Electric multipole moment, dipole and quadrupole (hyper)polarizability derivatives for HF (X 1 Σ +)

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Electric multipole moment, dipole and quadrupole (hyper)polarizability derivatives for HF ($X^1\Sigma^+$)

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Abstract

We report accurate values for the electric properties and property derivatives of hydrogen fluoride. Our approach is based on finite-field Møller–Plesset perturbation theory and coupled cluster calculations performed with large, carefully optimised basis sets of gaussian-type functions. All basis sets used in this study are of well-evidenced near-Hartree–Fock quality for all properties of interest. Our best values are obtained from CCSD(T) calculations (all electrons correlated) with a (16s11p8d4f/10s6p3d2f) basis set at the experimental bond length $R_e = 1.7328a_0$: dipole, $\mu = 0.7043ea_0$, quadrupole, $\Theta = 1.71ea_0^2$, octopole, $\Omega = 2.50ea_0^3$, and hexadecapole, $\Phi = 4.83ea_0^3$, moment, mean $\bar{\alpha} = 5.60$ and anisotropy, $\Delta\alpha = 1.14e^2a_0^2E_h^{-1}$ of the dipole polarizability, mean first, $\bar{\beta} = -7.4e^3a_0^3E_h^{-2}$ and second, $\bar{\gamma} = 512e^4a_0^4E_h^{-3}$ hyperpolarizability, mean quadrupole, $\bar{C} = 10.61e^2a_0^4E_h^{-1}$ polarizability. The R-dependence around R_e is obtained for all properties. At the CCSD(T)/[9s6p5d4f/6s4p3d1f] level of theory (all electrons correlated) $\bar{\alpha}$ and $\Delta\alpha$ vary around R_e as

$$\bar{\alpha}(R)/e^2a_0^2E_h^{-1} = 5.66 + 2.92(R - R_e) + 1.10(R - R_e)^2 + 0.24(R - R_e)^3 - 0.01(R - R_e)^4$$

$$\Delta\alpha(R)/e^2a_0^2E_h^{-1} = 1.12 + 4.30(R - R_e) + 2.97(R - R_e)^2 + 0.78(R - R_e)^3 + 0.07(R - R_e)^4$$

For the mean higher polarizabilities we report CCSD(T)/[9s6p5d4f/6s4p3d1f] (all electrons correlated) first derivatives, $(\frac{d\bar{\beta}}{dR})_e = 12.4e^3a_0^2E_h^{-2}$, $(\frac{d\bar{\gamma}}{dR})_e = 437e^4a_0^3E_h^{-3}$ and $(\frac{d\bar{C}}{dR})_e = 8.02e^2a_0^3E_h^{-1}$. At the MP2/[9s6p5d4f/6s4p3d1f] level of theory, the dipole–quadrupole ($A_{\alpha,\beta\gamma}$) polarizability varies around R_e as:

$$A_{z,zz}(R)/e^2a_0^3E_h^{-1} = 4.33 + 10.83(R - R_e) + 8.69(R - R_e)^2 + 2.99(R - R_e)^3 + 0.19(R - R_e)^4$$

$$A_{x,zx}(R)/e^2a_0^3E_h^{-1} = 1.32 + 2.27(R - R_e) + 1.30(R - R_e)^2 + 0.27(R - R_e)^3 + 0.07(R - R_e)^4$$

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1. Introduction

Electric polarizability has been recognized early enough as a fundamental property of atoms and molecules [1–4]. The relevance of this property to the rational approach to a wide range of phenomena has been carefully analysed and presented in depth by many authors [5–8]. Of particular importance are specific fields and research activities as nonlinear optics [9], Raman [10] and Hyper-Raman [11,12] spectroscopy, collision- and interaction-induced spectroscopies [13] and simulation studies [14]. Awareness of reliable polarizability, hyperpolarizability and higher (quadrupole) polarizability values is a key element to rigorous intermolecular interaction studies [15–17], analysis of spectroscopic observations [18–21] and simulations of phases [22–26]. In addition to polarizability values, there is currently additional interest in their derivatives with respect to geometrical molecular parameters. This interest extends not only to dipole polarizability [27,28] but also to hyperpolarizability [29–33] and quadrupole polarizability derivatives [19,34–35]. Although the experimental determination of polarizabilities and their derivatives has made considerable progress [36], not all of these properties are amenable to experiment [7]. As theory is, in most cases, the only way to their estimation, comprehensive reviews have examined and presented various aspects of the theoretical approach [37–46]. The convergence of experimental and theoretical endeavours has also been a subject of considerable interest [47]. It is worth noticing that the available experimental polarizability derivatives are deduced from Raman spectroscopic observations and are limited to a few molecules [48–52]. These derivatives are almost exclusively dipole polarizability data. A few notable exceptions are known for molecules of relatively high symmetry. Estimates of dipole–quadrupole and dipole–octopole polarizability derivatives for CF_4 have been obtained form collision-induced depolarized scattering measurements [34].

In this paper we report an extensive investigation of the electric multipole moment and (hyper)polarizability derivatives of hydrogen fluoride. Numerous studies have been reported for the electric properties of this important molecule, a system quite often used as testing ground for computational methods. In an early paper McLean and Yoshimine [53] used Slater-type basis sets to calculate the axial components of the (hyper)polarizability. In their pioneering paper, Bartlett and Purvis [54] estimated the electric correlation effects on the dipole (hyper)-polarizability. All the independent components of electric multipole moment, dipole and quadrupole (hyper)polarizability tensors, up to the fourth-rank, were obtained from self-consistent field (SCF) calculations with large basis sets of gaussian-type functions (GTF) by Bishop and Maroulis [55]. Derivative Hartree–Fock (DHF) studies of the electric properties of HF and the vibrational effects on these properties were reported by Liu and Dykstra [56] and Malik [57]. More recently, Feller and Peterson [58] reported a comprehensive study of the properties of HF, including the dipole (hyper)polarizability. Last, we mention a recent study by Kondo et al. [59] who obtained the bond-length dependence of the dipole and quadrupole moment and the axial component of the dipole (hyper)polarizability and the quadrupole polarizability. Our contribution comprises three steps. First, we design large basis sets observing closely their convergence to the Hartree–Fock limit. This near-Hartree–Fock quality extends to all properties under consideration. Second, we obtain reliable estimates of the electron correlation effects at the experimental bond length, R_e. Third, the bond-length or R-dependence of the electric properties is obtained from a set of calculations performed at various internuclear separations around R_e. Thus, we estimate electron correlation effects not only for the R_e value of the electric properties (P_e) but also for the respective derivatives $\left(\frac{dP}{dR}\right)_e$. Our work relies on a finite-field approach [60], well-tested over number of atomic [61,62] and molecular systems [63–67].

2. Theory and methods of calculation

The perturbed energy and the induced multipole moments of an uncharged molecule interacting with a weak, static electric field can be

written as [5,68]

$$E^{\mathrm{p}} \equiv E^{\mathrm{p}}(F_\alpha, F_{\alpha\beta}, F_{\alpha\beta\gamma}, F_{\alpha\beta\gamma\delta}, \ldots)$$

$$= E^0 - \mu_\alpha F_\alpha - (1/3)\Theta_{\alpha\beta}F_{\alpha\beta}$$

$$- (1/15)\Omega_{\alpha\beta\gamma}F_{\alpha\beta\gamma} - (1/105)\Phi_{\alpha\beta\gamma\delta}F_{\alpha\beta\gamma\delta}$$

$$+ \cdots - (1/2)\alpha_{\alpha\beta}F_\alpha F_\beta - (1/3)A_{\alpha,\beta\gamma}F_\alpha F_{\beta\gamma}$$

$$- (1/6)C_{\alpha\beta,\gamma\delta}F_{\alpha\beta}F_{\gamma\delta} - (1/15)E_{\alpha,\beta\gamma\delta}F_\alpha F_{\beta\gamma\delta}$$

$$+ \cdots - (1/6)\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma$$

$$- (1/6)B_{\alpha\beta,\gamma\delta}F_\alpha F_\beta F_{\gamma\delta} + \cdots$$

$$- (1/24)\gamma_{\alpha\beta\gamma\delta}F_\alpha F_\beta F_\gamma F_\delta + \cdots \qquad (1)$$

$$\mu_\alpha^{\mathrm{p}} = \mu_\alpha + \alpha_{\alpha\beta}F_\beta + (1/3)A_{\alpha,\beta\gamma}F_{\beta\gamma}$$

$$+ (1/2)\beta_{\alpha\beta\gamma}F_\beta F_\gamma + (1/3)B_{\alpha\beta,\gamma\delta}F_\beta F_{\gamma\delta}$$

$$+ (1/6)\gamma_{\alpha\beta\gamma\delta}F_\beta F_\gamma F_\delta + \cdots \qquad (2)$$

$$\Theta_{\alpha\beta}^{\mathrm{p}} = \Theta_{\alpha\beta} + A_{\gamma,\alpha\beta}E_\gamma + C_{\alpha\beta,\gamma\delta}F_{\gamma\delta}$$

$$+ (1/2)B_{\gamma\delta,\alpha\beta}F_\gamma F_\delta + \cdots \qquad (3)$$

$$\Omega_{\alpha\beta\gamma}^{\mathrm{p}} = \Omega_{\alpha\beta\gamma} + E_{\delta,\alpha\beta\gamma}F_\delta + \cdots \qquad (4)$$

where F_α, $F_{\alpha\beta}$, $F_{\alpha\beta\gamma}$, etc., are the field, field gradient, etc. at the origin. E^0, μ_α, $\Theta_{\alpha\beta}$, $\Omega_{\alpha\beta\gamma}$ and $\Phi_{\alpha\beta\gamma\delta}$ are the energy and the permanent dipole, quadrupole, octopole and hexadecapole moment of the free molecule. The second, third and fourth-order properties are the dipole polarizability ($\alpha_{\alpha\beta}$), the first ($\beta_{\alpha\beta\gamma}$) and second ($\gamma_{\alpha\beta\gamma\delta}$) dipole hyperpolarizability, the dipole–quadrupole ($A_{\alpha,\beta\gamma}$) and dipole–octopole ($E_{\alpha,\beta\gamma\delta}$) polarizability, the quadrupole polarizability ($C_{\alpha\beta,\gamma\delta}$) and the dipole–dipole–quadrupole hyperpolarizability ($B_{\alpha\beta,\gamma\delta}$). The subscripts denote Cartesian components and a repeated subscript implies summation over x, y and z. For a polar linear molecule (with z as the molecular axis) there is only one independent component of any order, μ_z, Θ_{zz}, Ω_{zzz} and Φ_{zzzz} [5]. Hereafter, we drop the subscript and write $\mu \equiv \mu_z$, $\Theta_{zz} \equiv \Theta$, $\Omega_{zzz} \equiv \Omega$ and $\Phi_{zzzz} \equiv \Phi$. The number of independent components for the electric polarizability tensors is regulated by symmetry [5,69]. In

addition to the Cartesian components we also compute mean values and anisotropies for some polarizabilities, defined as [5],

$$\bar\alpha = (\alpha_{zz} + 2\alpha_{xx})/3 \qquad \Delta\alpha = \alpha_{zz} - \alpha_{xx}$$

$$\bar\beta = (3/5)(\beta_{zzz} + 2\beta_{zxx}) \qquad \Delta\beta = \beta_{zzz} - 3\beta_{zxx}$$

$$\bar\gamma = (3\gamma_{zzzz} + 8\gamma_{xxxx} + 12\gamma_{xxzz})/15$$

$$\Delta_1\gamma = 3\gamma_{zzzz} - 4\gamma_{xxxx} + 3\gamma_{xxzz}$$

$$\Delta_2\gamma = \gamma_{zzzz} + \gamma_{xxxx} - 6\gamma_{xxzz} \qquad (5)$$

$$\bar C = (C_{zz,zz} + 8C_{xz,xz} + 8C_{xx,xx})/10$$

$$\Delta_1 C = 5C_{zz,zz} + 4C_{xz,xz} - 8C_{xx,xx}$$

$$\Delta_2 C = 2C_{zz,zz} - 4C_{xz,xz} + C_{xx,xx}$$

$$\bar B = (2/15)(B_{zz,zz} + 4B_{xz,xz} + B_{xx,zz} + 4B_{xx,xx})$$

These quantities are particular useful in comparisons of theoretical predictions to experimental values. They are also of value in the analysis of basis set or electron correlation effects on the components of some polarizabilities.

The expansions of Eqs (1)–(4) converge rapidly for very weak fields. Thus, relying on Eq. (1), it is possible to extract electric moment or polarizability values from a limited number of perturbed energy calculations [63,65]. Alternatively, induced multipole moments can be used for the calculation of polarizabilities [55,70]. Detailed presentations to our approach to the calculation of electric properties have been given elsewhere [63–67]. In this paper only a few essential points are brought to the attention of the reader.

Electron correlation effects were obtained via Møller–Plesset perturbation theory (MP) and coupled-cluster (CC) techniques. Analytical presentations of these theoretical tools and their relative merit in molecular property calculations can be found in standard textbooks and comprehensive reviews [71–76]. The MP methods used in this work are MP2 and MP4. We also use SDQ-MP4, a partial fourth-order approach much more economical than the complete fourth-order one. We lean heavily on the predictive capability of the CC methods, CCSD

and CCSD(T). The latter includes an estimate of connected triple excitations obtained via a perturbational treatment.

We have used Eq. (1) for the calculation of SCF, MP and CC values of μ, Θ, Ω, Φ, $\alpha_{\alpha\beta}$, $\beta_{\alpha\beta\gamma}$, $\gamma_{\alpha\beta\gamma\delta}$ and $C_{\alpha\beta,\gamma\delta}$. MP2 values for $A_{\alpha,\beta\gamma}$ and $E_{\alpha,\beta\gamma\delta}$ were calculated from the induced quadrupole and octopole moments obtained through the MP2 density [77]. We define the total electron correlation correction (ECC) as,

$$ECC = CCSD(T) - SCF \tag{6}$$

3. Computational details

We have designed large, flexible basis sets for our calculations. Their construction follows a computational philosophy presented elsewhere (see Ref. [65] and references therein). We have employed three different substrates. Basis sets Q1, Q2 and Q3 were built upon a (12s7p/6s) primitive set contracted to [7s4p/4s] [78]. Their composition is succinctly given as,

Q1 ≡ [9s6p5d4f/6s4p3d1f], 120 GFT from [7s4p/4s] + F: s (0.098212, 0.036195), p(0.063959, 0.022446), d(1.2293, 0.4782, 0.1860, 0.0724, 0.0281), f(0.4782, 0.1860, 0.0724, 0.0281) + H: s(0.031302, 0.010891), p(0.8666, 0.3939, 0.1790, 0.0814), d(0.3939, 0.1790, 0.0814), f(0.1790)

Q2 ≡ [10s7p6d5f/7s5p4d1f], 145 GFT from Q1 + F: s(0.013339), p(0.007877), d(0.7668), f(0.7668) + H: s(0.0037891), p(0.0370), d(0.8666)

Q2 ≡ [11s8p7d6f/8s6p5d3f], 184 GFT from Q1 + F: s(0.004916), p(0.002764), d(0.1160), f(0.1160) + H: s(0.001318), p(0.00760), d(0.0370), f(0.8666,0.0370)

A different type of substrate, an uncontracted basis set (14s9p/9s) [79,80] was used for the construction of PA1,

PA1 ≡ [16s11p8d4f/10s6p3d2f], 174 GFT from (14s9p/9s) [79,80] + F: s(0.091326, 0.036254), p(0.055227, 0.021952), d(3.1417, 1.9635, 1.2271, 0.6557, 0.3503, 0.1872, 0.0731, 0.0286), f(1.2271, 0.3503,0.1872, 0.0731) + H: s(0.0280548), p(1.9197, 0.8605, 0.3857, 0.1729,

0.0775, 0.0347), d(0.8605, 0.1729, 0.0775), f(0.8605, 0.1729)

For PA2 and PA3 we used an even larger (17s12p/9s) substrate contracted to [12s9p/9s] [79,80]:

PA2 ≡ [19s15p10d7f/12s7p4d2f], 230 GFT from [12s9p/9s] [79,80] + F: s(0.082950, 0.036011, 0.015633, 0.006787, 0.002946, 0.001279, 0.000555), p(0.046800, 0.021107, 0.009520, 0.004294, 0.001936, 0.000873), d(8.543687, 3.909019, 1.788505, 1.209766, 0.8183, 0.374399, 0.1713, 0.078375, 0.035859, 0.007507), f(1.788505, 1.209766, 0.8183, 0.374399, 0.1713, 0.035859, 0.007507) + H: s(0.0280548, 0.0117535, 0.0049241), p(4.659143, 1.991096, 0.8509, 0.1554, 0.028381, 0.005183, 0.000947), d(0.8509, 0.1554, 0.005183, 0.000947), f(0.8509, 0.1554)

PA3 ≡ [19s15p10d8f/12s9p5d2f], 248 GFT from PA2 + F: f(0.078375) + H: p(0.3636, 0.0664), d(0.3636)

5D and 7F GTF were used in all calculations. All optimizations were performed at the experimental bond length $R_e = 1.7328a_0$ [81].

Weak homogeneous electric fields of $0.005e^{-1}a_0^{-1}E_h$ were used in the calculation of dipole moments and (hyper)polarizabilities. For the calculation of the quadrupole moment and polarizability we simulated [63] weak quadrupolar fields of $|Q/R^3| = 0.0001e^{-1}a_0^{-2}E_h$. For the octopole and hexadecapole moment the magnitude of the simulated fields [65] was $0.0001e^{-1}a_0^{-3}E_h$ and $0.000000032e^{-1}a_0^{-4}E_h$.

All calculations were performed with the GAUSSIAN 92 [82] and GAUSSIAN 94 [83] set of programmes.

Atomic units are used throughout this paper. Conversion factors to SI units are, Energy, $1E_h = 4.3597482 \times 10^{-18}$ J, Length, $1a_0 = 0.529177249 \times 10^{-10}$ m, μ, $1ea_0 = 8.478358 \times 10^{-30}$ C m, Θ, $1ea_0^2 = 4.486554 \times 10^{-40}$ C m^2, Ω, $1ea_0^3 = 2.374182 \times 10^{-50}$ C m^3, Φ, $1ea_0^4 = 1.256363 \times 10^{-60}$ C m^4, α, $1e^2a_0^2E_h^{-1} = 1.648778 \times 10^{-41}$ C^2 m^2 J^{-1}, β, $1e^3a_0^3E_h^{-2} = 3.206361 \times 10^{-53}$ C^3 m^3 J^{-2}, γ, $1e^4a_0^4E_h^{-3} = 6.235378 \times 10^{-65}$ C^4 m^4 J^{-3}, A, $1e^2a_0^3E_h^{-1} = 8.724958 \times 10^{-52}$ C^2 m^3 J^{-1} ,

C or E, $1e^2a_0^4E_h^{-1} = 4.617048 \times 10^{-62}$ C^2 m^4 J^{-1}, B, $1e^3a_0^4E_h^{-2} = 1.696733 \times 10^{-63}$ C^3 m^4 J^{-2}.

4. Results and discussion

4.1. SCF results

SCF results calculated with all basis sets are given in Table 1. We expect our PA3 values to be quite close to the Hartree–Fock limit. This is easily seen by a direct comparison to the available numerical Hartree–Fock (NHF) data [84] for the electric moments calculated at $R_e = 1.7328a_0$. We obtain for PA3, $\mu/ea_0 = 0.7561$, $\Theta/ea_0^2 = 1.73$, $\Omega/ea_0^3 = 2.59$ and $\Phi/ea_0^4 = 5.03$. The accurate NHF values are 0.7561, 1.7321, 2.5924 and 5.0188, respectively. The agreement is excellent. Agreement with the other basis sets is significantly better than 1%.

Table 1
Convergence of SCF results for HF $(X^1\Sigma^+)$

Property	Q1	Q2	Q3	PA1	PA2	PA3
μ	0.7593	0.7583	0.7583	0.7564	0.7562	0.7561
Θ	1.74	1.73	1.73	1.73	1.73	1.73
Ω	2.60	2.60	2.59	2.59	2.60	2.59
Φ	4.95	4.98	4.98	5.02	5.03	5.03
α_{zz}	5.75	5.75	5.75	5.75	5.76	5.75
α_{xx}	4.48	4.48	4.48	4.49	4.49	4.49
$\bar{\alpha}$	4.90	4.90	4.90	4.91	4.91	4.91
$\Delta\alpha$	1.26	1.27	1.27	1.27	1.27	1.27
β_{zzz}	-8.5	-8.5	-8.5	-8.4	-8.5	-8.4
β_{zxx}	-0.5	-0.5	-0.5	-0.5	-0.5	-0.5
$\bar{\beta}$	-5.6	-5.6	-5.7	-5.6	-5.6	-5.6
$\Delta\beta$	-7.1	-7.1	-7.1	-7.0	-7.1	-7.1
γ_{zzzz}	275	275	274	272	270	272
γ_{xxxx}	331	329	330	330	327	330
γ_{xxzz}	94	94	94	94	93	94
$\bar{\gamma}$	306	306	306	306	303	306
$\Delta_1\gamma$	-218	-206	-215	-222	-217	-222
$\Delta_2\gamma$	43	40	41	38	37	38
$A_{z,zz}$	3.96	3.97	3.96	3.97	3.98	3.97
$A_{x,zx}$	0.94	0.91	0.94	0.84	0.94	0.91
$C_{zz,zz}$	7.45	7.44	7.44	7.41	7.39	7.41
$C_{xz,xz}$	4.40	4.40	4.41	4.40	4.39	4.41
$C_{xx,xx}$	5.93	5.92	5.93	5.91	5.88	5.91
$\bar{C}$	9.01	9.00	9.01	8.99	8.96	9.00
$\Delta_1 C$	7.35	7.46	7.42	7.34	7.47	7.39
$\Delta_2 C$	3.25	3.19	3.17	3.11	3.10	3.10
$E_{z,zzz}$	6.59	6.53	6.53	6.46	6.46	6.49
$E_{x,xxx}$	-0.77	-0.84	-0.87	-0.84	-0.87	-0.84
$B_{zz,zz}$	-54	-54	-54	-53	-52	-52
$B_{xz,xz}$	-34	-35	-34	-34	-34	-34
$B_{xx,zz}$	28	25	26	26	27	28
$B_{xx,xx}$	-48	-47	-48	-48	-47	-48
$\bar{B}$	-47	-47	-47	-47	-46	-47

Experimental geometry $R_e = 1.7328a_0$.

We turn our attention to the dipole (hyper)polarizability. We readily observe that the dipole polarizability values are almost perfectly stable. This is also the case for the first hyperpolarizability. For the second hyperpolarizability $\gamma_{\alpha\beta\gamma\delta}/e^4 a_0^4 E_h^{-3}$ our PA3 values are $\gamma_{zzzz} = 272$, $\gamma_{xxxx} = 330$, $\gamma_{xxzz} = 94$ and $\bar{\gamma} = 306$. Agreement with all other basis sets is very good. All basis sets yield for the Cartesian components values different 1% at most from the abovementioned.

Stable values are also obtained for the quadrupole (hyper)polarizabilities. For $C_{\alpha\beta,\gamma\delta}$ and $B_{\alpha\beta,\gamma\delta}$ the calculated mean values for PA3 are $\bar{C} = 9.00 e^2 a_0^4 E_h^{-1}$ and $\bar{B} = -47 e^3 a_0^4 E_h^{-2}$. All other values are remarkably close to these. Our best values for the dipole–quadrupole ($A_{\alpha,\beta\gamma}/e^2 a_0^3 E_h^{-1}$) and the dipole–octopole ($E_{\alpha,\beta\gamma\delta}/e^2 a_0^4 E_h^{-1}$) polarizability are $A_{z,zz} = 3.97$ and $A_{x,zx} = 0.91$, $E_{z,zzz} = 6.49$ and $E_{x,xxx} = -0.84$. The differences with

the values obtained with the other basis sets are small in absolute terms.

4.2. Electron correlation corrections

In Tables 2–6 we show CCSD(T) values for the electric moments, the dipole (hyper)polarizability and the quadrupole polarizability calculated with basis sets Q1, Q2 and PA1. MP2 values for the dipole–quadrupole and dipole–octopole polarizability and the quadrupole hyperpolarizability, obtained with Q1 and Q2, are given in Table 7.

Electron correlation reduces the magnitude of the electric moments. The effect is small. Our best CCSD(T)/PA1 results are (ECC in parentheses), $\mu/ea_0 = 0.7043(-0.0521)$, $\Theta/ea_0^2 = 1.71(-0.03)$, $\Omega/ea_0^3 = 2.50(-0.10)$ and $\Phi/ea_0^4 = 4.83(-0.19)$. All methods predict reliable values for all properties,

Table 2
Electron correlation effects on the multipole moments of HF ($X^1\Sigma^+$)

Basis set	Method	μ	Θ	Ω	Φ
Q1 ≡ [9s6p5d4f/6s4p3d1f]	SCF	0.7593	1.74	2.60	4.95
	MP2	0.7094	1.73	2.53	4.77
	SDQ-MP4	0.7090	1.72	2.50	4.75
	MP4	0.7000	1.72	2.50	4.73
	CCSD	0.7115	1.71	2.50	4.76
	CCSD(T)	0.7050	1.71	2.50	4.74
	ECC	**− 0.0542**	**− 0.03**	**− 0.11**	**− 0.21**
Q2 ≡ [10s7p6d5f/7s5p4d1f]	SCF	0.7583	1.73	2.60	4.98
	MP2	0.7089	1.73	2.53	4.81
	SDQ-MP4	0.7091	1.71	2.50	4.79
	MP4	0.6999	1.71	2.50	4.77
	CCSD	0.7114	1.71	2.50	4.79
	CCSD(T)	0.7049	1.71	2.49	4.78
	ECC	**− 0.0534**	**− 0.02**	**− 0.10**	**− 0.21**
PA1 ≡ (16s11p8d4f/10s6p3d2f)	SCF	0.7564	1.73	2.59	5.02
	MP2	0.7084	1.73	2.53	4.87
	SDQ-MP4	0.7092	1.71	2.51	4.85
	MP4	0.6995	1.71	2.50	4.83
	CCSD	0.7113	1.71	2.50	4.85
	CCSD(T)	0.7043	1.71	2.50	4.83
	ECC	**− 0.0521**	**− 0.03**	**− 0.10**	**− 0.19**

All MO correlated.

Table 3
Electron correlation effects on the dipole polarizability of HF ($X^1\Sigma^+$)

Basis set	Method	α_{zz}	α_{xx}	$\bar{\alpha}$	$\Delta\alpha$
Q1 ≡ [9s6p5d4f/6s4p3d1f]	SCF	5.75	4.48	4.90	1.26
	MP2	6.42	5.36	5.71	1.06
	SDQ-MP4	6.36	5.23	5.61	1.13
	MP4	6.52	5.43	5.80	1.09
	CCSD	6.30	5.16	5.54	1.14
	CCSD(T)	6.41	5.28	5.66	1.12
	ECC	**0.66**	**0.80**	**0.76**	**− 0.14**
Q2 ≡ [10s7p6d5f/7s5p4d1f]	SCF	5.75	4.48	4.90	1.27
	MP2	6.40	5.34	5.69	1.07
	SDQ-MP4	6.33	5.20	5.58	1.14
	MP4	6.50	5.40	5.76	1.10
	CCSD	6.28	5.13	5.51	1.15
	CCSD(T)	6.38	5.25	5.63	1.13
	ECC	**0.63**	**0.77**	**0.72**	**− 0.14**
PA1 ≡ (16s11p8d4f/10s6p3d2f)	SCF	5.75	4.49	4.91	1.27
	MP2	6.38	5.31	5.67	1.07
	SDQ-MP4	6.29	5.14	5.53	1.15
	MP4	6.46	5.35	5.72	1.11
	CCSD	6.24	5.09	5.47	1.16
	CCSD(T)	6.36	5.22	5.60	1.14
	ECC	**0.60**	**0.73**	**0.69**	**− 0.13**

All MO correlated.

although MP2 tends to underestimate the correlation effects.

Our best CCSD(T)/PA3 values for the components of $\alpha_{\alpha\beta}/e^2a_0^2E_{\mathrm{h}}^{-1}$ are (SCF values in parentheses) $\alpha_{zz} = 6.36(5.75)$, $\alpha_{xx} = 5.22(4.49)$, $\bar{\alpha} = 5.60(4.91)$ and $\Delta\alpha = 1.14(1.27)$. The total effect for the Cartesian components represents a sizeable 10.4 and 16.3%, for α_{zz} and α_{xx}, respectively. The ECC for the mean value decreases slightly in the direction Q1 → Q2 → PA1, while it remains practically stable for the anisotropy. Overall, the MP2 method overestimates slightly both Cartesian components. The other post-Hartree–Fock methods yield reasonable values for all components.

All three basis sets predict stable ECC values for all components of $\beta_{\alpha\beta\gamma}/e^3a_0^3E_{\mathrm{h}}^{-2}$. The CCSD(T)/PA1 values for the mean and the anisotropy (ECC in parentheses) are $\bar{\beta} = -7.4(-1.7)$ and $\Delta\beta = -5.0(2.1)$. These changes are, in absolute terms, 30.4 and 30.0%, respectively, of the SCF

values. We observe that the MP4 method over-estimates the electron correlation effect for all components of this tensor.

Electron correlation effects are very large for the second hyperpolarizability $\gamma_{\alpha\beta\gamma\delta}/e^4a_0^4E_{\mathrm{h}}^{-3}$. The effect on the Cartesian components is not uniform. The most affected is the transversal one. Consequently, we observe a drastic rearrangement of the mean and the anisotropies. Our best values (ECC in parentheses) are $\bar{\gamma} = 512(206)$, $\Delta_1\gamma = -742(-520)$ and $14(-24)$. For the mean hyperpolarizability the ECC represents an increase of 67.3% of the SCF value. Electron correlation more than triples the magnitude of the first anisotropy. The magnitude of the second anisotropy is strongly reduced. The performance of the post-Hartree–Fock methods is characterized by strong variations. Both MP2 and MP4 overestimate the electron correlation effects. It is worth noticing the inconsistency by a comparison of the MP4 and CCSD values. For the PA1 basis set we obtain $\bar{\gamma} = 577$

Table 4
Electron correlation effects on the first dipole hyperpolarizability of HF ($X^1\Sigma^+$)

Basis set	Method	β_{zzz}	β_{zxx}	$\bar{\beta}$	$\Delta\beta$
Q1 ≡ [9s6p5d4f/6s4p3d1f]	SCF	−8.5	−0.5	−5.6	−7.1
	MP2	−9.0	−1.5	−7.2	−4.5
	SDQ-MP4	−9.4	−1.4	−7.4	−5.1
	MP4	−10.0	−1.9	−8.3	−4.3
	CCSD	−9.1	−1.2	−6.9	−5.4
	CCSD(T)	−9.4	−1.5	−7.4	−5.0
	ECC	**−1.0**	**−1.0**	**−1.8**	**2.1**
Q2 ≡ [10s7p6d5f/7s5p4d1f]	SCF	−8.5	−0.5	−5.6	7.1
	MP2	−8.9	−1.5	−7.1	−4.5
	SDQ-MP4	−9.4	−1.4	−7.3	−5.1
	MP4	−10.0	−1.9	−8.3	−4.3
	CCSD	−9.0	−1.2	−6.9	−5.5
	CCSD(T)	−9.4	−1.4	−7.4	−5.1
	ECC	**−0.9**	**−1.0**	**−1.7**	**2.1**
PA1 ≡ (16s11p8d4f/10s6p3d2f)	SCF	−8.4	−0.5	−5.6	−7.0
	MP2	−8.9	−1.5	−7.1	−4.4
	SDQ-MP4	−9.3	−1.4	−7.3	−5.2
	MP4	−9.9	−1.9	−8.2	−4.3
	CCSD	−9.0	−1.2	−6.8	−5.5
	CCSD(T)	−9.4	−1.5	−7.4	−5.0
	ECC	**−0.9**	**−1.0**	**−1.7**	**2.1**

All MO correlated.

(MP4) and 461 (CCSD), the respective difference represents more than 50% of the total ECC.

For the quadrupole polarizability $C_{\alpha\beta,\gamma\delta}/e^2 a_0^4 E_h^{-1}$ we report CCSD(T)/PA1 values (ECC in parentheses) $C_{zz,zz} = 8.46(1.05)$, $C_{xz,xz} = 5.20(0.80)$, $C_{xx,xx} = 7.00(1.09)$ and $\bar{C} = 10.61(1.62)$. The changes show an almost uniform electron correlation effect on these properties. The size of the first anisotropy decreases while the second one remains practically unchanged. Considering the basis set effect on the ECC we notice that the magnitude of the effect reduces slightly with basis set size. For the mean $\bar{C}$ we obtain ECC values of 1.79 (Q1), 1.70 (Q2) and 1.62 (PA1). This is also true for the anisotropies.

Our MP2 values for the dipole–octopole polarizability $A_{\alpha,\beta\gamma}/e^2 a_0^3 E_h^{-1}$ show that electron correlation increases the magnitude for both components of this tensor. For Q2 we obtain $A_{z,zz} = 4.33$ and $A_{x,zx} = 1.32$. These values are 9.1 and 45.1% above the respective SCF results of 3.97 and 0.91. Similar

numbers are obtained with basis Q1. For the dipole–octopole polarizability $E_{\alpha,\beta\gamma\delta}/e^2 a_0^4 E_h^{-1}$ the opposite trend is observed. The magnitude of both components is reduced by electron correlation. Last, for $B_{\alpha\beta,\gamma\delta}/e^3 a_0^4 E_h^{-2}$ we report MP2/Q2 values of $B_{zz,zz} = -64$, $B_{xz,xz} = -49$, $B_{xx,zz} = 39$, $B_{xx,xx} = -72$ and $\bar{B} = -68$. Comparison with the respective SCF values shows important electron correlation effects for the components of this tensor. The MP2/Q1 results are quite similar.

4.3. Bond-length dependence of the electric properties

Table 8 lists part of our calculated values for bond lengths $\Delta R \equiv (R - R_e)/a_0 = 0$, ± 0.2, ± 0.4, ± 0.6 and ± 0.8. These are CCSD(T)/Q results for μ, Θ, Ω, Φ, $\alpha_{\alpha\beta}$, $\beta_{\alpha\beta\gamma}$, $\gamma_{\alpha\beta\gamma\delta}$ and $C_{\alpha\beta,\gamma\delta}$ and MP2/Q1 for $A_{\alpha,\beta\gamma}$, $E_{\alpha,\beta\gamma\delta}$ and $B_{\alpha\beta,\gamma\delta}$. In Table 9 we show the level-of-theory dependence of the first derivative $(\frac{dP}{dR})_e$.

Table 5
Electron correlation effects on the second dipole hyperpolarizability of HF ($X^1\Sigma^+$)

Basis set	Method	γ_{zzzz}	γ_{xxxx}	γ_{xxzz}	$\bar{\gamma}$	$\Delta_1\gamma$	$\Delta_2\gamma$
Q1 ≡ [9s6p5d4f/6s4p3d1f]	SCF	275	331	94	306	−218	43
	MP2	385	603	163	529	−768	10
	SDQ-MP4	385	593	161	522	−735	14
	MP4	432	686	186	601	−892	1
	CCSD	361	550	150	485	−666	12
	CCSD(T)	388	605	164	532	−762	8
	ECC	**113**	**274**	**70**	**225**	**−544**	**−35**
Q2 ≡ [10s7p6d5f/7s5p4d1f]	SCF	275	329	94	306	−206	40
	MP2	384	594	162	523	−736	5
	SDQ-MP4	381	578	159	511	−691	6
	MP4	428	670	184	590	−844	−5
	CCSD	360	534	148	475	−614	6
	CCSD(T)	388	590	163	523	−703	−3
	ECC	**113**	**261**	**69**	**217**	**−497**	**−43**
PA1 ≡ (16s11p8d4f/10s6p3d2f)	SCF	272	330	94	306	−222	38
	MP2	377	593	161	520	−758	4
	SDQ-MP4	368	561	153	495	−681	10
	MP4	415	658	179	577	−848	−3
	CCSD	344	524	141	461	−641	23
	CCSD(T)	373	584	157	512	−742	14
	ECC	**101**	**253**	**63**	**206**	**−520**	**−24**

All MO correlated.

Using our CCSD(T)/Q1 results for the multipole moments we calculate the following R-dependence for these properties around R_e :

$$\mu(R)/ea_0 = 0.7050 + 0.3101(R - R_e)$$
$$- 0.0053(R - R_e)^2 - 0.0677(R - R_e)^3$$
$$- 0.0140(R - R_e)^4 \qquad (7)$$

$$\Theta(R)/ea_0^2 = 1.71 + 1.59(R - R_e) + 0.39(R - R_e)^2$$
$$- 0.23(R - R_e)^3 - 0.09(R - R_e)^4 \qquad (8)$$

$$\Omega(R)/ea_0^3 = 2.50 + 4.30(R - R_e) + 2.21(R - R_e)^2$$
$$- 0.11(R - R_e)^3 - 0.34(R - R_e)^4 \qquad (9)$$

$$\Phi(R)/ea_0^4 = 4.73 + 10.79(R - R_e) + 8.25(R - R_e)^2$$
$$+ 1.74(R - R_e)^3 - 0.47(R - R_e)^4 \qquad (10)$$

The magnitude of the SCF first derivatives is slightly reduced by electron correlation. All methods predict more or less stable values. Overall, all moments increase rapidly with increasing bond length. In Fig. 1 we have traced for the higher moments the SCF and ECC values for $-0.8 < \Delta R/a_0 < 0.8$. We observe that the ECC decreases monotonically with increasing ΔR, while the opposite trend is evidenced for the SCF values.

The mean and the anisotropy of the dipole polarizability vary as

$$\bar{\alpha}(R)/e^2a_0^2E_h^{-1} = 5.66 + 2.92(R - R_e)$$
$$+ 1.10(R - R_e)^2 + 0.24(R - R_e)^3$$
$$- 0.01(R - R_e)^4 \qquad (11)$$

$$\Delta\alpha(R)/e^2a_0^2E_h^{-1} = 1.12 + 4.30(R - R_e)$$
$$+ 2.97(R - R_e)^2 + 0.78(R - R_e)^3$$
$$+ 0.07(R - R_e)^4$$

Table 6
Electron correlation effects on the quadrupole polarizability of HF ($X^1\Sigma^+$)

Basis set	Method	$C_{zz,zz}$	$C_{xz,xz}$	$C_{xx,xx}$	$\bar{C}$	$\Delta_1 C$	$\Delta_2 C$
Q1 ≡ [9s6p5d4f/6s4p3d1f]	SCF	7.45	4.40	5.93	9.01	7.35	3.25
	MP2	8.67	5.37	7.30	11.00	6.37	3.18
	SDQ-MP4	8.55	5.22	7.10	10.71	6.86	3.29
	MP4	8.85	5.46	7.41	11.18	6.82	3.25
	CCSD	8.42	5.12	6.96	10.51	6.91	3.31
	CCSD(T)	8.61	5.27	7.15	10.80	6.94	3.30
	ECC	**1.17**	**0.88**	**1.22**	**1.79**	**−0.42**	**0.05**
Q2 ≡ [10s7p6d5f/7s5p4d1f]	SCF	7.44	4.40	5.92	9.00	7.46	3.19
	MP2	8.23	5.00	6.76	10.23	7.08	3.24
	SDQ-MP4	8.47	5.19	7.01	10.60	7.03	3.19
	MP4	8.77	5.43	7.32	11.08	7.01	3.15
	CCSD	8.35	5.09	6.88	10.41	7.07	3.21
	CCSD(T)	8.54	5.24	7.07	10.70	7.10	3.20
	ECC	**1.10**	**0.84**	**1.15**	**1.70**	**−0.36**	**0.01**
PA1 ≡ (16s11p8d4f/10s6p3d2f)	SCF	7.41	4.40	5.91	8.99	7.39	3.11
	MP2	8.53	5.32	7.18	10.85	6.46	2.98
	SDQ-MP4	8.35	5.12	6.90	10.45	7.03	3.11
	MP4	8.66	5.37	7.23	10.95	6.98	3.06
	CCSD	8.25	5.04	6.80	10.30	7.06	3.13
	CCSD(T)	8.46	5.20	7.00	10.61	7.07	3.11
	ECC	**1.05**	**0.80**	**1.09**	**1.62**	**−0.32**	**0.00**

All MO correlated.

Table 7
SCF and MP2 results for the dipole–quadrupole ($A_{\alpha,\beta\gamma}$), dipole–octopole ($E_{\alpha,\beta\gamma\delta}$) polarizability and dipole–dipole–quadrupole ($B_{\alpha\beta,\gamma\delta}$) hyperpolarizability of HF ($X^1\Sigma^+$)

Property	Q1 ≡ [9s6p5d4f/6s4p3d1f]		Q2 ≡ [10s7p6d5f/7s5p3d1f]	
	SCF	MP2	SCF	MP2
$A_{z,zz}$	3.96	4.33	3.97	4.33
$A_{x,zx}$	0.94	1.32	0.91	1.32
$E_{z,zzz}$	6.59	6.03	6.53	6.04
$E_{x,xxx}$	−0.77	−0.55	−0.84	−0.58
$B_{zz,zz}$	−54	−65	−54	−64
$B_{xz,xz}$	−34	−50	−35	−49
$B_{xx,zz}$	28	40	25	39
$B_{xx,xx}$	−48	−74	−47	−72
$\bar{B}$	−47	−69	−47	−68

The innermost MO was kept frozen.

Table 8
R-dependence of the electric properties of $HF(X^1\Sigma^+)$. CCSD(T)/Q1[a] results for μ, Θ, Ω, Φ, $\alpha_{\alpha\beta}$, $\beta_{\alpha\beta\gamma}$, $\gamma_{\alpha\beta\gamma\delta}$ and $C_{\alpha\beta,\gamma\delta}$; MP2/Q1[b] results for $A_{\alpha,\beta\gamma}$, $E_{\alpha,\beta\gamma\delta}$ and $B_{\alpha\beta,\gamma\delta}$.

Property	−0.8	−0.6	−0.4	−0.2	0	0.2	0.4	0.6	0.8
μ	0.4823	0.5299	0.5839	0.6432	0.7050	0.7663	0.8234	0.8727	0.9093
Θ	0.77	0.93	1.15	1.41	1.71	2.04	2.39	2.75	3.08
Ω	0.39	0.69	1.13	1.73	2.50	3.44	4.56	5.81	7.16
Φ	0.30	0.78	1.60	2.90	4.74	7.24	10.39	14.55	19.32
α_{zz}	3.37	3.89	4.54	5.37	6.41	7.70	9.27	11.17	13.41
α_{xx}	4.16	4.43	4.71	4.99	5.28	5.59	5.90	6.21	6.52
$\bar{\alpha}$	3.90	4.25	4.65	5.12	5.66	6.29	7.02	7.86	8.82
$\Delta\alpha$	−0.79	−0.55	−0.17	0.38	1.12	2.11	3.37	4.95	6.89
β_{zzz}	−0.2	−1.3	−3.1	−5.7	−9.4	−14.2	−19.6	−23.9	−24.0
β_{zxx}	−1.6	−1.6	−1.6	−1.5	−1.5	−1.4	−1.3	−1.2	−0.9
$\bar{\beta}$	−2.0	−2.7	−3.7	−5.3	−7.4	−10.2	−13.3	−15.8	−15.5
$\Delta\beta$	4.4	3.5	1.6	−1.1	−5.0	−10.0	−15.6	−20.4	−21.2
γ_{zzzz}	129	166	211	293	388	498	614	668	585
γ_{xxxx}	333	394	457	531	605	683	768	866	932
γ_{xxzz}	79	100	114	140	164	192	229	273	316
$\bar{\gamma}$	267	324	377	454	532	618	715	814	867
$\Delta_1\gamma$	−705	−780	−854	−822	−762	−663	−542	−639	−1025
$\Delta_2\gamma$	−15	−40	−15	−17	8	28	10	−105	−378
$C_{zz,zz}$	3.92	4.55	5.44	6.73	8.61	11.36	15.34	21.06	29.16
$C_{xz,xz}$	3.19	3.54	3.98	4.55	5.27	6.19	7.34	8.80	10.63
$C_{xx,xx}$	4.69	5.14	5.68	6.33	7.15	8.20	9.55	11.33	13.69
$\bar{C}$	6.70	7.40	8.27	9.38	10.80	12.64	15.05	18.21	22.37
$\Delta_1 C$	−5.13	−4.21	−2.28	1.18	6.94	15.99	29.68	49.82	78.79
$\Delta_2 C$	−0.25	0.09	0.64	1.60	3.30	6.17	10.87	18.25	29.49
$A_{z,zz}$	−0.22	0.34	1.20	2.50	4.33	6.86	10.25	14.63	20.16
$A_{x,zx}$	0.22	0.38	0.60	0.91	1.32	1.83	2.45	3.21	4.13
$E_{z,zzz}$	−2.94	−2.22	−0.76	1.81	6.03	12.64	22.31	36.08	54.95
$E_{x,xxx}$	1.60	1.40	1.03	0.39	−0.55	−1.80	−3.55	−5.86	−8.80
$B_{zz,zz}$	−18	−25	−33	−45	−65	−91	−123	−159	−193
$B_{xz,xz}$	−26	−30	−35	−41	−50	−59	−71	−85	−103
$B_{xx,zz}$	25	28	33	36	40	45	49	56	62
$B_{xx,xx}$	−45	−52	−59	−65	−74	−80	−89	−100	−112
$\bar{B}$	−37	−43	−50	−58	−69	−80	−95	−113	−132

[a] All MO correlated.
[b] The innermost MO is kept frozen.

The SCF first derivative are $(\frac{\mathrm{d}\bar{\alpha}}{\mathrm{d}R})_e = 2.57$ and $(\frac{\mathrm{d}\Delta\alpha}{\mathrm{d}R})_e = 4.35 e^2 a_0 E_h^{-1}$. Electron correlation increases strongly the derivative of the mean but has a smaller effect on the derivative of the anisotropy. We show in Fig. 2 the R-dependence of the SCF and ECC quantities for the Cartesian components of the dipole polarizability. Both SCF values increase very rapidly with ΔR ($\alpha_{zz} > \alpha_{xx}$ in the range of values considered here) but the effect is considerably less important for the total electron correlation.

The SCF, MP2, MP4 and CCSD(T) $\bar{\beta}(R)$ curves in Fig. 3 show that at the SCF level this property decreases strongly for $\Delta R/a_0 > 0$. The post-Hartree–Fock methods display a quite different behaviour for $\Delta R/a_0 > 0.4$. The $(\frac{\mathrm{d}\bar{\beta}}{\mathrm{d}R})_e$ results in

Table 9
Level-of-theory dependence of $\left(\frac{\mathrm{d}P}{\mathrm{d}R}\right)_e$ for HF ($X^1\Sigma^+$)

Property	SCF	MP2	SDQ-MP4	MP4	CCSD	CCSD(T)
$\left(\frac{d\mu}{dR}\right)_e$	0.4031	0.3353	0.3179	0.3053	0.3200	0.3101
$\left(\frac{d\Theta}{dR}\right)_e$	1.71	1.65	1.61	1.60	1.60	1.59
$\left(\frac{d\Omega}{dR}\right)_e$	4.73	4.43	4.34	4.32	4.34	4.30
$\left(\frac{d\Phi}{dR}\right)_e$	11.60	11.01	10.91	10.82	10.85	10.79
$\left(\frac{d\bar{\alpha}}{dR}\right)_e$	2.57	2.94	2.93	3.09	2.85	2.92
$\left(\frac{d\Delta\alpha}{dR}\right)_e$	4.35	4.00	4.24	4.16	4.33	4.30
$\left(\frac{d\bar{\beta}}{dR}\right)_e$	−15.1	−11.0	−12.3	−12.3	−12.5	−12.4
$\left(\frac{d\bar{\gamma}}{dR}\right)_e$	257	426	441	528	398	437
$\left(\frac{d\bar{C}}{dR}\right)_e$	6.74	8.21	8.05	8.61	7.73	8.02
$\left(\frac{dA_{z,zz}}{dR}\right)_e$	10.52	10.83				
$\left(\frac{dA_{x,zx}}{dR}\right)_e$	1.93	2.27				
$\left(\frac{dE_{zz,zz}}{dR}\right)_e$	25.84	26.42				
$\left(\frac{dE_{x,xxx}}{dR}\right)_e$	−5.19	−5.46				
$\left(\frac{d\bar{B}}{dR}\right)_e$	−42	−56				

Basis set Q1 ≡ [9s6p5d4f/6s4p3d1f]. See Table 8.

Table 9 have been obtained from fits to values obtained in the range $-0.8 < \Delta R/a_0 < 0.4$. The magnitude of the SCF value is strongly reduced by electron correlation but the higher methods yield remarkably stable values.

The components of the second hyperpolarizability display different behaviour for relatively large internuclear separations. In Figs. 4 and 5 we have traced the R-dependence of the longitudinal and transversal components for the SCF, MP2, MP4 and CCSD(T) methods. The SCF curve for γ_{zzzz} shows a rapid monotonic increase while the MP2, MP4 and CCSD(T) levels display an inversion of this trend for $\Delta R/a_0 > 0.6$. This is not the case for γ_{xxxx} as for all methods represented in Fig. 5 a smooth monotonic increase is immediately obvious. The $\left(\frac{d\bar{\gamma}}{dR}\right)_e$ values reveal a strong electron correlation effect with an ECC of $180e^4a_0^3E_h^{-3}$, an increase of 70% for the SCF of 257. The MP2 value is quite close to the most accurate CCSD(T) one but the MP4 method overestimates the effect.

As shown in Fig. 6, the components of the quadrupole polarizability vary smoothly with the internuclear separation. The axial component
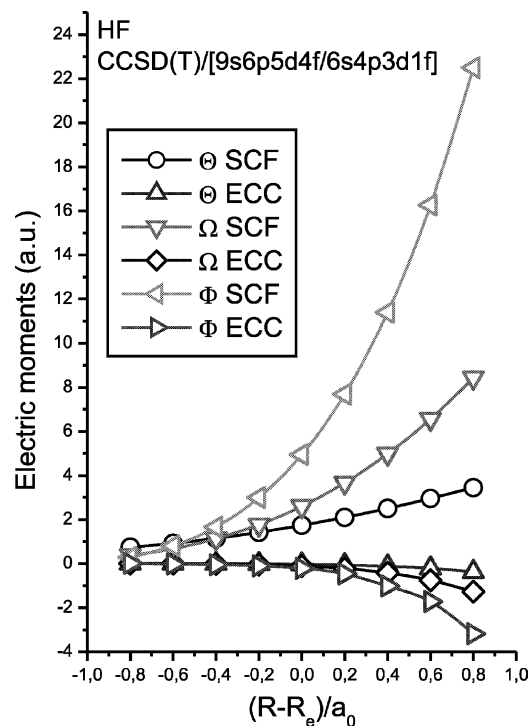
Fig. 1. R-dependence of the SCF and ECC values for the components of the higher electric moments (Θ, Ω, Φ) of hydrogen fluoride. Basis set Q1.
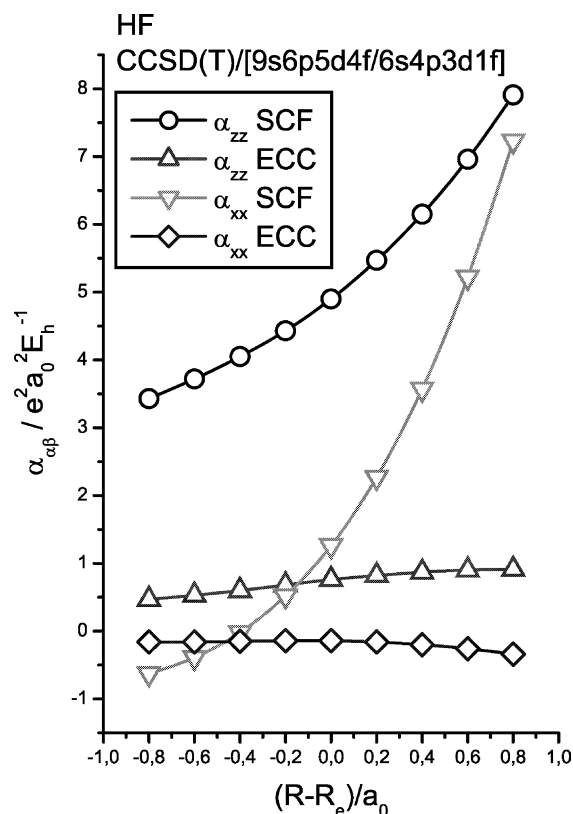
Fig. 2. *R*-dependence of the SCF and ECC values for the components of the dipole polarizability of hydrogen fluoride. Basis set Q1.

$C_{zz,zz}$ seems to be the most affected by the geometry changes. This is present in both the SCF and ECC curves. The mean varies at the CCSD(T)/Q1 level of theory as

$$\bar{C}(R)/e^2 a_0^4 E_h^{-1} = 10.80 + 8.02(R-R_e) + 5.23(R-R_e)^2$$

$$+2.76(R-R_e)^3 + 0.95(R-R_e)^4 \quad (12)$$

The SCF value of the first derivative is $\left(\dfrac{d\bar{C}}{dR}\right)_e = 6.74 e^2 a_0^3 E_h^{-1}$. The CCSD(T) value is 8.02, or 19.0% higher. All other methods are in fair agreement with the CCSD(T) result.

In Fig. 7 we have plotted the *R*-dependence of the MP2 values of the dipole–quadrupole and dipole–octopole polarizability. Both properties exhibit strong *R*-dependence. This is most true for
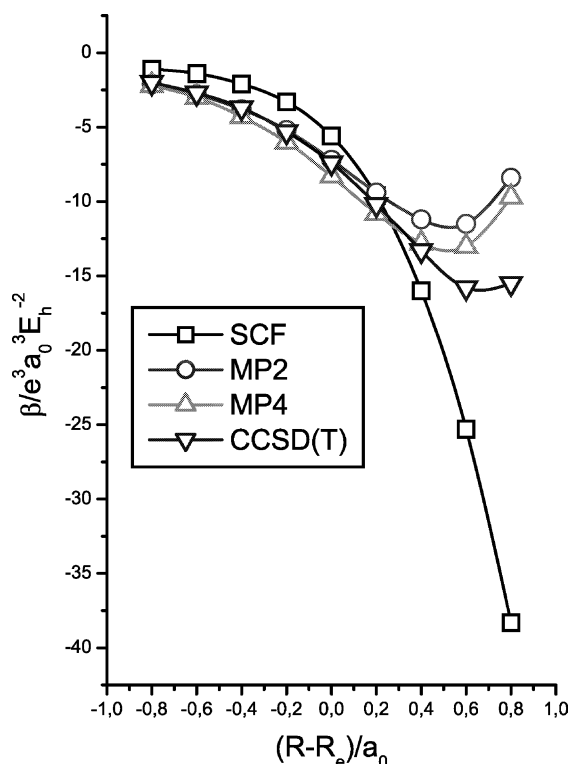
Fig. 3. *R*-dependence of the mean first hyperpolarizability of hydrogen fluoride. Basis set Q1.

the axial components which show enhanced values for $\Delta R/a_0 > 0$. The values of the first derivatives are very large for both $A_{z,zz}$ and $E_{z,zzz}$. We find that the variation of the dipole–octopole polarizability is very well represented by

$$A_{z,zz}(R)/e^2 a_0^3 E_h^{-1} = 4.33 + 10.83(R-R_e) + 8.69(R-R_e)^2$$

$$+2.99(R-R_e)^3 + 0.19(R-R_e)^4$$

$$A_{x,zx}(R)/e^2 a_0^3 E_h^{-1} = 1.32 + 2.27(R-R_e) + 1.30(R-R_e)^2$$

$$+0.27(R-R_e)^3 + 0.07(R-R_e)^4 \quad (13)$$

For the components of the dipole–octopole polarizability the *R*-dependence is best given as

$$[E_{z,zzz}(R) - E_{z,zzz}(R_e)]/e^2 a_0^4 E_h^{-1}$$

$$= 26.42(R-R_e) + 29.01(R-R_e)^2 + 15.25(R-R_e)^3$$

$$+3.39(R-R_e)^4$$
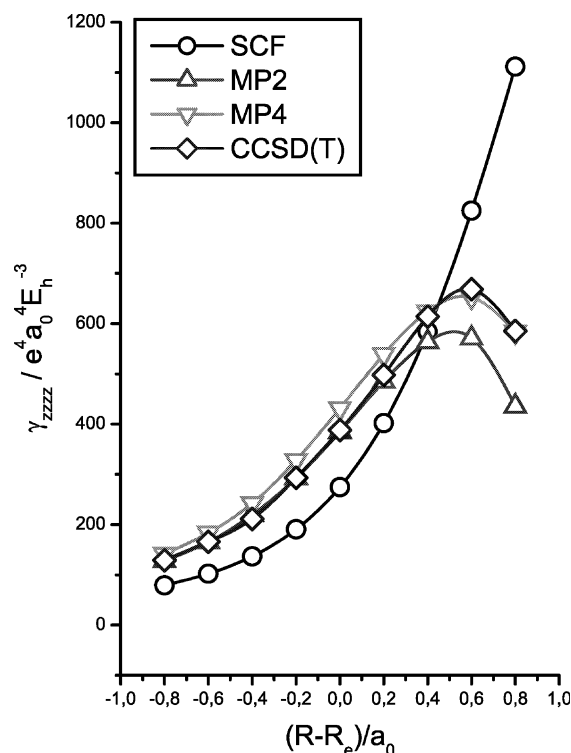
Fig. 4. R-dependence of the longitudinal component of the second hyperpolarizability of hydrogen fluoride. Basis set Q1.
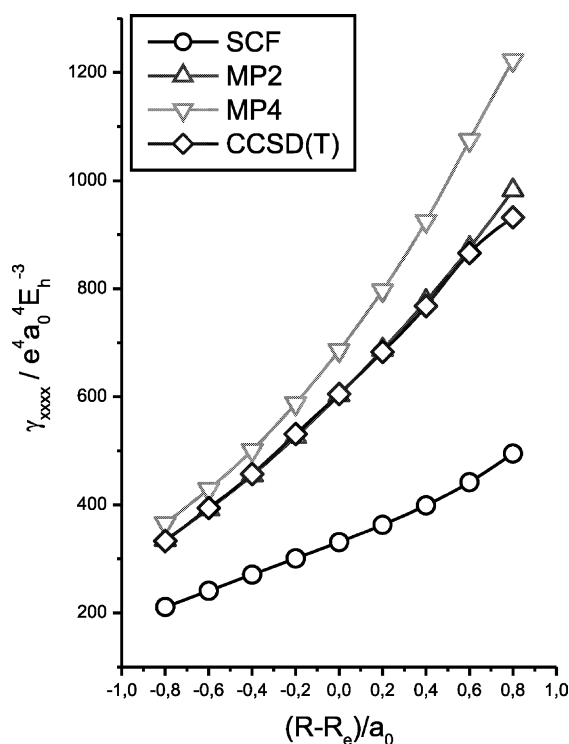

Fig. 5. R-dependence of the transversal component of the second hyperpolarizability of hydrogen fluoride. Basis set Q1.

$$[E_{z,zzz}(R) - E_{z,zzz}(R_e)]/e^2 a_0^4 E_h^{-1}$$

$$= -5.46(R-R_e) - 4.57(R-R_e)^2 - 1.63(R-R_e)^3$$

$$- 0.37(R-R_e)^4 \qquad (14)$$

The magnitude of the components of $B_{\alpha\beta,\gamma\delta}$ increases monotonically with increasing bond length. Fig. 8 shows clearly that this change is more pronounced for the axial component $B_{zz,zz}$. Overall, the R-dependence of the mean is best represented by the following polynomial:

$$[\bar{B}(R) - \bar{B}(R_e)]/e^3 a_0^4 E_h^{-2} = -56(R-R_e) - 28(R-R_e)^2$$
$$- 6(R-R_e)^3 + 4(R-R_e)^4 \quad (15)$$

4.4. Rovibrational corrections

This problem has been treated in some depth by Bishop [38,40] and more recently by Seth et al.

[85], Ingamells et al. [86] and Ruud et al. [87]. In this work we follow a simple approach [88] which has been successfully tested on similar systems [65]. We rely on experimental spectroscopic constants for hydrogen fluoride [81] to obtain the value of property P at vJ rovibrational state as,

$$P_{vJ} - P_e = \left(0.059317\left(\frac{dP}{dR}\right)_e + 0.015205\left(\frac{d^2P}{dR^2}\right)_e\right)$$
$$\times \left(v + \frac{1}{2}\right) + 0.000178\left(\frac{dP}{dR}\right)_e J(J+1) \qquad (16)$$

By inserting in Eq. (16) the respective derivatives (obtained from Table 8) we obtain estimates of P_{vJ} for all properties. For the electric moments

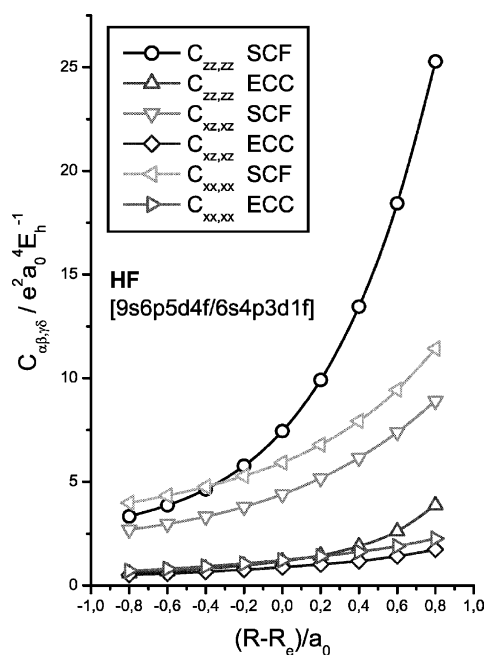Fig. 6. R-dependence of the SCF and ECC values of the Cartesian components of the quadrupole polarizability of hydrogen fluoride. Basis set Q1.
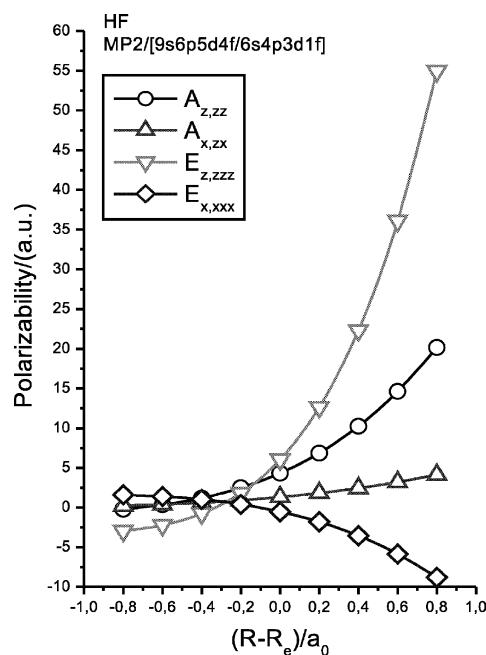

Fig. 7. R-dependence of the MP2 values of the dipole–quadrupole ($A_{\alpha,\beta\gamma}$) and dipole–octopole ($E_{\alpha,\beta\gamma\delta}$) polarizability of hydrogen fluoride. Basis set Q1.

and the dipole polarizabilities we have

$$\mu_{vJ} - \mu_e = 0.0182\left(v + \frac{1}{2}\right) + 0.00055J(J+1);$$

$$\Theta_{vJ} - \Theta_e = 0.11\left(v + \frac{1}{2}\right) + 0.00028J(J+1);$$

$$\Omega_{vJ} - \Omega_e = 0.32\left(v + \frac{1}{2}\right) + 0.00076J(J+1);$$

$$\Phi_{vJ} - \Phi_e = 0.89\left(v + \frac{1}{2}\right) + 0.0019J(J+1);$$ (17)

$$\bar{\alpha}_{vJ} - \bar{\alpha}_e = 0.21\left(v + \frac{1}{2}\right) + 0.00052J(J+1);$$

$$\Delta\alpha_{vJ} - \Delta\alpha_e = 0.35\left(v + \frac{1}{2}\right) + 0.00076J(J+1)$$

The zero-point vibrational correction (ZPVC $\equiv$ $P_{00} - P_e$) is estimated at $0.0091ea_0$ for μ, $0.05ea_0^2$ for Θ, $0.16ea_0^3$ for Ω, $0.45ea_0^4$ for Φ, 0.10 for $\bar{\alpha}$ and $0.17e^2a_0^2E_h^{-1}$ for $\Delta\alpha$, $-0.5e^3a_0^3E_h^{-2}$ for $\bar{\beta}$, $15e^4a_0^4E_h^{-3}$ for $\bar{\gamma}$, $0.32e^2a_0^4E_h^{-1}$ for $\bar{C}$, 0.45 for $A_{z,zz}$ and $0.09e^2a_0^3E_h^{-1}$ for $A_{x,zx}$, 1.22 for $E_{z,zzz}$ and $-0.23e^2a_0^4E_h^{-1}$ for $E_{x,xxx}$,
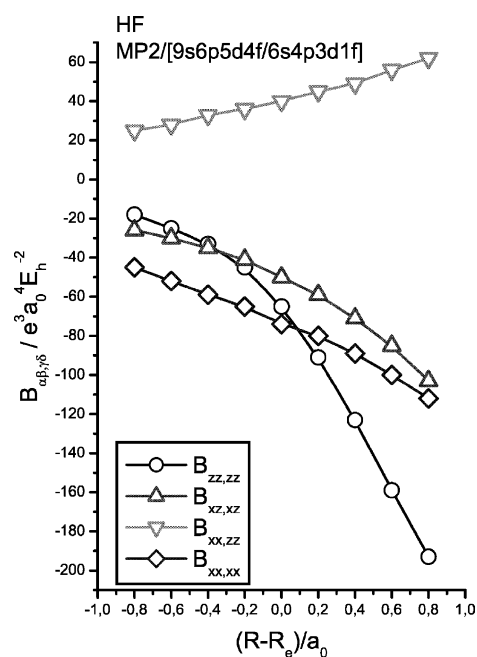
Fig. 8. R-dependence of the MP2 of the Cartesian components of the of the dipole–dipole–quadrupole ($B_{\alpha\beta,\gamma\delta}$) polarizability of hydrogen fluoride. Basis set Q1.

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Table 10
Theoretical predictions and experimental data for the electric properties of hydrogen fluoride

Property	Theory			Experiment
	Present[a]		Previous	
	SCF	CCSD(T)		
μ	0.7561	0.7043	0.7038[b], 0.700[c], 0.7141[d], 0.756[e], 0.708[f], 0.7121[g], 0.715[h], 0.72[i], 0.7096[j]	0.7093[k]
$(\frac{d\mu}{dR})_e$	0.4031	0.3101	0.3159[l]	0.3197k
Θ	1.73	1.71	1.7204[m], 1.727[c], 1.641[d], 1.711[n], 1.716[h], 1.7121[o]	1.75 ± 0.02[p]
$(\frac{d\Theta}{dR})_e$	1.71	1.59		
Ω	2.59	2.50	2.460[c], 2.500[n]	
$(\frac{d\Omega}{dR})_e$	4.73	4.30		
Φ	5.03	4.83		
$(\frac{d\Phi}{dR})_e$	11.60	10.79		
$\bar{\alpha}$	4.91	5.60	5.573[b], 5.68[c], 4.863[d], 4.91[e], 5.58[f], 5.94[g], 5.345[h], 5.43[i], 5.816[q], 5.538[j], 5.598[r]	5.601 [s], 5.398[t]
$(\frac{d\bar{\alpha}}{dR})_e$	2.57	2.92	2.64[l], 3.10[q], 2.938[r]	
$\Delta\alpha$	1.27	1.14	1.158[b], 1.08[c], 1.370[d], 1.26[e], 1.13[f], 1.07[g], 1.252[h], 1.13[i], 1.273[q], 1.142[j], 1.157[r]	1.485 ± 0.135[u], 1.31 ± 0.13[v]
$(\frac{d\Delta\alpha}{dR})_e$	4.35	4.30	4.47[l], 4.68[q], 4.32[r]	
$\bar{\beta}$	-5.6	-7.4	-4.40[w], -7.179[c], -6.94[d], -5.63[e], -7.22[f], -7.92[x], -9.57[g], -6.70[i], -7.48[y], -6.93[z], -7.18[j]	-11.0 ± 1.0[aa]
$(\frac{d\beta}{dR})_e$	-15.1	-12.4	-15.8[l], -14.47[w]	
$\bar{\gamma}$	306	512	509[b], 543[c], 305[e], 516[f], 558[x], 665.5[g], 410[z], 447.9[i], 488[j]	842 ± 142[aa]
$(\frac{d\bar{\gamma}}{dR})_e$	257	437		
$\bar{C}$	9.00	10.61	10.21[m], 7.54[c], 7.213[d], 8.939[h]	
$(\frac{d\bar{C}}{dR})_e$	6.74	8.02		

[a] PA3 for SCF and CCSD(T)/PA1 for post-Hartree–Fock R_e values. All derivatives were obtained with the Q1 basis set.

[b] Chong and Langhoff [89], CCSD(T)/[8s6p4d3f/5s3p2d].

[c] From unrelaxed coupled cluster density matrix calculations of (induced) multipole moments with a [5s3p2d/3s2p] basis set. Pluta et al. [90].

[d] Cartier et al. [91]. SD-CI/[7s5p2d1f/5s2p1d] results.

[e] Complete basis set limit (CBS) SCF values by Feller and Petersen [58].

[f] Estimated CBS limit at the CCSD(T) level. Feller and Peterson [58].

[g] Calaminici et al. [92], VWN-DFT calculations with TZVP-FIP1 ($\alpha_{\alpha\beta}$ and $\beta_{\alpha\beta\gamma}$) and TZVP-FIP2 ($\gamma_{\alpha\beta\gamma\delta}$) basis sets.

[h] Hesselmann and Jansen [93], BCCD/aug-cc-pVQZ.

[i] CASSCF/t-aug-cc-pVTZ results by Bishop and Norman [94].

[j] Explicitly correlated coupled cluster calculations with a 21s15p9d8f/8s5p4d basis set, Franke et al. [95].

[k] Ogilvie [106].

[l] The dipole moment derivative from a ACCD curve by Dykstra. The (hyper)polarizability derivatives are SCF results, see Kirtman and Bishop [96].

[m] Diercksen and Sadlej [97], MBPT(4)/[8s5p3d1f/4s2p1d].

[n] Multireference CI calculations by Feller and Peterson [58].

[o] Full CI basis set limit Re value by Halkier and Coriani [98]

[p] Molecular beam electric resonance spectroscopy (MBER) by De Leeuw and Dymanus [107].

[q] Time-dependent gauge-invariant (TDGI) approach by Merawa and Dargelos [99] (Basis B2).

$-2e^3a_0^4E_\mathrm{h}^{-2}$ for $\bar{B}$. Some of these ZPVC are fairly sizeable, we note the case of Φ (9.5% of the R_e value), $\bar{\beta}$ (6.8% of the R_e value) and $E_{z,zzz}$ (20.2% of the R_e value).

4.5. Comparison with previous theoretical predictions

Only a representative selection of previous theoretical predictions has been included in Table 10. More can be found in Bishop and Maroulis [55] or Feller and Peterson [58].

Previous values for μ/ea_0 include a 0.7038 CCSD(T) value [89], a 0.700 unrelaxed CC density matrix calculation (UCCDM) [90] and a 0.7141 SD-CI result [91]. Feller and Peterson [58] estimated the complete basis set (CBS) SCF limit at 0.756. Our SCF/PA3 value is in excellent agreement with this CBS estimate. The CCSD(T)/CBS estimate is 0.708 [58], barely 0.5% above our CCSD(T)/PA1 value. We also mention a density functional theory (DFT) value of 0.7121 [92], a Brueckner CC doubles (BCCD) result of 0.715 [93], a complete active space SCF (CASSCF) value of 0.72 [94] and the explicitly correlated CC (CC-R12) result of 0.7096 [95]. Our CCSD(T) is in very good agreement with the CC-R12 value. For the derivative $(\frac{\mathrm{d}\mu}{\mathrm{d}R})_\mathrm{e}$ the approximate CCD (ACCD) value $0.3159e$ by Dyskstra (referenced by Bishop and Kirtman [96]) is very close to ours.

For Θ/ea_0^2 we mention the early MBPT(4) calculation of 1.7204 [97], the UCCDM of 1.727 [90], the SD-CI of 1.641 [91], the multireference CI (MRCI) of 1.711 [58] and the BCCD of 1.716 [93]. Halkier and Coriani [98] have obtained a full CI basis set limit estimate of 1.7121. This last value is in excellent agreement with our CCSD(T)/PA1 of 1.71.

For Ω/ea_0^3 the UCCDM value of Pluta et al. [90] is slightly below our CCSD(T)/PA1 value. The MRCI

value of Feller and Peterson [58] is 2.500, in perfect agreement with our aforementioned value.

Turning our attention to the dipole polarizability $\alpha_{\alpha\beta}/e^2a_0^2E_\mathrm{h}^{-1}$, we observe that our SCF/PA3 values for the mean (4.91) and the anisotropy (1.27) are in excellent agreement with the SCF/CBS results of Feller and Peterson [58], 4.91 and 1.26, respectively. More results for $\bar{\alpha}$ and $\Delta\alpha$, include: 5.573 and 1.158, CCSD(T) [89], 5.68 and 1.08, UCCDM [90], 4.863 and 1.370, SD-CI [91], 5.58 and 1.13, CCSD(T)/CBS [58], 5.94 and 1.07, DFT [92], 5.345 and 1.252, BCCD [93], 5.43 and 1.13, CASSCF [94], 5.816 and 1.273, TDGI (time-dependent gauge invariant) [99], 5.538 and 1.142, CC-R12 [95], 5.598 and 1.157, CCSD [100]. We note again the excellent agreement of our CCSD(T)/PA1 values with the CCSD(T)/CBS [58] and CC-R12 [95] results. For the respective derivatives $(\frac{\mathrm{d}\alpha_{\alpha\beta}}{\mathrm{d}R})_\mathrm{e}/e^2a_0E_\mathrm{h}^{-1}$, Bishop and Kirtman [96] reported SCF values of 2.64 and 4.47 for the mean and the anisotropy, respectively. The TDGI [99] results are 3.10 and 4.68, respectively. Our CCSD(T)/Q1 values are in excellent agreement with the CCSD values of 2.938 and 4.320 reported by Pecul and Rizzo [100].

For the mean of the first dipole hyperpolarizability $\bar{\beta}/e^3a_0^3E_\mathrm{h}^{-2}$, Feller and Peterson reported a SCF/CBS value of -5.63. Our SCF/PA3 is -5.6. The coupled-Hartree–Fock (CHF) value of Lazzeretti et al. [101] is somewhat lower at -4.40. We mention also the CCSD(T) of -7.179 [89], the UCCMD of -6.94 [90], the CCSD(T)/CBS of -7.22 [58], the EOM-CC (equation-of-motion CC) of -7.92 [102], the DFT of -9.57 [92], the CASSCF of -6.70 [94], the CC3 of -7.48 [103], the DFT-LB94 of -6.93 [104] and the CC-R12 of -7.18 [95]. We readily observe that the most accurate results are in the region of -7.18 to -7.48 [58,89,95,103], a range of values that

[r] Pecul and Rizzo [100], CCSD/d-aug-cc-pVQZ.
[s] Dipole oscillator strength distributions (DOSD) by Kumar and Meath [108].
[t] Static values, extrapolation of refractivity data for liquid HF, see Russell and Spackman [109].
[u] MBER spectroscopy by Muenter [111].
[v] MBER value [111] corrected for vibrational effects by Bishop et al. [112].
[w] Lazzeretti et al. [101], CPHF/[9s6p3d1f/6s2p1d].
[x] EOM-CC/t-aug-cc-pVTZ calculations by Rozyczko and Bartlett [102].
[y] Gauss et al. [103]. CC3/t-aug-cc-pVTZ calculation.
[z] DFT calculations with the van Leuwen-Baerends (LB94) potential. Van Gisbergen et al. [104].
[aa] ESHG at 694.3 nm, see Shelton and Rice [47].

includes our CCSD(T)/PA1 of -7.4. It should be noted that Franke et al. [95] recommend a final $\bar{\beta} = -7.33 \pm 0.165$, a value quite close to our best result cited above. Considerably little has been published on the derivative $(\frac{d\bar{\beta}}{dR})_e/e^3a_0^2E_h^{-2}$. The old CHF of Lazzeretti et al. [101] is -14.47 and the SCF of Bishop and Kirtman [96] -15.8, both close to our SCF/Q1 value of -15.1.

The accurate calculation of the mean second hyperpolarizability $\bar{\gamma}/e^4a_0^4E_h^{-3}$ has recently emerged as quite a challenge. Starting from the SCF values we note that the available SCF/CBS of 305 [58] is in excellent agreement with our reference SCF/PA3 value of 306. Chong and Langhoff [89] reported a CCSD(T) value of 509. The UCCDM value of Pluta et al. [90] is higher at 543. The CCSD(T)/CBS estimate of Feller and Peterson [58] is 516. Rozyczko and Bartlett [102] reported an EOM-CC of 558. The DFT of Calaminici et al. [92] is higher at 665.5. The DFT-LB94 of Van Gisbergen et al. [104] is relatively low, as is the CASSCF of 447.9 reported by Bishop and Norman [94]. Last, we mention a CC-R12 value of 488 by Franke et al. [95]. The same authors recommend a value of $\bar{\gamma} = 501 \pm 12$. This last value in close agreement with our CCSD(T)/PA1, the CCSD(T)/CBS estimate [58] and the CCSD(T) value of 509 [89]. We are not aware of previous values of the derivative $(\frac{d\bar{\gamma}}{dR})_e$.

The old value of $\bar{C}/e^2a_0^4E_h^{-1}$ reported by Diercksen and Sadlej [97] is 10.21, in fair agreement with our respective values. We have obtained a MP4/PA1 value of 10.95 (see Table 6). Other post-Hartree–Fock values are lower at 7.54 (Pluta et al. [90]), 7.213 (Cartier et al. [91]) and 8.939 (Hesselmann and Jansen [93]). We are not aware of pervious values of the first derivative of the quadrupole polarizability.

The UCCDM study of the higher polarizabilities by Pluta et al. [90] is almost unique as the authors have reported post-Hartree–Fock values for all quadrupole (hyper)polarizabilities. They have used a small [5s3p2d/3s2p] basis set. Their SCF values for $A_{\alpha,\beta\gamma}$ and $E_{\alpha,\beta\gamma\delta}$ are rather reasonably close to ours. The divergence is more apparent for $B_{\alpha\beta,\gamma\delta}$. Their post-Hartree–Fock values for $A_{\alpha,\beta\gamma}$ show the same trend as ours. This is not the case for the axial component of the dipole–octopole polarizability. For $B_{\alpha\beta,\gamma\delta}$ their correlated values follow the same pattern as ours. They report a UCCDM value of $\bar{B} = -57.8e^3a_0^4E_h^{-2}$. Last we mention the $A_{\alpha,\beta\gamma}$ values of Cartier et al. [91]. The authors have produced an extensive study of basis set effects is their work on hydrogen fluoride (a much earlier study by the same school was the first to attempt a rationalization of basis set effects on $A_{\alpha,\beta\gamma}$ and $C_{\alpha\beta,\gamma\delta}$ [105], see Ref. [55]). Their SD-CI values are $A_{z,zz} = 2.755$ and $A_{x,zx} = 0.281e^2a_0^3E_h^{-1}$. They predict a negative electron correlation effect on the axial component.

4.6. Comparison with experiment

In order to compare our values to the available experimental data we add to our CCSD(T)/PA1 results the ZPVC calculated at the CCSD(T)/Q1 level.

For the experimental dipole moment and the respective derivative we adopt the values resulting from Ogilvie's analysis [106], $\mu_e = 0.7093ea_0$ and the derivative $(\frac{d\mu}{dR})_e = 0.3197$. Our CCSD(T)/PA1 value for the former is $0.7043ea_0$, 0.7% below the experimental result. Our value CCSD(T)/Q1 for the derivative is 0.3101, again slightly lower than that deduced by Ogilvie [106].

Adding the estimated ZPVC of 0.50 to our $\Theta_e = 1.71$ we obtain a ground vibrational state value $\Theta_{00} = 1.76ea_2^0$. The Θ_{01} value should be only $\approx 0.0006ea_0^2$ above this value. Thus, the theoretical prediction is quite close to the experimental value $\Theta_{01} = 1.75 \pm 0.2ea_0^2$ [107].

For the mean dipole polarizability Kumar and Meath [108] deduced from dipole-oscillator strength distributions (DOSD) [108] an experimental value of $\bar{\alpha} = 5.601e^2a_0^2E_h^{-1}$. Russell and Spackman [109] reference a static value of 5.398 obtained from an extrapolation to infinite wavelength of liquid-phase refractivity data [110]. Our equilibrium value (in agreement with best available theoretical efforts) augmented with the ZPVC of 0.10 would result in ground-state estimate of $5.70e^2a_0^2E_h^{-1}$, above the semiempirical and liquid-phase results. The experimental value of $\Delta\alpha$ is $1.485 \pm 0.135e^2a_0^2E_h^{-1}$ [111]. Corrected for pure vibrational effects by Bishop et al. [112] this value reduces to $1.31 \pm 0.13e^2a_0^2E_h^{-1}$. Our estimate is

$1.14 + 0.17 = 1.31 e^2 a_0^2 E_h^{-1}$, in excellent agreement with the above value.

The discrepancy between theory and experiment for the hyperpolarizability of hydrogen fluoride has been closely analyzed [47,102,113]. The available experimental data are dynamic ESHG values pertaining at 694.3 nm, $\bar{\beta} = -11.0 \pm 1.0 e^3 a_0^3 E_h^{-2}$ and $\bar{\gamma} = 842 \pm 142 e^4 a_0^4 E_h^{-3}$. Our values confirm previous estimates of the static limit of both properties. Hence, the present results corroborate the discrepancy.

5. Conclusions

In this study we have reported a comprehensive study of the electric properties of hydrogen fluoride. We have designed large, carefully optimized Reference near-Hartree–Fock values are obtained for all properties. Very large basis sets have been used for the accurate determination of the electron correlation effects. Much of the material presented in this paper is new, or represents an essential refinement of previous work.

We have determined the R-dependence of the dipole polarizability around the experimental bond length R_e as

$$[\bar{\alpha}(R) - \bar{\alpha}(R_e)]/e^2 a_0^2 E_h^{-1}$$
$$= 2.92(R - R_e) + 1.10(R - R_e)^2 + 0.24(R - R_e)^3$$
$$- 0.01(R - R_e)^4$$

$$[\Delta\alpha(R) - \Delta\alpha(R_e)]/e^2 a_0^2 E_h^{-1}$$
$$= 4.30(R - R_e) + 2.97(R - R_e)^2 + 0.78(R - R_e)^3$$
$$+ 0.07(R - R_e)^4$$

For the dipole hyperpolarizabilities and their derivatives we recommend $\bar{\beta} = -7.4 \pm 0.1 e^3 a_0^3 E_h^{-2}$ and $\left(\dfrac{d\bar{\beta}}{dR}\right)_e = -12.4 \pm 0.6 e^3 a_0^2 E_h^{-2}$, $\bar{\gamma} = 512 \pm 10 e^4 a_0^4 E_h^{-3}$ and $\left(\dfrac{d\bar{\gamma}}{dR}\right)_e = 437 \pm 22 e^4 a_0^3 E_h^{-3}$.

We have also obtained for the first time the R-dependence of the quadrupole (hyper)polarizabilities $A_{\alpha,\beta\gamma}$, $E_{\alpha,\beta\gamma\delta}$ and $B_{\alpha\beta,\gamma\delta}$. For the dipole–quadrupole and the dipole–octopole polarizability we report MP2 curves

$$[A_{z,zz}(R) - A_{z,zz}(R_e)]/e^2 a_0^3 E_h^{-1}$$
$$= 10.83(R - R_e) + 8.69(R - R_e)^2 + 2.99(R - R_e)^3$$
$$+ 0.19(R - R_e)^4$$

$$[A_{x,zx}(R) - A_{z,zz}(R_e)]/e^2 a_0^3 E_h^{-1}$$
$$= 2.27(R - R_e) + 1.30(R - R_e)^2 + 0.27(R - R_e)^3$$
$$+ 0.07(R - R_e)^4$$

and

$$[E_{z,zzz}(R) - E_{z,zzz}(R_e)]/e^2 a_0^4 E_h^{-1}$$
$$= 26.42(R - R_e) + 29.01(R - R_e)^2$$
$$+ 15.25(R - R_e)^3 + 3.39(R - R_e)^4$$

$$[E_{z,zzz}(R) - E_{z,zzz}(R_e)]/e^2 a_0^4 E_h^{-1}$$
$$= -5.46(R - R_e) - 4.57(R - R_e)^2 - 1.63(R - R_e)^3$$
$$- 0.37(R - R_e)^4$$

New experimental investigations on the mean dipole (hyper)polarizability are highly desirable. An accurate gas-phase determination of the static value of $\bar{\alpha}$ is in order. The measurement of the dispersion of the hyperpolarizability would allow for a more unambiguous rapprochement of experiment with theory on this important matter.

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