Theoret. Chim. Acta (Berl.) 63, 69–82 (1983)

THEORETICA CHIMICA ACTA

Finite-Field Many-Body Perturbation Theory

IV. Basis Set Optimization in MBPT Calculations of Molecular Properties. Molecular Quadrupole Moments

Geerd H. F. Diercksen

Max-Planck-Institut für Physik und Astrophysik, Institut für Astrophysik,
Karl-Schwarzschild-Str. 1. D-8046 Garching bei München, Federal Republic of Germany

Andrzej J. Sadlej

Physical Chemistry 2, Chemical Center, University of Lund, P.O.B. 740, S-220 07 Lund 7, Sweden

The choice of truncated basis sets and their optimization for MBPT calculations of molecular properties are discussed. It is pointed out that computing the correlation corrections to some *k*th order property by using the MBPT approach requires the knowledge of accurate perturbed orbitals through the *k*th order. Hence, it is argued that the basis set functions can be optimized with respect to the perturbed energies calculated within the coupled Hartree–Fock method. The proposed procedure is illustrated by MBPT calculations of quadrupole moments of H_2 and FH. Additionally, also some estimates of the quadrupole polarizability tensor components for these molecules are obtained.

Key words: Finite-field many-body perturbation theory – Basis sets – Quadrupole moments – Quadrupole polarizabilities – H_2 – FH.

1. Introduction

In most cases fairly accurate results for atomic and molecular properties [1] can be obtained within the SCF HF approximation. However, in order to exploit the predictive power of quantum mechanical calculations a careful consideration of the electron correlation effects is unavoidable. Recent studies of the electron correlation contribution to properties of many-electron systems have shown that the genuine correlation effects [2] can be accounted for by using relatively simple methods [2–7]. Among them the many-body perturbation theory (MBPT) approach [8], based on what is known as the coupled Hartree–Fock (CHF) [9, 10] solutions for the perturbed one-electron problem [2], has been found particularly convenient [2, 3]. Considerable attention has been given to the CHF-based MBPT scheme restricted to the intermediate states which result from single (S) and double (D) substitutions (SD-MBPT) in the reference function [11, 12]. Recent calculations [12–14] seem to indicate that the CHF-based SD-MBPT approach is capable of yielding the major part of the correlation contribution to different properties of many-electron systems.

Most calculations of the electron correlation contribution to atomic and molecular properties are carried out within the algebraic approximation, i.e. by using some truncated set of one-electron functions. The choice of the basis set is of principal importance and to a large extent determines the accuracy of the final results. The calculation of correlation corrections to the SCF HF (CHF) values of atomic and molecular properties imposes certain specific requirements with regard to the basis set composition.

In the present paper the basis set composition is analysed in terms of the structure of the MBPT correlation corrections to properties and a method for the basis set optimization is proposed. This method is utilized for the optimization of basis sets in accurate MBPT calculations of molecular quadrupole moments. The calculations are carried out by using the finite-field perturbation theory (FPT) approach.

2. Correlation Corrections to Properties of Many-Electron Systems. Requirements Concerning the Basis Set Composition

The present paper forms a part of the project aimed at a systematic determination of basis sets suitable for highly accurate calculations of molecular quadrupole moments. The analysis of the basis set problem in calculations of correlation corrections to properties is most conveniently carried out by invoking the relevant expressions of the CHF-based MBPT formalism [2, 3, 12]. The nth order correlation correction Q_n to some kth order property Q can be defined as a quantity proportional to the kth order derivative of the μ-dependent nth order correlation energy $E_n(\mu)$:

$$Q_n \sim E_n^{(k)} = \frac{1}{k!}\left(\frac{\partial^k E_n(\mu)}{\partial \mu^k}\right)_{\mu=0}, \tag{1}$$

where μ is the strength of the external perturbation pertinent for the given property Q [1], and $E_n^{(k)}$ is the perturbed energy of the (k, n)th order. By virtue of using the μ-dependent SCF HF orbitals in what is called the CHF-based MBPT approach [2, 3], the correlation perturbation series for the total correlation correction Q_{corr} to the property Q begins with the second-order term, i.e.

$$Q_{\text{corr}} = Q_2 + Q_3 + Q_4 + \cdots. \tag{2}$$

The differentiation of the μ-dependent correlation energy formulae [2, 3] shows that the correlation corrections to the kth order property will involve the perturbed CHF orbitals through the kth order with respect to the external perturbation strength. Hence, for the accurate calculation of $E_n^{(k)}$ one needs to know the accurate perturbed CHF functions for both the occupied and virtual orbitals which enter the correlation energy expressions [15].

In general there are no variational bounds available for separate contributions Q_n to the total correlation correction Q_{corr}. Hence, the optimization of basis set functions can hardly be accomplished with respect to Q_n and it appears that the best one can do is to use the most accurate perturbed CHF orbitals [9, 10]. It is proposed therefore that the optimization of basis set functions should be carried out with respect to the perturbed CHF energies. Obviously, this procedure will mainly affect the basis set functions which contribute mostly to the occupied SCF HF orbitals and the CHF perturbation corrections to virtual orbitals will come out as a by-product of the CHF procedure [9]. This limitation of the procedure suggested in this paper can be removed to some extent when using the multi-configuration (MC) reference functions in the MBPT approach [16] with the perturbed single-particle states determined according to the MC-CHF perturbation scheme [17]. However, there are some indications [18, 19] that the contribution of the perturbed SCF HF virtual orbitals to the correlation corrections Q_n is of secondary importance compared to that which follows from the perturbed occupied SCF HF states.

In spite of its incapability to yield optimized virtual orbitals the CHF approach gives at least some idea about the general requirements concerning the basis set composition. Consider for example a many-electron system whose reasonable description of the SCF HF level of accuracy can be achieved by using a basis set involving atomic functions with the highest value of the angular momentum quantum number equal to l. Let the external perturbation be expressible in terms of the L-pole moment one-electron operators [1]. Then the minimum requirement concerning the basis set composition for the calculation of Q_n leads to the conclusion that the initial basis set has to be augmented by atomic functions with the angular momentum quantum numbers through $l + k \times L$. Hence, if the (s, p) basis set is sufficient at the SCF HF level of accuracy for the unperturbed system, the calculation of correlation corrections to the quadrupole moment requires the use of a (s, p, d, f) basis set.

For obvious reasons the basis set size has to be kept as small as possible and this can be achieved either by making the given basis set explicitly dependent on the perturbation strength [20, 21] or by optimizing a few higher angular momentum functions. In the case of correlation corrections to quadrupole moments the use of appropriate field-gradient-dependent basis sets [21] requires the calculation of non-standard eliptic integrals. For this reason standard perturbation-independent basis sets appear to be preferable. Their optimization is to be carried out via the optimization of orbital exponents with respect to the perturbed CHF energies. Moreover, the optimization should be principally performed for those atomic functions which are expected to give a dominant contribution to the perturbed CHF orbitals of a given order.

3. Basis Set Optimization for Molecular Quadrupole Moments

The quadrupole moment tensor $\theta_{\mu\nu}$ can be regarded as the first-order electric property which arises from the field-gradient perturbation [1]. Since the truncated MBPT expansion violates the Hellmann–Feynman theorem [22] the corresponding calculation of correlation corrections to the SCF HF values of $\theta_{\mu\nu}$ requires both the unperturbed SCF HF and the first-order perturbed CHF orbitals. The latter follow from the consideration of the one-electron perturbation operator [1]:

$$\hat{\theta}_{\mu\nu} = \tfrac{1}{2}(3x_\mu x_\nu - \delta_{\mu\nu} r^2) \tag{3}$$

and the minimization of the corresponding second-order perturbed CHF energy $E^{(2),\mathrm{CHF}}_{\mu\nu,\mu\nu}$ [9, 10]. The second-order perturbed energy $E^{(2)}_{\mu\nu,\mu\nu}$ is proportional to the diagonal $(\mu\nu, \mu\nu)$ component of the quadrupole polarizability tensor $C_{\mu\nu,\mu\nu}$ [1, 23]. The corresponding definitions follow those of Buckingham [1]. A useful summary of different definitions of the quadrupole moment and quadrupole polarizability tensors has recently been given by Rivail and Cartier [23].

The calculations reported in this paper have been carried out for H_2 and FH. First, the hydrogen atom GTO/CGTO basis set has been partly optimized with respect to the quadrupole polarizability of the hydrogen molecule. The initial $(7s2p)$ GTO basis set derived from the $(6s)$ GTO set of Huzinaga [24] and augmented with two p-type GTO's with orbital exponents selected according to Werner and Meyer [4] has been contracted to the $[4s2p]$ CGTO set and further augmented with a single d-type GTO. Since the SCF HF orbital of H_2 is mainly composed of s-type atomic functions, its first-order perturbation due to the operator (3) will mostly involve d-type components. Hence, only the d-type GTO exponent has been optimized with respect to quadrupole polarizability tensor components. The optimization has been carried out independently for $C_{xx,xx}$ and $C_{zz,zz}$, where the z-axis is assumed to be taken along the H—H bond. This results in two different values of the d-type GTO exponent, $\eta_{xx}(d_\mathrm{H}) = \eta_{yy}(d_\mathrm{H})$ and $\eta_{zz}(d_\mathrm{H})$. The final MBPT calculations have been performed with the $[4s2p1d]$ CGTO basis set with the d-type GTO exponent taken as a simple average:

$$\eta(d_\mathrm{H}) = \tfrac{1}{3}(\eta_{xx}(d_\mathrm{H}) + \eta_{yy}(d_\mathrm{H}) + \eta_{zz}(d_\mathrm{H})), \tag{4}$$

and the corresponding basis set is listed in Table 1. The dependence of the quadrupole polarizability tensor components on the d-type GTO exponent is shown in Fig. 1.

A similar procedure has been used in order to optimize the fluorine atom basis set for the calculation of correlation corrections to the quadrupole moment of FH. The hydrogen atom basis set has been taken the same as that determined for the hydrogen molecule. The initial $(12s8p3d)$ GTO set for F is chosen according to the rules devised by Reinsch and Meyer [25] which are applied to the $(11s7p)$ GTO basis set of Huzinaga [24]. This set has been contracted to

Table 1. GTO/CGTO basis sets of H and F for MBPT calculations of quadrupole moments of H_2 and FH

	CGTO No.	$H[7s2p1d/4s2p1d]$ $c_i(\eta_i)$ [a]		CGTO No.	$F[12s8p3d1f/8s5p3d1f]$ $c_i(\eta_i)$ [a]
s:	1	0.023653526(68.16)	s:	1	0.0049432634(37736.0)
		+0.17976680(10.2465)			+0.036991691(5867.08)
		+0.86080283(2.34648)			+0.19663837(1332.47)
					+0.82769142(369.441)
	2	0.39241463(0.67332)		2	0.29720969(116.843)
		+0.65630447(0.22466)			+0.74248828(40.3488)
	3	1.0(0.082217)		3	1.0(14.9663)
	4	1.0(0.030338)		4	1.0(5.87593)
				5	1.0(1.65334)
				6	1.0(0.610836)
				7	1.0(0.233289)
				8	1.0(0.0933157)
p:	1	1.0(0.7)	p:	1	0.030024639(102.2620)
					+0.21454060(23.9384)
					+0.83446861(7.52059)
	2	1.0(0.2)		2	0.44901329(2.77246)
					+0.61160453(1.10005)
				3	1.0(0.446775)
				4	1.0(0.171870)
				5	1.0(0.0687480)
d:	1	1.0(0.075) [b]	d:	1	1.0(1.64995)
				2	1.0(0.412488)
				3	1.0(0.137496)
			f:	1	1.0(0.275) [c]

[a] Contraction coefficients (c_i) and GTO exponents (η_i)

[b] Average optimized value of the d-type GTO exponent obtained from CHF calculations of the xx, xx and zz, zz components of the quadrupole polarizability tensor for H_2. See text

[c] Average optimized value of the f-type GTO exponent obtained from CHF calculations of the xx, xx and zz, zz components of the quadrupole polarizability tensor for FH. See text

the $[8s5p3d]$ CGTO basis set and then augmented with the f-type GTO whose orbital exponent has been optimized with respect to $C_{xx,xx}$ and $C_{zz,zz}$. The two different values of $\eta(f_F)$, i.e. $\eta_{xx}(f_F) = \eta_{yy}(f_F)$ and $\eta_{zz}(f_F)$, have been averaged according to:

$$\eta(f_F) = \tfrac{1}{3}(\eta_{xx}(f_F) + \eta_{yy}(f_F) + \eta_{zz}(f_F)), \tag{5}$$

and the final $[8s5p3d1f]$ CGTO basis set for the fluorine atom which is used in our MBPT calculations has been given in Table 1. The f-type GTO exponent dependence of $C_{xx,xx}$ and $C_{zz,zz}$ for FH is shown in Fig. 2.

All CHF calculations reported in this paper have been carried out by using the FPT scheme for the field-gradient perturbation. The optimized values of orbital exponents have been obtained from the appropriate parabolic fits for the components of the quadrupole polarizability tensor. The value of the field-gradient

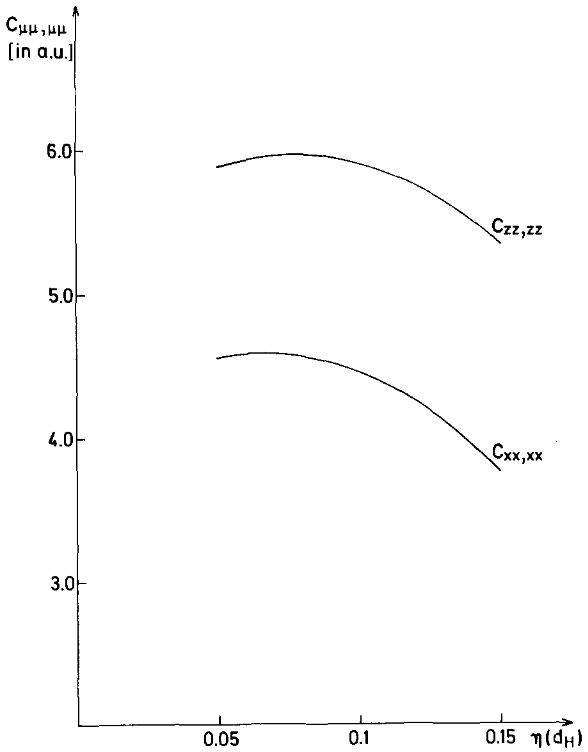

Fig. 1. SCF HF (CHF) calculations of the quadrupole polarizability tensor $C_{\mu\mu,\mu\mu}$ for the hydrogen molecule. Dependence of $C_{xx,xx}$ and $C_{zz,zz}$ on the orbital exponent $\eta(d_H)$ of the d-type GTO for H

strength ($V_{\mu\nu}$) employed in the FPT SCF HF optimization of orbital exponents has been taken as equal to 0.005 a.u. for both H_2 and FH. Since the SCF HF method satisfies the Hellmann–Feynman theorem, the accuracy of our calculations could have been checked by comparing: (1) the average values of the quadrupole moment operator with the appropriate first-order derivatives of the field-gradient-dependent SCF energies, $E_{SCF}(V_{\mu\nu})$, and (2) the first-order derivatives of the induced quadrupole moments $\theta_{\mu\nu}(V_{\mu\nu})$ with the corresponding second-order derivatives of $E_{SCF}(V_{\mu\nu})$. In both cases the differences amount to less than 0.2 per cent of the total value of a given quantity.

According to the discussion presented in Section 2 the main attention has been paid to the optimization of those atomic functions which, by simple perturbation theory arguments, are expected to make the dominant contribution to the first-order perturbed CHF orbitals. No optimization of the d-type GTO's has been attempted for the fluorine atom. Above all the corresponding orbital exponents have already been selected [25] for the calculation of quadrupole polarizabilities. Moreover, they describe the first-order field-gradient perturbation of the s-type functions. The latter are not expected to be highly important for the calculation of correlation corrections to the quadrupole moment of FH

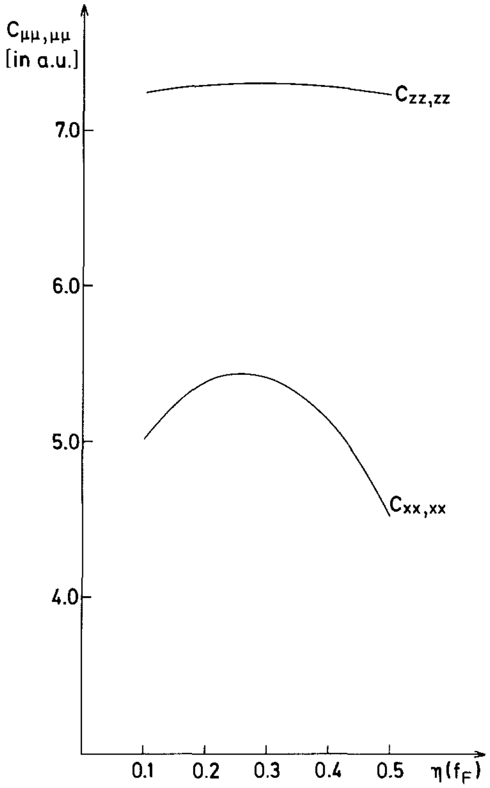

Fig. 2. SCF HF (CHF) calculations of the quadrupole polarizability tensor $C_{\mu\mu,\mu\mu}$ for the hydrogen fluoride molecule. Dependence of $C_{xx,xx}$ and $C_{zz,zz}$ on the orbital exponent $\eta(f_F)$ of the f-type GTO on F

[13, 14]. Hence, for the present purpose optimizing the f-type GTO for F and the d-type GTO for H appears to be sufficient.

4. Fourth-Order FPT SD-MBPT Calculations of the Quadrupole Moment of H_2 and FH

All calculations reported in this section have been performed with the GTO/CGTO basis sets for H and F given in Table 1. For both H_2 and FH the experimental values of the equilibrium bond length ($R_{HH} = 1.4$ a.u., $R_{FH} = 1.73288$ a.u.) have been assumed. Since the correlation corrections to the SCF HF values of the quadrupole moment of both molecules are relatively small, the value of the field-gradient strength has been a little decreased compared to that used for the optimization of orbital exponents. The calculations for H_2 have been performed with $V = V_{\mu\nu} = 0.002$ a.u., while for FH we used $V = V_{\mu\nu} = 0.003$ a.u.

The SD-MBPT expansion for correlation corrections to atomic and molecular properties has been described and analysed in our previous papers [12–14]. It consists of all terms which arise due to singly and doubly substituted intermediate states in the correlation energy series and can be written as:

$$Q_{\mathrm{corr}}^{\mathrm{SD\text{-}MBPT}} = Q_2^D + Q_3^D + Q_{4d}^{SD} + Q_{4r,cj}^D + \cdots, \tag{6}$$

where we use the same notation as in Ref. [13]. It has been found [12–14] that the correlation perturbation series (6) truncated at the fourth-order gives a good approximation for the total correlation correction to properties of many-electron systems. Usually only the first three terms of the expansion (6) are retained leading to the following estimate of the property value:

$$Q \simeq Q^{\mathrm{SD\text{-}MBPT}}(4) = Q_{\mathrm{SCF}} + Q_{\mathrm{corr}}^{\mathrm{SD\text{-}MBPT}}(4), \tag{7}$$

where

$$Q_{\mathrm{corr}}^{\mathrm{SD\text{-}MBPT}}(4) = Q_2^D + Q_3^D + Q_{4d}^{SD}. \tag{8}$$

Neglecting the contribution due to the conjoint renormalization term $Q_{4r,cj}^D$ follows from the observation that the direct fourth-order contribution due to quadruply excited intermediate states is nearly cancelled out by the fourth-order renormalization term. However, no such cancellation will occur for systems containing less than four electrons. Hence, for the hydrogen molecule it is more appropriate to use the complete fourth-order Rayleigh–Schrödinger perturbation theory (SD-RSPT) formula:

$$Q^{\mathrm{SD\text{-}RSPT}}(4) = Q_{\mathrm{SCF}} + Q_{\mathrm{corr}}^{\mathrm{SD\text{-}RSPT}}(4), \tag{9}$$

where

$$Q_{\mathrm{corr}}^{\mathrm{SD\text{-}RSPT}}(4) = Q_{\mathrm{corr}}^{\mathrm{SD\text{-}MBPT}}(4) + Q_{4r}^D \tag{10}$$

and Q_{4r}^D represents the total of the fourth-order renormalization term [12–15] which can be partitioned into conjoint and disjoint contributions [15, 26]. For systems with less than four electrons only conjoint diagrams will contribute to Q_{4r}^D, i.e. for these systems $Q_{4r}^D = Q_{4r,cj}^D$ [15, 26, 27].

It is also appropriate to mention that Eq. (10) is the fourth-order PT approximation for the correlation correction to Q_{SCF} in the configuration interaction scheme limited to singly and doubly substituted configurations (SD-CI), i.e.

$$Q_{\mathrm{corr}}^{\mathrm{SD\text{-}RSPT}}(4) = Q_{\mathrm{corr}}^{\mathrm{SD\text{-}CI}}(4). \tag{11}$$

Different terms which contribute to either SD-MBPT or SD-RSPT expansion for the correlation energy can be easily obtained from subsequent iterations in what is known as the direct CI scheme [28]. This method has also been employed in our calculation of the field-gradient-dependent correlation energy contributions.

In order to complete the information about the quality of our calculations let us mention that the SCF energies obtained for the GTO/CGTO basis sets of Table 1 are equal to −1.132256 a.u. for H_2 and −100.065591 a.u. for FH. For the hydrogen molecule the fourth-order SD-RSPT correlation energy is −0.035817 a.u. and the corresponding SD-CI result amounts to −0.036715 a.u.

Table 2. SCF and correlation contributions to the quadrupole moment of H_2 and FH. All values in a.u.

Contribution [a]	H_2 [b]	FH [c]
Q_{SCF}	0.4865	1.7422
Q_2^D	−0.0282	−0.0015
Q_3^D	−0.0094	−0.0207
Q_{4d}^D	−0.0050	−0.0030
Q_{4r}^D	+0.0008	+0.0038
$Q_{corr}^{SD\text{-}MBPT}(4)$	−0.0427	−0.0252
$Q_{corr}^{SD\text{-}RSPT}(4)$	−0.0418	−0.0214
$Q_{corr}^{SD\text{-}CI}$	−0.0451	−0.0200

[a] The symbol Q has the meaning of the molecular quadrupole moment θ which is equal to the zz-component of the quadrupole moment tensor with the x-axis taken along the bond. The nuclear contribution is included in Q_{SCF}

[b] Calculated with the origin of the coordinate system at the nuclear center of mass. $R_{HH} = 1.4$ a.u.

[c] Calculated with the origin of the coordinate system at the nuclear center of mass. $R_{FH} = 1.73288$ a.u.

In the case of FH the fourth-order SD-MBPT scheme results in $E_{corr}^{SD\text{-}MBPT}(4) = -0.27995$ a.u., while the SD-CI approach gives $E_{corr}^{SD\text{-}CI} = -0.26730$ a.u., indicating a rather important contribution due to disjoint renormalization diagrams. It is worth while to note that for FH the fourth-order renormalization term E_{4r}^D is equal to +0.01370 a.u., and hence, $E_{corr}^{SD\text{-}CI} \simeq E_{corr}^{SD\text{-}CI}(4)$.

Different contributions to the quadrupole moment ($\theta = \theta_{zz}$) of H_2 and FH and estimates of the total correlation correction to the corresponding SCF values are presented in Table 2. All data reported in this table have been computed by the numerical differentiation of the field-gradient-dependent energy values [22]. For the given value of the field-gradient strength $V = V_{\mu\nu}$ the first-order derivatives follow from the energy values $E(-V)$ and $E(+V)$. The accuracy of this numerical procedure for the SCF HF method has already been discussed in Sect. 3. Since in our final MBPT calculations the values of V are even smaller than those employed for the optimization of orbital exponents, the difference between the SCF values for the quadrupole moment calculated as the energy derivative and those obtained by the direct application of the Hellmann–Feynman theorem has been made less than 0.0005 a.u.

Some check on the numerical accuracy of the calculated correlation corrections to the quadrupole moment can be obtained for the hydrogen molecule. In this particular case the SD-CI method is equivalent to a full CI. Hence, the Hellmann–Feynman theorem is satisfied [22] and the correlated value of the H_2 quadrupole moment computed as the first-order derivative of the SD-CI energy should be equal to the corresponding average value of the quadrupole moment operator. Indeed, the two values differ only by 0.0004 a.u., indicating again a very high accuracy of the numerical differentiation scheme employed in this paper.

Obviously, the Hellmann–Feynman theorem is not satisfied for the SD-CI wave function for FH. In this case the quadrupole moment calculated as the average value of the quadrupole moment operator is equal to 1.7197 a.u. and according to the data of Table 2 is by 0.0025 a.u. smaller than the corresponding energy derivative. Hence, the total contribution of what is known as the selfconsistency effects [22], which are completely neglected when applying the Hellmann–Feynman theorem to limited CI functions, can be estimated as equal to about −0.0025 a.u. (relative to the SD-CI energy derivative).

Computing the SD-CI property values via the differentiation of the perturbation dependent SD-CI energy represents the most legitimate procedure within the SD-CI approximation [22]. However, one should also remember that the property values calculated in this way still suffer from what is known as the erratic treatment of unlinked clusters [38, 39]. It has been shown [39] that the unlinked clusters can make a rather important contribution to the SD-CI values of properties and that the latter need to be corrected accordingly. Amos [32] has recently suggested that there may be some cancellation between the unwanted contributions due to unlinked clusters and the self-consistency effects. If so, the SD-CI values obtained directly from the Hellmann-Feynman theorem can be fairly close to the CHF-based SD-MBPT results. This suggestion appears to be confirmed by the present data. The total of the unlinked contributions can be estimated from the disjoint part of Q_{4r}^{D}. According to our calculations for FH the corresponding contribution is equal to 0.0020 a.u. and leads to the estimate of the corrected SD-CI value of the quadrupole moment equal to 1.7202 a.u., which is relatively close to both the fourth-order SD-CI result and the SD-CI value obtained from the Hellmann–Feynman theorem.

The final results of our quadrupole moment calculations are given in Table 3. They are compared with other theoretical results and with the experimental data. The comparison with the experimental values of the quadrupole moment is to some extent limited since the corresponding rovibrational corrections have not been taken into account in our calculations. However, they can be safely estimated from the existing data of other authors [32–34]. It can be seen from the results presented in Table 3 that our correlated values of quadrupole moments of H_2 and FH are very close to the corresponding estimates obtained from the experimental data. The smallness of the correlation contribution does not allow for definite conclusions concerning the superiority of the SD-MBPT scheme compared to other methods considered in this paper. However, the CHF-based SD-MBPT values appear to have been obtained by using the most sophisticated computational procedure. Above all they do not suffer from the erratic treatment of unlinked clusters. They also take full advantage of the variation optimization of the perturbed SCF orbitals. This is definitely the best one can do within the truncated MBPT expansion which is additionally limited to singly and doubly substituted intermediate states.

The appropriateness of the fourth-order CHF-based SD-MBPT approach for the calculation of properties of many-electron systems is based on the assumption

Table 3. Molecular quadrupole moments. Comparison of different theoretical and experimental results for H_2 and FH. All values in a.u. [a]

Method	H_2	FH
This work		
SCF	0.4865	1.7422
SD-MBPT(4) [b]	0.4438	1.7170
SD-RSPT(4) [c]	0.4447	1.7206
SD-CI	0.4414	1.7222
Reference results		
SCF	0.493 [d]	1.733 [e]
	0.4815 [31]	1.732 [37]
		1.7555 [32]
MC SCF		1.6865 [33]
SD-CI		1.7254 [32]
Exact	0.457 [34]	
Experimental	0.460±0.021 [f]	1.75±0.02 [35]
	(0.440±0.021) [g]	(1.72±0.02) [h]

[a] For the geometry data and related information see footnotes to Table 2. The calculated values do not include rovibrational corrections. Conversion factor: 1 a.u. of quadrupole moment $= 1.34491 \times 10^{-26}$ e.s.u. $= 4.4865 \times 10^{40}$ cm^2

[b] The fourth-order SD-MBPT result

[c] The fourth order SD-RSPT result

[d] Calculated from the accurate SCF wave function of Kołos and Roothaan [29]

[e] Results of accurate numerical SCF calculations of McCullough [30]

[f] Taken from Ref. [36]

[g] Estimated vibrationless value according to the data of Ref. [34]

[h] Estimated vibrationless value. See Ref. [32]

that the observed cancellations between Q_{4r} and the direct fourth-order contribution involving quadruply excited intermediate states [3] has a more general character. Moreover, the SD-MBPT approach assumes also that the contribution due to triply excited intermediate states is negligible. Both these assumptions need to be carefully checked. Also the higher order terms in the correlation perturbation series can be of some importance. Calculations intended to clarify the above-mentioned uncertainties are in progress [40].

5. Estimates of the Quadrupole Polarizability Tensor Components for H_2 and FH

It is obvious that according to the criteria discussed in Sect. 2 the GTO/CGTO basis sets employed in this study are not appropriate for highly accurate calculations of the quadrupole polarizability tensor. However, the data concerning the components of the quadrupole polarizability tensor are rather scarce. Since they come out as a by-product of our quadrupole moment calculations, it appears worth while to present them as well. The corresponding data are given in Table

Table 4. Components of the quadrupole polarizability tensor for H_2 and FH. Comparison of different theoretical results. All values in a.u. [a]

Method	$C_{xx,xx}$	$C_{xz,xz}$	$C_{zz,zz}$
H_2			
This work			
SCF	4.58	4.23	5.92
SD-RSPT(4)	4.45	4.22	5.97
SD-CI	4.44	4.22	5.97
Reference results			
SCF [31]	—	—	4.7
Sum-over-states [41]	4.94	4.26	5.93
[42]	5.08	4.28	6.00
[42]	4.89	3.97	5.69
FH			
This work			
SCF	5.46	4.21	7.31
SD-MBPT(4)	6.40	4.97	8.40
SD-RSPT(4)	6.14	4.80	8.08
SD-CI	6.14	4.75	8.07
Reference results			
SCF [37]	—	—	5.4
Variation-perturbation [b]	4.4	3.3	5.7

[a] For the geometry data and related information see footnote a to Table 2. The quadrupole polarizability tensor is defined according to Buckingham [1, 23]. Units for the quadrupole polarizability: 1 a.u. = $0.46170 \times 10^{-61}\,C^2\,m^2\,J^{-1} = 0.041496\,Å^5$

[b] Calculations by using the Kirkwood variation-perturbation method in the SCF approximation [23, 43]

4 and compared with other calculations. In most cases our SCF HF and correlated results for $C_{\mu\nu,\mu\nu}$ [1] are larger than the corresponding results reported by other authors. However, for the above-mentioned reasons one should not make definite conclusions concerning their superiority in comparison with other calculations. Nonetheless, for the FH molecule the present SD-MBPT results are, to our best knowledge, the only available data which include the correlation effects. Moreover, let us also point out that the electron correlation contribution to $C_{\mu\nu,\mu\nu}$ appears to be by no means negligible. For all components of the quadrupole polarizability tensor of FH this contribution amounts to more than ten per cent of the corresponding SCF values. Hence, the inclusion of the electron correlation effects in accurate calculations of quadrupole polarizabilities is at least as necessary as in the case of the dipole polarizability tensor [2–7, 12–14].

References

1. Buckingham, A. D.: Adv. Chem. Phys. **12**, 107 (1967); Swanstrøm, P., Hegelund, F.: In: Computational techniques in quantum chemistry and molecular physics, p. 299, G. H. F. Diercksen, B. T. Sutcliffe, A. Veillard, eds. Dordrecht: Reidel Publ. Co. 1975

2. Adamowicz, L., Sadlej, A. J.: Chem. Phys. Letters **53**, 377 (1978); Sadlej, A. J.: J. Chem. Phys. **75**, 320 (1981); Sadlej, A. J.: Acta Phys. Polon. A. **59**, 669 (1981); Sadlej, A. J.: Int. J. Quantum Chem., in press
3. Bartlett, R. J., Purvis III, G. D.: Phys. Rev. A. **20**, 1313 (1979); Purvis III, G. D., Bartlett, R. J.: Phys. Rev. A. **23**, 1594 (1981); Bartlett, R. J.: Ann. Rev. Phys. Chem. **32**, 359 (1981)
4. Werner, H.-J., Meyer, W.: Mol. Phys. **31**, 855 (1976); Werner, H.-J., Meyer, W.: Phys. Rev. A. **13**, 13 (1976)
5. Zeiss, G. D., Scott, W. R., Suzuki, N., Chong, D. P., Langhoff, S. R.: Mol. Phys. **37**, 1543 (1979); Amos, R. D.: Mol. Phys. **38**, 33 (1979); Morrison, M. A., Hay, P. J.: J. Chem. Phys. **70**, 4034 (1979); Martin, R. L., Davidson, E. R., Eggers, D. F., Jr.: Chem. Phys. **38**, 341 (1979); Daborn, G. T., Ferguson, W. I., Handy, N. C.: Chem. Phys. **50**, 255 (1980)
6. Karlström, G., Roos, B. O., Sadlej, A. J.: Chem. Phys. Letters **86**, 374 (1982); Roos, B. O., Sadlej, A. J.: J. Chem. Phys. **76**, 5444 (1982)
7. Nelin, C., Roos, B. O., Sadlej, A. J., Siegbahn, P. O.: J. Chem. Phys. **77**, 3607 (1982)
8. March, N. H., Young, W. H., Sampanthar, S.: The many-body problem in quantum mechanics. Cambridge: Cambridge University Press 1967; Kelly, H. P.: Adv. Chem. Phys. **14**, 129 (1969); Wilson, S.: Specialist Periodical Report: Theoretical Chem. **4**, 1 (1981)
9. Stevens, R. M., Pitzer, R. M., Lipscomb, W. N.: J. Chem. Phys. **38**, 550 (1963); Langhoff, P. W., Karplus, M., Hurst, R. P.: J. Chem. Phys. **44**, 505 (1966); Diercksen, G., McWeeny, R.: J. Chem. Phys. **44**, 3554 (1966); Dodds, J. L., McWeeny, R., Sadlej, A. J.: Mol. Phys. **34**, 1779 (1977)
10. Caves, T. C., Karplus, R.: J. Chem. Phys. **50**, 3649 (1969); Rossky, P. J., Karplus, M.: J. Chem. Phys. **72**, 6085 (1980)
11. Bartlett, R. J., Shavitt, I.: Chem. Phys. Letters **50**, 190 (1977); Bartlett, R. J., Shavitt, I.: Int. J. Quantum. Chem. **11**, 165 (1977); Purvis, G. D., Bartlett, R. J.: J. Chem. Phys. **68**, 2114 (1978)
12. Diercksen, G. H. F., Sadlej, A. J.: Chem. Phys. **61**, 229 (1981)
13. Diercksen, G. H. F., Sadlej, A. J.: Chem. Phys. Letters **84**, 390 (1982); Diercksen, G. H. F., Sadlej, A. J.: Chem. Phys. **65**, 407 (1982); Diercksen, G. H. F., Sadlej, A. J.: Chem. Phys. Letters **89**, 423 (1982); Diercksen, G. H. F., Sadlej, A. J.: Theoret. Chim. Acta (Berl.) **61**, 485 (1982)
14. Diercksen, G. H. F., Sadlej, A. J.: Phys. Rev. A., in press
15. Paldus, J., Čižek, J.: Adv. Quantum Chem. **9**, 105 (1975); Bartlett, R. J., Purvis, G. D.: Int. J. Quantum Chem. **14**, 561 (1978); Wilson, S., Silver, D. M.: Int. J. Quantum Chem. **15**, 683 (1979)
16. Brandow, B. H.: Rev. Mod. Phys. **39**, 771 (1967); Brandow, B. H.: Adv. Quantum Chem. **10**, 187 (1977); Lindgren, I.: J. Phys. B.: At. Mol. Phys. **7**, 2441 (1974); Lindgren, I.: Int. J. Quantum Chem. Symp. **12**, 33 (1978)
17. Jaszuński, M., Sadlej, A. J.: Theoret. Chim. Acta (Berl.) **40**, 157 (1975); Jaszuński, M., Sadlej, A. J.: Int. J. Quantum Chem. **11**, 233 (1977)
18. Roos, B. O., Taylor, P. R., Siegbahn, P. E. M.: Chem. Phys. **48**, 157 (1980); Roos, B. O.: Int. J. Quantum Chem. Symp. **14**, 175 (1980)
19. Diercksen, G. H. F., Sadlej, A. J.: Mol. Phys. **47**, 33 (1982)
20. Sadlej, A. J.: Chem. Phys. Lett. **47**, 50 (1977); Sadlej, A. J.: Mol. Phys. **34**, 731 (1977); Sadlej, A. J.: Acta Phys. Polon. A **53**, 297 (1978); Epstein, S. T., Sadlej, A. J.: Int. J. Quantum Chem. **15**, 147 (1979)
21. Woliński, K., Sadlej, A. J.: Chem. Phys. Letters **64**, 51 (1979); Woliński, K., Sadlej, A. J.: Acta Phys. Polon. A **56**, 681 (1979); Woliński, K., Sadlej, A. J.: Mol. Phys. **41**, 1419 (1980)
22. Nerbrant, P.-O., Roos, B. O., Sadlej, A. J.: Int. J. Quantum. Chem. **15**, 135 (1979); Diercksen, G. H. F., Roos, B. O., Sadlej, A. J.: Chem. Phys. **59**, 29 (1981)
23. Rivail, J. L., Cartier, A.: Mol. Phys. **36**, 1085 (1978)
24. Huzinaga, S.: Approximate atomic functions. Technical Report: Division of Theoretical Chemistry, Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada 1971
25. Reinsch, E.-A., Meyer, W.: Phys. Rev. A. **18**, 1793 (1978)
26. Čársky, P., Urban, M.: Ab initio calculations, Lecture Notes in Chemistry, Vol. 16. Berlin-Heidelberg-New York: Springer 1980

27. Diercksen, G. H. F., Jaszuński, M., Sadlej, A. J.: Chem. Phys. **71**, 105 (1982)
28. Roos, B.: Chem. Phys. Letters **15**, 153 (1972); Roos, B. O., Siegbahn, P. E. M.: In: Modern theoretical chemistry, Vol. 3, Methods of electronic structure theory, p. 277, H. F. Schaefer, ed. New York: Plenum Press 1977
29. Kołos, W., Roothaan, C. C. J.: Rev. Mod. Phys. **32**, 219 (1960)
30. Christiansen, P. A., McCullough, E. A., Jr.: Chem. Phys. Letters **55**, 439 (1978); McCullough, E. A., Jr.: Mol. Phys. **42**, 943 (1981)
31. McLean, A. D., Yoshimine, M.: J. Chem. Phys. **46**, 3682 (1967)
32. Amos, R. D.: Chem. Phys. Letters **87**, 23 (1982)
33. Amos, R. D.: Mol. Phys. **35**, 1765 (1978)
34. Kołos, W., Wolniewicz, L.: J. Chem. Phys. **43**, 2429 (1965)
35. Leeuw de, F. H., Dymanus, A.: J. Mol. Spectr. **48**, 427 (1973); Muenter, J. S.: J. Chem. Phys. **56**, 5409 (1972)
36. McLean, A. D., Yoshimine, M.: J. Chem. Phys. **45**, 3676 (1966)
37. McLean, A. D., Yoshimine, M.: J. Chem. Phys. **47**, 3256 (1967)
38. Davidson, E. R.: In: The world of quantum chemistry, R. Daudel, B. Pullman, eds. Dordrecht: Reidel Publ. Co. 1974; Langhoff, S. R., Davidson, E. R.: Int. J. Quantum Chem. **8**, 6 (1974); Siegbahn, P. E. M.: Chem. Phys. Letters **55**, 386 (1978)
39. Diercksen, G. H. F., Kraemer, W. P., Sadlej, A. J.: Chem. Phys. Letters **82**, 117 (1981)
40. Diercksen, G. H. F., Kellö, V., Sadlej, A. J.: to be published
41. Meyer, W.: Chem. Phys. **17**, 27 (1976)
42. Mulder, F., Avoird van der, A., Wormer, P. E. S.: Mol. Phys. **37**, 159 (1979)
43. Sadlej,. A. J.: Mol. Phys. **40**, 509 (1980)

Received November 25, 1982