),$$

$$\text{M2: } \text{M1} + \text{C}(n_d = 0.029833),$$

$$\text{M3: } \text{M2} + \text{C}(n_d = 1.808217).$$

$$\text{M4: } \text{M2} + \text{C}(n_d = 0.350128, n_f = 0.350128).$$

The large M5 set contains additional diffuse functions on C ( $n_s = 0.004521, n_p = 0.003715$ ) and H ( $n_s = 0.003566$ ). The p-GTF on H have exponents  $n_p = 1.077410, 0.289269, 0.077665$ . It contains the same d-GTF on C as M3. The f-GTF on C and the d-GTF on H have the same exponents as in the afore-described M1. Lastly,

$$\text{M6: } \text{M5} + \text{C}(n_d = 0.350128, n_f = 0.154069).$$

The dipole polarizabilities were calculated from the molecular energies in the presence of weak homogeneous fields,  $F = 0.005 \text{ e}^{-1} a_0^{-1} E_h$ . The quadrupole polarizabilities were obtained from energies perturbed by the presence of arrays of charges placed

sufficiently far from the molecule and producing a quasi-quadrupolar field with  $|Q/R^3|=0.0001\text{ e}^{-1}a_0^{-2}E_h$ . Much weaker fields were used in the calculation of molecular polarizabilities from the induced multipole moments.

The experimental value of Gray and Robiette [23] for the equilibrium bond length of  $\text{CH}_4$ ,  $R_e=2.052a_0$ , was used in this work.

All calculations were performed with GAUSSIAN 86 and GAUSSIAN 92 [24].

#### 4. Results and discussion

**SCF.** We list SCF values obtained with sets M1–M6 in Table 1, along with previous findings by other authors. Our results pertain to a bond length of  $2.052a_0$ , while other values in Table 1 were calculated at slightly different distances. The comparison of the M5 values to those obtained with M6 shows little change. We expect M6, a set rich in d-GTF, to provide SCF values close to the Hartree–Fock limit for all properties. Remarkably stable values are obtained for  $\alpha$ ,  $\beta$ ,

$A$  and  $B_{\alpha\beta,\gamma\delta}$ . We draw attention to the M6 values for the multipole moments  $\Omega=2.4095\text{ e}a_0^3$  and  $\Phi=-7.690\text{ e}a_0^4$ , the quadrupole polarizability  $\bar{C}=58.16\text{ e}^2a_0^4E_h^{-1}$  and the hyperpolarizability  $\bar{\gamma}=1884\text{ e}^4a_0^4E_h^{-3}$ . Previous SCF calculations, most frequently, pertain to a bond length of  $2.061a_0$ . An interpolation, using the values obtained with M3 (see Table 4), gave  $\alpha=16.06\text{ e}^2a_0^3E_h^{-1}$ ,  $\beta=-11.62\text{ e}^3a_0^3E_h^{-2}$  and  $\bar{\gamma}=1852\text{ e}^4a_0^4E_h^{-3}$  at  $R_e=2.061a_0$ . The interpolated value of the dipole polarizability agrees well with previous findings in Table 1. The SCF results of Liu and Dykstra [3], converted to conform to Buckingham's definitions, are in good agreement with ours.

**Electron correlation corrections.** Electron correlation corrections to the SCF values of  $\alpha$ ,  $\beta$ ,  $\gamma_{\alpha\beta,\gamma\delta}$  and  $C_{\alpha\beta,\gamma\delta}$  were calculated with basis sets M1, M3 and M4. MP4 calculations were performed with M1 (Table 2). M4 was used in the CCSD(T) calculations (Table 3). M3 was used in SDQ-MP4 calculations of the dipole properties for five bond lengths,  $R_e$ ,  $R_e\pm 0.1$  and  $R_e\pm 0.2a_0$  (Table 4). It is interesting to notice that M1, M3 and M4 provide similar results at the MP4

Table 1  
SCF electric moments, polarizabilities and hyperpolarizabilities of methane calculated with various basis sets

P	M1 <sup>a</sup>	M2 <sup>b</sup>	M3 <sup>c</sup>	M4 <sup>d</sup>	M5 <sup>e</sup>	M6 <sup>f</sup>	A <sup>g</sup>	DS <sup>h</sup>	LD <sup>i</sup>	FLZ <sup>j</sup>
$\Omega$	2.4601	2.4215	2.4543	2.4559	2.4156	2.4095	2.527	2.48	2.5153	2.49
$\phi$	-7.984	-7.854	-8.039	-8.031	-7.679	-7.690	-8.278	-7.90		-7.81
$\alpha$	15.91	15.95	15.91	15.94	15.96	15.98	15.648	16.10	16.000	16.05
$\beta$	-11.31	-11.21	-11.33	-11.31	-11.13	-11.10	-9.98		-11.032	
$\gamma_{zzzz}$	1669	1750	1757	1768	1786	1806			1678.6	
$\gamma_{xxxx}$	644	632	640	638	665	667			612.98	
$\bar{\gamma}$	1774	1808	1822	1826	1870	1884			1743	
$A$	9.52	9.46	9.50	9.48	9.49	9.46	9.86	9.71	9.84	10.35
$E$	-18.88	-18.28	-18.31	-18.38	-19.54	-19.67	-17.98	-19.49	-19.36	-20.28
$C_{zz,zz}$	34.46	34.47	34.51	34.72	34.85	34.89	35.954	34.62	32.614	31.35
$C_{xx,xz}$	30.64	30.67	30.65	30.84	30.98	31.03	23.825		30.078	29.00
$\bar{C}$	57.44	57.49	57.49	57.84	58.09	58.16	50.162		55.662	53.61
$B_{zz,zz}$	-248	-256	-254	-256	-256	-256	-194		-250.8	
$B_{xx,xz}$	-214	-212	-214	-214	-219	-219			-211.0	

<sup>a</sup> Basis set [6s4p2d1f/4s2p1d], 95 contracted GTF. <sup>b</sup> Basis set [6s4p3d1f/4s2p1d], 100 CGTF.

<sup>c</sup> Basis set [6s4p4d1f/4s2p1d], 105 CGTF. <sup>d</sup> Basis set [6s4p4d2f/4s2p1d], 112 CGTF.

<sup>e</sup> Basis set [7s5p4d1f/5s3p1d], 125 CGTF. <sup>f</sup> Basis set [7s5p5d2f/5s3p1d], 137 CGTF.

<sup>g</sup> Ref. [1], basis [6s4p3d/3s1p] at  $2.0665a_0$  for  $C_{\alpha\beta,\gamma\delta}$ . All other properties at  $2.052a_0$ .

<sup>h</sup> Ref. [25], basis [8s5p3d1f/4s2p1d] at  $2.061a_0$ . <sup>i</sup> Ref. [3], basis [7s5p3d/4s2p] at  $2.061a_0$ .

<sup>j</sup> Ref. [26], basis [8s5p4d/6s3p].

Table 2

Electron correlation corrections to  $\alpha$ ,  $\beta$ ,  $\gamma_{\alpha\beta\gamma\delta}$  and  $C_{\alpha\beta\gamma\delta}$  for  $\text{CH}_4$  calculated with basis M1, [6s4p2d1f/4s2p1p] <sup>a</sup>

P	SCF	MP2	MP3	DQ-MP4	SDQ-MP4	MP4
$\alpha$	15.91	16.49	16.32	16.26	16.30	16.43
$\beta$	-11.33	-8.13	-8.69	-8.85	-8.66	-8.21
$\gamma_{zzzz}$	1665	2081	1940	1908	1958	2072
$\gamma_{xxxx}$	643	771	713	703	722	763
$\bar{\gamma}$	1770	2173	2019	1989	2042	2158
$C_{zz,zz}$	34.46	34.14	36.43	36.25	36.36	36.84
$C_{xz,xz}$	30.65	32.24	31.75	31.65	31.73	32.05
$\bar{C}$	57.45	60.97	59.95	59.73	59.89	60.56

<sup>a</sup> The following SDQ-MP4 quadrupole polarizabilities were obtained with basis M3:  $C_{zz,zz}=36.41$ ,  $C_{xz,xz}=31.73$  and  $\bar{C}=59.93$   $e^2 a_0^4 E_h^{-1}$ .

Table 3

Electron correlation corrections to  $\alpha$ ,  $\beta$ ,  $\gamma_{\alpha\beta\gamma\delta}$  and  $C_{\alpha\beta\gamma\delta}$  for  $\text{CH}_4$  calculated with basis M4, [6s4p4d2f/4s2p1p]

P	SCF	MP2	MP3	DQ-MP4	SDQ-MP4	MP4	CCSD	CCSD(T)
$\alpha$	15.94	16.49	16.31	16.25	16.28	16.42	16.26	16.39
$\beta$	-11.31	-8.14	-8.72	-8.90	-8.74	-8.28	-8.73	-8.31
$\gamma_{zzzz}$	1768	2295	2138	2099	2150	2276	2138	2254
$\gamma_{xxxx}$	638	809	758	747	765	805	763	800
$\bar{\gamma}$	1826	2348	2193	2155	2207	2332	2198	2312
$C_{zz,zz}$	34.72	37.25	36.49	36.30	36.39	36.87	36.33	36.77
$C_{xz,xz}$	30.84	32.29	31.77	31.67	31.74	32.06	31.70	31.99
$\bar{C}$	57.84	61.09	60.02	59.78	59.92	60.59	59.84	60.45

level of theory. The SDQ-MP4 values for  $\alpha$  are 16.30, 16.30 and 16.28  $e^2 a_0^4 E_h^{-1}$  for M1, M3 and M4, respectively. For  $\beta$  at the same level we obtain -8.66, -8.66 and -8.74  $e^3 a_0^3 E_h^{-2}$ . The difference is small even for  $\bar{\gamma}$ , in which case we have 2158, 2231 and 2207  $e^4 a_0^4 E_h^{-3}$ . Compare also the values for  $\bar{C}$ : 59.89, 59.93 and 59.92  $e^2 a_0^4 E_h^{-1}$ . Thus, a small but carefully optimized basis set may be expected to yield reasonable values even for the quadrupole polarizability or the dipole hyperpolarizability. It is instructive to compare the fourth-order triples contribution T4 calculated with M1 and the substantially larger M4 set. The triples contribution for M4 (basis M1 values in parentheses) are  $\alpha=0.14$  (0.13)  $e^2 a_0^4 E_h^{-1}$ ,  $\beta=0.46$  (0.46)  $e^3 a_0^3 E_h^{-2}$ ,  $\bar{\gamma}=125$  (117)  $e^4 a_0^4 E_h^{-3}$  and  $\bar{C}=0.67$  (0.67)  $e^2 a_0^4 E_h^{-1}$ . A rather remarkable agreement. Lastly, we note the difference between the CCSD and CCSD(T) values. The CCSD(T)  $\alpha$ ,  $\beta$ ,  $\bar{\gamma}$

and  $\bar{C}$  are 0.8%, 4.8%, 5.2% and 1.0% higher than the CCSD results.

We have also studied the dependence of the calculated dipole properties on the bond length. Using the values listed in Table 4, we obtain the following derivatives for the symmetric stretching of the C-H bond at the SDQ-MP4 level of theory (SCF values in parentheses):  $(d\alpha/dR)_e=15.7$  (16.3)  $e^2 a_0 E_h^{-1}$ ,  $(d\beta/dR)_e=-25.3$  (-32.2)  $e^3 a_0^2 E_h^{-2}$  and  $(d\bar{\gamma}/dR)_e=37.4 \times 10^2$  ( $33.7 \times 10^2$ )  $e^4 a_0^3 E_h^{-3}$ .

In previous work [13,28] we relied on accurate SCF values and estimates of the electron correlation correction in order to propose estimates of electric multipole moments and polarizabilities. The results in Table 2 provide evidence for the validity of such a scheme. For  $\alpha$ ,  $\beta$ ,  $\bar{\gamma}$  and  $\bar{C}$  it is easily verified that  $\text{SDQ-MP4} < \text{CCSD(T)} < \text{MP4}$ . Thus, accurate SCF values, reliable D2+D3+SDQR4 corrections and reasonably accurate values of T4 might be used to de-

Table 4

Bond-length dependence (symmetric stretch) of correlated dipole polarizability and hyperpolarizability values of methane calculated with basis M3, [6s4p4d1f/4s2p1d]

Method	$\alpha$	$\beta$	$\gamma_{xxxx}$	$\gamma_{xxxx}$	$\bar{\gamma}$
$R=1.852 a_0$					
SCF	12.94	−6.17	1226	431	1252
MP2	13.52	−4.17	1612	557	1635
MP3	13.40	−4.60	1510	518	1528
DQ-MP4	13.36	−4.73	1485	511	1505
SDQ-MP4	13.39	−4.60	1525	525	1545
$R=1.952 a_0$					
SCF	14.36	−8.46	1469	525	1512
MP2	14.94	−5.91	1936	685	1983
MP3	14.80	−6.38	1811	646	1862
DQ-MP4	14.75	−6.53	1781	637	1833
SDQ-MP4	14.79	−6.37	1828	654	1882
$R=2.052 a_0$					
SCF	15.91	−11.33	1757	640	1822
MP2	16.49	−8.12	2304	819	2365
MP3	16.32	−8.68	2150	768	2212
DQ-MP4	16.26	−8.85	2113	756	2175
SDQ-MP4	16.30	−8.66	2166	776	2231
$R=2.152 a_0$					
SCF	17.62	−14.94	2097	776	2189
MP2	18.17	−10.80	2736	979	2817
MP3	17.96	−11.46	2541	915	2623
DQ-MP4	17.89	−11.64	2496	902	2580
SDQ-MP4	17.93	−11.43	2557	924	2642
$R=2.252 a_0$					
SCF	19.50	−19.42	2496	936	2620
MP2	19.99	−13.99	3240	1174	3353
MP3	19.74	−14.77	2977	1097	3114
DQ-MP4	19.66	−14.95	2943	1082	3064
SDQ-MP4	19.70	−14.71	3011	1105	3132

duce estimates for the electric properties. The availability of CCSD(T) values suggests an even simpler approach. Combining the M6 SCF results with the M4 CCSD(T) corrections we obtain

$$\alpha = 16.42 e^2 a_0^2 E_h^{-1},$$

$$\beta = -8.09 e^3 a_0^3 E_h^{-2},$$

$$\bar{\gamma} = 2370 e^4 a_0^4 E_h^{-3},$$

$$\bar{C} = 60.77 e^2 a_0^4 E_h^{-1},$$

expecting, as we may, these values to be within a few percent of the static limit values at  $R_e$ .

Table 5

Comparison of theoretical predictions and experimental data for the dipole polarizabilities of methane

Method	$\alpha$	$\beta$	$\bar{\gamma}$
SD-CI <sup>a</sup>	16.13	−7.17	
SDQ-MP4 <sup>b</sup>	16.30	−8.66	2231
MP4 <sup>c</sup>	16.43	−8.21	2158
CCSD <sup>d</sup>	16.26	−8.73	2198
CCSD(T) <sup>d</sup>	16.39	−8.31	2312
DOSD	17.27 <sup>e</sup>		
Kerr effect			2887 ± 144 <sup>f</sup>
ESHG		± 1.2 <sup>g</sup>	2590 <sup>h</sup>

<sup>a</sup> Ref. [1] at 2.052  $a_0$ . <sup>b</sup> Present investigation, basis set M3 [6s4p4d1f/4s2p1d].

<sup>c</sup> Present investigation, basis set M1 [6s4p2d1f/4s2p1d].

<sup>d</sup> Present investigation, basis set M4 [6s4p4d2f/4s2p1d].

<sup>e</sup> Dipole oscillator strength distributions [27]. <sup>f</sup> Ref. [6] at 632.8 nm.

<sup>g</sup> Refs. [1,5]. <sup>h</sup> Static value, Ref. [8].

*Comparison with previous theoretical results and experiment.* We refer to Amos [1], Gough [29], Wong et al. [30] and Wolinski and Sadlej [31] for a discussion and presentation of previous theoretical endeavours on the dipole polarizability of methane. We limit this discussion to post-Hartree–Fock efforts going beyond the dipole polarizability. The SD-CI value of  $\beta$  reported by Amos [1] is  $-7.17 e^3 a_0^3 E_h^{-2}$  (Table 5), somewhat smaller in magnitude than our correlated values. We are not aware of previous correlated values of either  $\gamma_{\alpha\beta\gamma\delta}$  or  $C_{\alpha\beta\gamma\delta}$ .

Wong et al. [30] have reported an extensive study of the polarizability derivatives of methane. Using ACPF (averaged pair functional theory) they obtained  $\alpha = 16.3130 e^2 a_0^2 E_h^{-1}$  and  $(d\alpha/dR)_e = 15.54 e^2 a_0 E_h^{-1}$  with a [6s4p2d/4s2p] basis set at  $R_e = 2.05196 a_0$ . The same authors report values of  $\alpha = 16.3621 e^2 a_0^2 E_h^{-1}$  and  $(d\alpha/dR)_e = 15.50 e^2 a_0 E_h^{-1}$  obtained with the larger [8s5p3d1f/4s2p1d] basis used by Diercksen and Sadlej [25]. Both sets of values agree quite well with our SDQ-MP4 results.

The recent experimental value of  $\alpha = 17.26 e^2 a_0^2 E_h^{-1}$  by Hohm and Kerl [32] is close to the  $17.27 e^2 a_0^2 E_h^{-1}$  deduced by Thomas and Meath [27] from dipole oscillator strength distributions (DOSD). If we add to our static limit estimate of  $16.42 e^2 a_0^2 E_h^{-1}$  the accurate vibrational correction of  $0.884 e^2 a_0^2 E_h^{-1}$  [30], we arrive at a ground-state

theoretical prediction  $\alpha = 17.30 \text{ e}^2 a_0^2 E_h^{-1}$ . A much simpler procedure, adopted by Amos [1], is used to obtain estimates of the magnitude of the vibrational correction for  $\beta$  and  $\bar{\gamma}$ . The properties are calculated at the vibrationally averaged bond length  $\langle R \rangle = 2.082 a_0$ . An interpolation of the results in Table 4 yields corrections of  $-0.78 \text{ e}^3 a_0^3 E_h^{-2}$  and  $115 \text{ e}^4 a_0^4 E_h^{-3}$  for  $\beta$  and  $\bar{\gamma}$ , respectively. This should not be considered to be more than a crude estimate of the quantity. It is worth mentioning that a recent SCF study by Marti et al. [33] estimates the vibrational correction for  $\gamma$  at  $175 \text{ e}^4 a_0^4 E_h^{-3}$ . The correction will increase the magnitude of  $\beta$ , resulting in a discrepancy between the theoretical prediction and the experimental value of  $\pm 1.2 \text{ e}^3 a_0^3 E_h^{-2}$  [5]. A new, more accurate measurement of the first dipole hyperpolarizability is needed to resolve the discrepancy. A Kerr effect measurement at 632.8 nm by Buckingham and Orr [6] gave a  $\bar{\gamma}$  value of  $2887 \pm 144 \text{ e}^4 a_0^4 E_h^{-3}$ . Shelton's efforts [8] have produced a static value of  $\bar{\gamma} = 2590 \text{ e}^4 a_0^4 E_h^{-3}$ . Our static limit estimate at  $R_e$  is  $2370 \text{ e}^4 a_0^4 E_h^{-3}$ . Based on the above presented estimates, a vibrational correction of  $2 \times 10^2 \text{ e}^4 a_0^4 E_h^{-3}$  for  $\bar{\gamma}$  seems plausible enough. It would lead to a ground-state theoretical value of  $26 \times 10^2 \text{ e}^4 a_0^4 E_h^{-3}$ . A rather conservative, as we readily admit, estimate. However, it unquestionably points to an accord between theory and experiment.

## 5. Conclusions

We have obtained electric polarizabilities and hyperpolarizabilities for methane from finite-field SCF, MP4 and CCSD(T) calculations with large Gaussian-function basis sets. A large [7s5p5d2f/5s3p1d] basis set is expected to provide accurate SCF values for all multipole moment and polarizability tensors up to the fourth rank.

Our estimates for the static values of  $\alpha$ ,  $\beta$ ,  $\bar{\gamma}$  and  $\bar{C}$  at  $R_e$  are

$$\alpha = 16.42 \text{ e}^2 a_0^2 E_h^{-1},$$

$$\beta = -8.09 \text{ e}^3 a_0^3 E_h^{-2},$$

$$\bar{\gamma} = 2370 \text{ e}^4 a_0^4 E_h^{-3},$$

$$\bar{C} = 60.77 \text{ e}^2 a_0^4 E_h^{-1}.$$

In addition, we obtained the following polarizability derivatives for the symmetric stretch of the C–H bond:

$$(d\alpha/dR)_e = 15.7 \text{ e}^2 a_0 E_h^{-1},$$

$$(d\beta/dR)_e = -25.3 \text{ e}^3 a_0^2 E_h^{-2},$$

$$(d\bar{\gamma}/dR)_e = 37.4 \times 10^2 \text{ e}^4 a_0^3 E_h^{-3}.$$

Agreement with experiment is observed for both  $\alpha$  and  $\bar{\gamma}$ , but not for  $\beta$ .

We are not aware of previous correlated values for  $\gamma_{\alpha\beta\gamma\delta}$  or  $C_{\alpha\beta,\gamma\delta}$ .

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## Appendix

Conversion factors from atomic to SI units.

Energy,  $1 E_h = 4.3597482 \times 10^{-18} \text{ J}$ ;

length,  $1 a_0 = 0.529177249 \times 10^{-10} \text{ m}$ ;

$\Omega$ ,  $1 e a_0^3 = 2.374182 \times 10^{-50} \text{ C m}^3$ ;

$\Phi$ ,  $1 e a_0^4 = 1.256363 \times 10^{-60} \text{ C m}^4$ ;

$\alpha$ ,  $1 e^2 a_0^2 E_h^{-1} = 1.648778 \times 10^{-41} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}$ ;

$\beta$ ,  $1 e^3 a_0^3 E_h^{-2} = 3.206361 \times 10^{-53} \text{ C}^3 \text{ m}^3 \text{ J}^{-2}$ ;

$\gamma$ ,  $1 e^4 a_0^4 E_h^{-3} = 6.235378 \times 10^{-65} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$ ;

$A$ ,  $1 e^2 a_0^3 E_h^{-1} = 8.724958 \times 10^{-52} \text{ C}^2 \text{ m}^3 \text{ J}^{-1}$ ;

$C$  or  $E$ ,  $1 e^2 a_0^4 E_h^{-1} = 4.617048 \times 10^{-62} \text{ C}^2 \text{ m}^4 \text{ J}^{-1}$ ;

$B$ ,  $1 e^3 a_0^4 E_h^{-2} = 1.696733 \times 10^{-63} \text{ C}^3 \text{ m}^4 \text{ J}^{-2}$ .

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