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ARTICLE *in* CHEMICAL PHYSICS LETTERS · JULY 2011

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# Validation and application of auxiliary density perturbation theory and non-iterative approximation to coupled-perturbed Kohn–Sham approach for calculation of dipole–quadrupole polarizability

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## ARTICLE INFO

### Article history:

Available online 20 May 2011

## ABSTRACT

Recently, two non-iterative approaches have been proposed to calculate response properties within density functional theory (DFT). These approaches are auxiliary density perturbation theory (ADPT) and the non-iterative approach to the coupled-perturbed Kohn–Sham (NIA-CPKS) method. Though both methods are non-iterative, they use different techniques to obtain the perturbed Kohn–Sham matrix. In this Letter, for the first time, both of these two independent methods have been used for the calculation of dipole–quadrupole polarizabilities. To validate these methods, three tetrahedral molecules viz.,  $P_4$ ,  $CH_4$  and adamantane ( $C_{10}H_{16}$ ) have been used as examples. The comparison with MP2 and CCSD proves the reliability of the methodology.

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## 1. Introduction

Electric properties such as multipole moments, polarizabilities and hyperpolarizability are studied widely [1,2], due to their applicability in predicting long range atomic and molecular interactions [3]. These fundamental properties play an important role in designing new non-linear optical materials [4]. The higher order polarizabilities such as, dipole–quadrupole polarizabilities ( $A$ ) and dipole–octupole polarizabilities ( $E$ ) have also gained attention in recent years [5,6]. These polarizabilities are important for the description of surface-enhanced Raman scattering and interaction induced light scattering spectra.  $A$ ,  $E$  and the derivatives of dipole–quadrupole polarizability with respect to Cartesian coordinates and vibrational normal coordinates ( $\partial A/\partial Q$ ) are determined experimentally using collision induced light scattering and high resolution infrared absorption spectroscopies [7]. Maroulis and Hohm have collaboratively studied dipole–quadrupole polarizability of some interesting tetrahedral molecules such as  $OsO_4$  [8],  $P_4$  [9] and group IV tetrachlorides [10]. They also performed a careful comparison between theory and experiment. However, their theoretical calculations are based on the finite-field (FF) approach in the framework of many body perturbations (MP) and coupled cluster (CC) methods [11,12]. An analytic approach was first presented by Amos to evaluate static ( $A$ ) values. This scheme is based on the coupled-perturbed Hartree–Fock method [13]. Quinet et al. have recently developed a procedure based on

the time dependent Hartree–Fock scheme for evaluating both frequency dependent electric dipole–quadrupole polarizability and first order derivative of dipole–quadrupole polarizability. The quantity ( $\partial A/\partial Q$ ) [14] is directly relevant to the determination of vibrational Raman optical activity (VROA) intensities. VROA spectroscopy is receiving increasing attention due to its broad range of applications including the characterization of conformational dynamics in proteins [15].

For studying large molecular systems, density functional theory (DFT) is an obvious choice because of simplicity in applications. However, response properties using DFT have been calculated mainly at the finite-field method. Recently, the non-iterative approaches to response properties using DFT i.e. auxiliary density perturbation theory (ADPT) [16] and the non-iterative approximation to the coupled-perturbed Kohn–Sham (NIA-CPKS) [17,18] method have been developed with application to large molecules in mind. Here, for the first time, we are presenting the implementation of NIA-CPKS derived from self-consistent perturbation (SCP) theory [19–24]. The details of older implementations of NIA-CPKS can be found in our previous Letters. The ADPT and NIA-CPKS methods have already been successfully applied in dipole–polarizability ( $\alpha$ ) calculations. Both methods are different from the widely used analytical coupled-perturbed Kohn–Sham (CPKS) approach. The CPKS equation system involves the derivative of the Kohn–Sham (KS) matrix. The construction of KS matrix derivatives is not straight forward as it requires evaluation of functional derivatives of the exchange–correlation potential. To obtain the first order response of the molecular density the CPKS equation system has to be solved iteratively. In NIA-CPKS, evaluation of the

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functional derivative of the exchange–correlation potential is avoided by using a finite-field approximation for the calculation of KS matrix derivatives from which the response density matrix is calculated. ADPT is an alternative approach to the CPKS method. Different to previous non-variational ad hoc expansions of molecular integrals in perturbation theory [25] ADPT is fully variational and, therefore, yields CPKS results. In ADPT the response density matrix is obtained non-iteratively by solving an inhomogeneous equation system with the dimension of the number of auxiliary functions used to expand the approximated density. Thus, both approaches can be applied efficiently to large molecules.

This has motivated us to extend these two non-iterative approaches to dipole–quadrupole polarizability calculation. In the present Letter, we have validated the NIA-CPKS and ADPT approach for the calculation of dipole–quadrupole polarizabilities. We also present an alternative NIA-CPKS implementation in the framework of self-consistent perturbation theory. Finite field MP2, CCSD and experimental results are reported for the purpose of comparison with our new methodologies. Calculations are performed on  $P_4$ ,  $CH_4$  and adamantane ( $C_{10}H_{16}$ ) molecules with tetrahedral symmetry. The Letter is organized in the following manner. In Section 2, theoretical details of ADPT and the new implementation of NIA-CPKS are described. Computational details are given in Section 3. Elaborate discussion of the results is presented in Section 4. Finally, concluding remarks are drawn in Section 5.

## 2. Theory

In the presence of an arbitrary uniform electric field, the electron distribution of a molecule is distorted. The Hamiltonian of such system can be expressed as [26],

$$H(F) = H^0 - \mu_i F_i - \frac{1}{3} \theta_{ij} F_{ij} - \dots \quad (1)$$

$H^0$  is the unperturbed Hamiltonian,  $\mu_i$  and  $\theta_{ij}$  are the dipole and quadrupole moment operators. Einstein summation is used throughout the Letter with  $i$  and  $j$  spanning  $x$ ,  $y$  and  $z$ .  $F_i$  represents an electric field component and  $F_{ij}$  an electric field gradient, which denotes the non-homogeneous nature of the electric field. Energy and multipole moments also show explicit dependence on the electric field. According to Buckingham [27] and McLean and Yoshimine [28] the energy, dipole and quadrupole moment of a molecule in terms of the static electric field can be written as,

$$\begin{aligned} E(F) - E^0 - \mu_i^0 F_i - \frac{1}{3} \theta_{ij}^0 F_{ij} - \frac{1}{15} \Omega_{ijk}^0 F_{ijk} - \frac{1}{105} \Phi_{ijkl}^0 F_{ijkl} + \dots \\ - \frac{1}{2} \alpha_{ij} F_i F_j - \frac{1}{3} A_{ijk} F_i F_j F_k - \frac{1}{6} C_{ijkl} F_{ij} F_{kl} \\ - \frac{1}{6} \beta_{ijk} F_i F_j F_k - \frac{1}{6} B_{ijkl} F_i F_j F_k F_l + \dots \end{aligned} \quad (2)$$

$$\mu_i = \mu_i^0 + \alpha_{ij} F_j + \frac{1}{3} A_{ijk} F_j F_k + \frac{1}{2} \beta_{ijk} F_j F_k + \frac{1}{3} B_{ijkl} F_j F_k F_l + \dots \quad (3)$$

$$\theta_{ij} = \theta_{ij}^0 + A_{ijk} F_k + C_{ijkl} F_{kl} + \frac{1}{2} B_{ijkl} F_k F_l \quad (4)$$

where  $E^0$ ,  $\mu^0$ ,  $\theta^0$ ,  $\Omega^0$  are the energy and permanent multiple moments of the free molecule,  $\alpha_{ij}$  its dipole polarizability and  $\beta_{ijk}$  the corresponding (first) hyperpolarizability.  $A_{kij}$  is the dipole–quadrupole polarizability and  $B_{ijkl}$  the dipole–dipole–quadrupole hyperpolarizability. For a molecule belonging to  $T_d$  symmetry, there exists only one component of the octupole ( $\Omega_{ijk}$ ) and hexadecapole ( $\Phi_{ijkl}$ ) moment as well as of the dipole ( $\alpha_{ij}$ ) and dipole–quadrupole ( $A_{kij}$ ) polarizability. In this Letter, we investigate dipole–quadrupole polarizabilities of  $T_d$  structures for which the only non-vanishing component is  $A_{x,y,z}$ .

In general, all possible components of the dipole–quadrupole polarizability  $A_{kij}$  can be obtained as a trace of the product of the response density matrix and quadrupole integrals.

$$A_{kij} = T_r(P^{(k)} \cdot \Theta_{ij}) \quad (5)$$

where  $P^{(k)}$  is the density matrix derivative with respect to the external electric field in  $x$ ,  $y$  or  $z$  direction.  $\theta_{ij}$  represents the quadrupole moment integral matrix. In this work, density matrix derivatives are either obtained by ADPT or NIA-CPKS.

### 2.1. Perturbation theory

In auxiliary density functional theory (ADFT) [29], as implemented in deMon2k [30], the approximated density is expanded into primitive Hermite Gaussian  $k(r)$  centred on atoms [31,32] as,

$$\tilde{\rho}(r) = \sum_k x_k \tilde{k}(r) \quad (6)$$

The primitive Hermite Gaussian auxiliary functions are denoted by a bar. The auxiliary density,  $\tilde{\rho}(r)$ , is used for the variational fitting of the Coulomb potential [33,34] as well as for the calculation of the exchange–correlation energy and potential. The ADFT energy expression is given as,

$$\begin{aligned} E_{SCF} = \sum_{\mu,\nu} P_{\mu\nu} H_{\mu\nu} + \sum_{\mu,\nu} \sum_k P_{\mu\nu} \langle \mu\nu || \bar{k} \rangle x_k - \frac{1}{2} \sum_{k,l} x_k x_l \langle \bar{k} || \bar{l} \rangle \\ + E_{xc}[\tilde{\rho}] \end{aligned} \quad (7)$$

The fitting coefficients  $x_k$  are obtained by variational minimization of the difference between the Kohn–Sham and auxiliary densities in a Coulomb metric according to Dunlap. No charge conservation constraint is employed [35]. The symbol  $||$  denotes the two-electron Coulomb operator. An alternative derivation, named model density approach (MDA), of ADFT is given in [36]. For a recent review on this field, we refer the interested reader to [37].

ADPT is derived from self-consistent Hartree–Fock perturbation (SCP) theory [19–24] in the framework of ADFT [16]. The perturbed closed-shell density matrix, assuming perturbation independent basis and auxiliary functions as it is the case here, takes the form

$$P_{\mu\nu}^{(\lambda)} = \frac{\partial P_{\mu\nu}}{\partial \lambda} = 2 \sum_i^{\text{occ}} \sum_a^{\text{uno}} \frac{\mathcal{K}_{ia}^{(\lambda)}}{\epsilon_i - \epsilon_a} (C_{\mu i} C_{va} + C_{\mu a} C_{vi}) \quad (8)$$

Here  $\lambda$  represents the perturbation parameter, which in our case is a component of the external electric field. The orbital energies of the  $i$ th occupied and  $a$ th unoccupied molecular orbital are denoted by  $\epsilon_i$  and  $\epsilon_a$ , respectively. The perturbed KS matrix  $\mathcal{K}_{ia}^{(\lambda)}$  is given in the molecular orbital representations as

$$\mathcal{K}_{ia}^{(\lambda)} = \sum_{\mu,\nu} C_{\mu i} C_{\nu a} Z_{\mu,\nu}^{(\lambda)} \quad (9)$$

In ADPT  $K_{\mu,\nu}^{(\lambda)}$  is calculated analytically and it is represented as follows,

$$K_{\mu,\nu}^{(\lambda)} = H_{\mu,\nu}^{(\lambda)} + \sum_k \langle \mu\nu || \bar{k} \rangle (x_k^{(\lambda)} + K_k^{(\lambda)}) \quad (10)$$

The perturbed exchange–correlation coefficients are given by

$$Z_k^{(\lambda)} = \sum_{lm} \langle \bar{k} || \bar{l} \rangle^{-1} \langle \bar{l} | f_{xc}[\tilde{\rho}] | \bar{m} \rangle x_m^{(\lambda)} \quad (11)$$

Here  $f_{xc}[\tilde{\rho}]$  denotes the exchange–correlation kernel calculated from the approximated density. The perturbed fitting coefficients are obtained by solving the following equation system [16]

$$(G - 4A - 4AF)x^{(\lambda)} = 4b^{(\lambda)} \quad (12)$$

With

$$G_{\bar{k}l} = \langle \bar{k} || \bar{l} \rangle \quad (13)$$

$$A_{\bar{k}l} = \sum_i^{\text{occ}} \sum_a^{\text{uno}} \frac{\langle \bar{k} || ia \rangle \langle ia || \bar{l} \rangle}{\varepsilon_i - \varepsilon_a} \quad (14)$$

$$F_{\bar{k}l} = \sum_m^{\text{occ}} \langle \bar{k} || m \rangle^{-1} \langle m || f_{xc} [\bar{p}] || \bar{l} \rangle \quad (15)$$

$$b_k^{(\lambda)} = \sum_i^{\text{occ}} \sum_a^{\text{uno}} \frac{\langle \bar{k} || ia \rangle \langle i || r_\lambda a \rangle}{\varepsilon_i - \varepsilon_a} \quad (16)$$

Because the dimension of this equation system (12) is given by the number of auxiliary functions a direct, non-iterative, solution is possible. Once the perturbed fitting coefficients are obtained the perturbed Kohn–Sham matrix (10) is calculated and transformed into molecular orbital representation (9). Back-substitution in (8) then yields the perturbed density matrix.

Within the NIA-CPKS approach the perturbed Kohn–Sham matrix is calculated numerically by finite-difference at a suitably chosen electric field as,

$$K_{\mu\nu}^{(\lambda)} = \frac{K_{\mu\nu}(+\Delta F_\lambda) - K_{\mu\nu}(-\Delta F_\lambda)}{2\Delta F} \quad (17)$$

Substituting this perturbed Kohn–Sham matrix into Eq. (8) yields the perturbed density matrix. This represents our new implementation of NIA-CPKS in deMon2k. Our earlier NIA-CPKS implementation was using the CPKS equations for obtaining perturbed molecular orbital coefficients and, thereby, the perturbed density matrix. Our new implementation can be seen as a NIA-CPKS version of self-consistent perturbation theory. Because ADPT is also based on SCP this simplifies considerably the implementation effort in our perturbation branch of deMon2k. Once the perturbed density matrix is calculated, the dipole–quadrupole polarizability tensor elements are obtained from,

$$A_{\lambda,\eta\zeta} = \sum_{\mu,\nu} P_{\mu\nu}^{(\lambda)} \langle \mu || r_{\eta\zeta} || \nu \rangle \quad (18)$$

Here  $\lambda$  denotes the Cartesian component of the electric field and  $\eta\zeta$  that of the quadrupole moment integrals.

### 3. Computational details

Choice of proper basis set and geometry is crucial for electric property determination. We have used large basis sets along with adequate diffuse and polarization functions for dipole–quadrupole polarizability calculation. All calculations are performed in the (symmetry adapted) standard orientation. Geometry and basis sets for the studied molecules are as follows:

#### 3.1. $P_4$

$P_4$  molecule has a cage like structure. We have used the most recent experimental P–P bond length, 2.1958 Å [38]. Four different basis sets, P0 [6s5p2d], P1 [6s5p3d], P2 [6s5p3d1f] and P3 [6s5p4d2f] were constructed on a (14s9p)[5s4p] [39] substrate. The detailed construction of the basis set is given in Ref. [10].

#### 3.2. $CH_4$

In standard orientation geometry, C is at origin and the four C–H bonds lie along the directions defined by the origin and the points (1, 1, 1), (1, –1, –1), (–1, 1, –1) and (–1, –1, 1). The equilibrium geometrical parameters are used for calculations, C–H bond length is set to be 1.08587 Å [40]. We have used four basis sets M1 [6s4p2d1f/4s2p1d], M2 [6s4p3d1f/4s2p1d], M3 [6s4p4d1f/4s2p1d] and M4 [6s4p4d2f/4s2p1d] for dipole–quadrupole polarizability calculation. All four basis sets are constructed on (9sp/4s)/[4s2p/2s]. Details of the construction of the basis sets are given

in Ref. [11]. All basis sets have already proven to be of good quality for dipole–quadrupole polarizability calculations.

#### 3.3. Adamantane ( $C_{10}H_{16}$ )

Adamantane molecule also has a cage structure like  $P_4$ . C–C and C–H bond lengths used were 1.54024 Å and 1.1124 Å, respectively. These molecular parameters were obtained experimentally from electron diffraction measurements [41]. Here we have used the smallest, M1, and largest, M4, basis set which was constructed for the methane molecule.

To study the stability of our results with respect to the functional choice the local VWN [42] and the generalized gradient approximated PBE [43] functionals were used. For the density fitting the GEN-A2 and GEN-A2\* [44] auxiliary function sets were employed.

### 4. Results and discussions

In this section, we present the results of our calculations for the systems described above. For the validation of our methods, we also report finite field MP2 and CCSD  $A_{x,yz}$  values of dipole–quadrupole polarizabilities. The (FF) MP2 and (FF) CCSD values were calculated by taking a finite difference of quadrupole moments obtained from respective (full) MP2 and CCSD calculations at two different field values viz. 0.001 and –0.001 atomic units. Within the NIA-CPKS approach, we have used the same field value for the construction of the Kohn–Sham matrix derivatives. Two options, AUXIS and BASIS, mentioned in the tables, refer to the type of density used for the calculation of the exchange–correlation energy and potential. They can be calculated from either the auxiliary function (AUXIS) or the basis function (BASIS) density. Thus, the AUXIS and BASIS options refer to ADFT and RI-DFT calculations. By construction analytical ADPT dipole–quadrupole polarizabilities can only be calculated with the AUXIS option, whereas NIA-CPKS dipole–quadrupole polarizabilities were calculated for both options. All reported values are in atomic units.

In Table 1, our DFT calculated dipole–quadrupole polarizabilities of  $P_4$  for the four different basis sets are compared to corresponding (FF) MP2 and (FF) CCSD results. As this table shows,  $A_{x,yz}$  values calculated using the PBE functional and GEN-A2\* auxiliary function set are larger than those from VWN/GENA2\*. This trend is common to all four basis sets. The reverse trend is observed for the GEN-A2 auxiliary function set. Here the PBE values are smaller than those of VWN. We also observe that  $A_{x,yz}$  is usually increasing with the addition of polarization functions. This trend is independent from the used functional and methodology from the P0 to the P2 basis set. However, from P2 to P3 exceptions are observed. In case of ADPT, dipole–quadrupole polarizabilities calculated with GEN-A2 are consistently larger than calculated with GEN-A2\* for all basis sets and both functionals. NIA-CPKS also follows the same trend except for the P3 basis with the PBE functional. Here GEN-A2\* values are larger than GEN-A2 ones. Quadrupole polarizabilities calculated with the BASIS option within NIA-CPKS are closed to the corresponding AUXIS/NIA-CPKS/GEN-A2\* results. In general, ADPT and NIA-CPKS are in good agreement with each other for dipole–quadrupole polarizability. In particular, ADPT/GEN-A2\* results are in excellent agreement with NIA-CPKS BASIS results. This underlines the quality of the ADPT approach. The same was observed in our previous study of dipole–quadrupole polarizabilities [45]. The  $A_{x,yz}$  values calculated with (FF) MP2 are within the range of our DFT values. The corresponding CCSD values are larger than MP2. Our DFT results are in better agreement with the CCSD results than with the MP2 ones. Both CCSD and MP2 values are close to NIA-CPKS/VWN/BASIS and ADPT/VWN/GEN-A2\*

**Table 1**  
Static dipole–quadrupole polarizability ( $A_{xyz}$ ) of  $P_4$  [a.u.].

Basis	Basis functions	Functional	ADPT		NIA-CPKS			MP2	CCSD
			GEN-A2	GEN-A2*	GEN-A2	GEN-A2*	BASIS		
P0 <sup>1</sup>	132	PBE	85.4600	83.5986	84.7874	83.9818	83.3726	81.7878	82.7363
		VWN	86.2040	81.1477	86.0756	81.2707	81.5881		
P1 <sup>2</sup>	156	PBE	87.3610	85.8753	86.3950	86.3161	85.1419	82.3996	83.0694
		VWN	89.0184	83.9323	88.6108	84.5174	84.1123		
P2 <sup>3</sup>	196	PBE	88.3394	87.2405	87.7090	87.5432	86.2429	82.6886	83.6203
		VWN	90.8808	85.1816	90.2155	85.5836	85.5854		
P3 <sup>4</sup>	260	PBE	88.1526	87.0432	87.0288	87.2131	86.1470	83.1699	84.0828
		VWN	90.4400	84.7702	89.9586	85.6880	85.7363		

<sup>1</sup> [6s5p2d].<sup>2</sup> [6s5p3d].<sup>3</sup> [6s5p3d1f].<sup>4</sup> [6s5p3d2f].

quadrupole polarizabilities. The reported  $A_{xyz}$  values by Maroulis et al. using (FF) MP2 for the P0, P1 and P2 basis are 83.6, 85.4 and 85.1, respectively [10]. Their values are different from our (FF) MP2 values. This is because our calculations were done with a P–P bond length of 2.1958 Å, which is the most recently reported experimental bond length and their calculations were performed using an older experimental bond length (2.2228 Å). The other reason for this disagreement is that the number of basis functions is different even though the basis set is the same. Because we chose a Cartesian orbital representation in deMon2k, 6d and 10f functions are used in the calculation which results in a larger number of basis functions compared to those used by Maroulis et al. Moreover, our calculations are based on full MP2 level of theory whereas Maroulis et al. have frozen the 20 inner most MOs in their MP2 calculation. The experimental obtained from depolarized collision induced light scattering measurement [46] is  $77 \pm 26$  atomic units. Our theoretical results of  $A_{xyz}$  component are in good agreement with experiment, considering experimental error bars.

In Table 2 we compare our calculated DFT dipole–quadrupole polarizability of  $CH_4$  with (FF) MP2 and (FF) CCSD results. The used basis sets were designed by Maroulis for electric response property calculations [11] and have proven already reliable for post Hartree–Fock dipole–quadrupole polarizability calculations. As already observed for  $P_4$  the ADPT and NIA-CPKS results at the same level of theory are very similar. However, different to  $P_4$  the use of the GEN-A2\* auxiliary function set increases the dipole–quadrupole polarizability of  $CH_4$ . The NIA-CPKS BASIS results are lying always in between the corresponding AUXIS GEN-A2 and GEN-A2\* values. This indicates that the GEN-A2\* auxiliary functions set is still not fully saturated. We attribute this mainly to the hydrogen

atoms. However, the effect is small and does not alter significantly the quality of the DFT results. Comparison between DFT and (FF) MP2 and (FF) CCSD is best at the PBE/BASIS level of theory. Also ADPT/VWN/GEN-A2\* and NIA-CPKS/VWN/GEN-A2\* results show good agreement with the post Hartree–Fock calculations. The experimentally measured dipole–quadrupole polarizability of  $CH_4$  is 11.3 atomic units [47]. This is in good agreement with our theoretical results.

The  $P_4$  and  $CH_4$  validations show that our DFT implementations yield dipole–quadrupole polarizabilities that are comparable to corresponding (FF) MP2 and (FF) CCSD results. In the case of  $P_4$  and  $CH_4$ , the theoretical dipole–quadrupole polarizabilities are also in reasonable agreement with the experimental measurements. For adamantane the situation is different. Here the experimental upper value for the dipole–quadrupole polarizability of  $102.0 \pm 7.8$  a.u. is much larger than theoretical results by Maroulis et al. [48] and Quinet et al. [14], the absolute values are  $8.0 \pm 1.5$  a.u. and 9.736843 a.u. respectively. The experimental values reported by Maroulis et al. were determined from collision induced light scattering (CILS) measurements. The details about the experimental set up are given in [48]. These experimental measurements are characterized to low signal-to-noise ratio. It is also possible that the CILS spectrum is disturbed by three-body interactions and vibrational combination bands. The occurrence of these effects clearly limits accurate determination of dipole–quadrupole polarizabilities. The details discussion about these issues regarding the experimental procedure, we suggest to refer [48]. In the theoretical calculations of Maroulis et al. [48], the basis set size was limited by the computational effort. With our new DFT implementations we can lift this limitation. Therefore, we calculated dipole–quadrupole

**Table 2**  
Static dipole–quadrupole polarizabilities ( $A_{xyz}$ ) of  $CH_4$  [a.u.].

Basis	Basis functions	Functional	ADPT		NIA-CPKS			MP2	CCSD
			GEN-A2	GEN-A2*	GEN-A2	GEN-A2*	BASIS		
M1 <sup>1</sup>	88	PBE	8.5383	9.6044	8.6818	9.5317	9.0860	9.2257	9.1882
		VWN	8.5619	9.5370	8.6640	9.5430	8.9051		
M2 <sup>2</sup>	94	PBE	8.5054	9.6011	8.6517	9.5012	9.0761	9.1833	9.1726
		VWN	8.4605	9.5245	8.6534	9.5256	8.9002		
M3 <sup>3</sup>	100	PBE	8.5067	9.6042	8.6819	9.4825	9.1047	9.1915	9.1793
		VWN	8.4300	9.5297	8.6499	9.5299	8.9256		
M4 <sup>4</sup>	110	PBE	8.5265	9.6147	8.7130	9.5062	9.0932	9.1246	9.1109
		VWN	8.6722	9.5008	8.6603	9.5145	8.9106		

<sup>1</sup> [6s4p2d1f/4s2p1d].<sup>2</sup> [6s4p3d1f/4s2p1d].<sup>3</sup> [6s4p4d1f/4s2p1d].<sup>4</sup> [6s4p4d2f/4s2p1d].



**Table 3**  
Static dipole–quadrupole polarizabilities ( $A_{x,yz}$ ) of adamantane [a.u.].

Basis	Basis functions	Functional	ADPT		NIA-CPKS		BASIS
			GEN-A2	GEN-A2*	GEN-A2	GEN-A2*	
M1	656	PBE	13.1082	9.4776	15.8529	9.3205	10.5451
		VWN	12.6258	10.8307	15.9183	10.5766	11.4226
M4	876	PBE	11.5483	8.8324	15.7236	8.9593	10.6512
		VWN	13.0564	11.3859	16.1264	10.9805	11.6553

polarizabilities of adamantane with the M1 and M4 basis for carbon and hydrogen that gave good results for  $\text{CH}_4$ . Table 3 presents our results for adamantane. As in our validation calculations on  $\text{CH}_4$  the NIA-CPKS BASIS values lie in between the corresponding AUXIS GEN-A2 and GEN-A2\* ones. Taking the BASIS results as our best estimate we see from Table 3 that basis size effects are negligible and that our results are one order of magnitude smaller than the experimentally suggested upper bound for the dipole–quadrupole polarizability of adamantane. Moreover, our results are in the same range as the previous theoretical studies by Maroulis et al. [48] and Quinet et al. [14]. Thus, basis set size effects can be excluded to be responsible for the existing mismatch between the experimental and theoretical dipole–quadrupole polarizability of adamantane.

## 5. Conclusion

In this Letter, we have presented two non-iterative approaches, viz. ADPT and NIA-CPKS, for DFT dipole–quadrupole polarizability calculations. For the first time we presented a NIA-CPKS implementation in the framework of self-consistent perturbation (SCP) theory. The described methods are implemented in deMon2k and applied to the tetrahedral molecules  $\text{P}_4$ ,  $\text{CH}_4$  and adamantane ( $\text{C}_{10}\text{H}_{16}$ ). The results obtained are compared with (FF) MP2, (FF) CCSD and experimental dipole–quadrupole polarizabilities. We have shown that both methods provide consistent results within a chosen methodology, i.e. given functionals, basis sets and AUXIS or BASIS option. Qualitatively the ordering of the dipole–quadrupole polarizabilities of all three molecules is the same for all methodologies. The ADPT and NIA-CPKS dipole–quadrupole polarizabilities show good agreement with (FF) MP2 and (FF) CCSD results as well as with the corresponding experimental values for  $\text{P}_4$  and  $\text{CH}_4$ . We also observed that GEN-A2\* auxiliary function sets are needed for quantitative accurate results, at least for small systems. These results highlight the stability of the ADPT and NIA-CPKS approach. In this study, we have focused on the validation of our non-iterative methods for static dipole–quadrupole polarizability calculations. To the best of our knowledge this is the first time that non-iterative methods are used for dipole–quadrupole polarizability calculations within DFT. These methods will facilitate the study of large molecular systems such as clusters and bio-molecules without compromising accuracy. We have touched this topic by the basis set study for the dipole–quadrupole polarizability of adamantane. The observed discrepancy between experimental and theoretical dipole–quadrupole polarizabilities for adamantane raises many questions, in particular on the temperature and frequency dependency of these values. So far only estimates are available in the literature. The methodology to obtain dynamic electric response is already developed within ADPT [49]. Thus it can be used for studying the dynamic dipole–quadrupole polarizabilities. The temperature effects can be added by first principle Born–Oppenheimer Molecular Dynamics (BOMD) simulations. This was already successfully applied to dipole-polarizabilities [50] and can be extended to dipole–quadrupole polarizabilities. Developments along these lines are currently underway in our laboratories.

## Acknowledgments

S.V.S. acknowledges financial support from the Council of Science and Industrial Research (CSIR), India. S.P. acknowledges partial financial support from the SSB grant of CSIR, India and the J.C. Bose fellowship grant of DST, India. Facilities at the Centre of Excellence in Scientific Computing at CSIR-NCL are acknowledged. A.M.K. gratefully acknowledges support from CONACyT (60117-F), ICyTDF (PIFUTP08-87) and CIAM (107310). This work was performed in the framework of the Indian–Mexican cooperation project J110.405.

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