

Behaviour of density functional theory for electric response properties at distorted geometries of molecules

Sapana V. Shedge · Sayali P. Joshi · Sourav Pal

Received: 17 May 2011 / Accepted: 1 August 2011 / Published online: 4 February 2012
© Springer-Verlag 2012

Abstract The role of exchange–correlation is well known for accurate calculations of electric response properties. The exchange–correlation functional in density functional theory (DFT) has been well studied for ground state equilibrium geometry. However, the behaviour of these functional in stretched geometries, where static correlation play an important role, has not been studied systematically, particularly for response electric properties. Thus, we present here the rigorous calculation of electric response properties at distorted geometries of the molecules. We have considered dipole polarizability and dipole–quadrupole polarizability for description of role of static and dynamic correlation for electric response properties. The calculations are performed with our new approach, non-iterative approximation to coupled-perturbed Kohn–Sham method. These DFT results are compared with higher level ab initio such as coupled perturbed singles and doubles and fully correlated full CI. We have studied single, double and triple-bonded systems at different inter-nuclear separation. We report here the dipole polarizability and dipole–quadrupole polarizability of HF, BH, H₂CO, CO and NO⁺. We also present the effect of basis and functional on polarizability and dipole–quadrupole polarizability.

Keywords NIA-CPKS · Dipole–quadrupole polarizability · Dipole–dipole polarizability · DFT · Distorted geometry

1 Introduction

The recent development in theoretical and computational chemistry has made the study of large molecular systems possible. A lot of interest lies in determining structure and properties of systems such as clusters, nano-materials, biomolecules and periodic systems. Density functional theory (DFT) has been proved to be a good tool for studying such systems efficiently and with reasonable accuracy. The theory is exact in principle for ground states and works well at low computational cost. Thus, DFT has been applied broadly in solid state physics and material chemistry for understanding a wide range of phenomenon [1, 2]. DFT has also been applied widely for electric and magnetic response properties [3–7]. Static and dynamic electric properties have been studied extensively during last few years [8–11]. A weak electric perturbation affects the electronic distribution of the molecule, and it can be analyzed with the study of electric response properties. Recently, two new approaches have been developed for efficient calculation of response of electric perturbation within DFT, namely non-iterative approximation to coupled-perturbed Kohn–Sham approach (NIA-CPKS) [12, 13] and auxiliary density perturbation theory (ADPT) [14, 15]. These two approaches have been implemented in the developers' version of deMon2 k [16] software for dipole polarizability. Both the approaches are well tested for dipole-polarizability calculations [17]. Recently, these approaches have been further extended for calculation of dipole–quadrupole polarizabilities, and their reliability has been verified by comparison with higher level ab initio methods [18]. Both the approaches have provided reasonably accurate and promising results in our earlier studies.

Electron correlation plays important role in accurate description of binding energies and electric response

Dedicated to Professor Eluvathingal Jemmis and published as part of the special collection of articles celebrating his 60th birthday.

S. V. Shedge · S. P. Joshi · S. Pal (✉)
Physical Chemistry Division,
National Chemical Laboratory, Pune 411008, India
e-mail: s.pal@ncl.res.in

properties of molecules and materials. Fundamentally DFT gives exact treatment of static and dynamic correlation [19–21]. Though DFT is exact in principle for ground state, its success in actual calculation lies in proper formulation of exchange–correlation functional. For ground state equilibrium geometry, a systematic study of exchange–correlation functional has been made in recent years. It is well known from systematic ab initio quantum chemical theories that the ground state equilibrium geometry is dominated by dynamic electron correlation. From this, it can be surmized that there exists reliable functional in DFT, which describes dynamic correlation efficiently. However, it is not clear whether the same functionals of DFT can describe the degenerate or near-degenerate states, open-shell systems, breaking of chemical bonds and strongly correlated systems that are dominated by static correlation. Preliminary studies point to inadequacy of these functionals in representing static correlation leading to incorrect density and energy [22, 23]. The new functional has been developed to cover static correlation in DFT, but it is still beyond the practical application [24]. The single determinant picture of DFT fails to take into account the static correlation. Bally et al. have studied the potential energy curve for H_2^+ [25] with DFT method. The H_2^+ potential has showed local minimum at infinity, which should be exactly zero. This wrong behaviour of DFT method is due to the self interaction error [26, 27]. Additionally, DFT gives the incorrect description of dissociation limit of H_2 [28, 29] molecule and some ionic systems such as LiF [30–32]. However, fewer studies are available on behaviour of DFT for response electric properties of molecules [12, 33]. Thus, we present here rigorous calculation of polarizability and quadrupole polarizability for a range of internuclear separation and careful analysis of behaviour of DFT for electric properties.

In present paper, we have considered single-bonded, double-bonded, triple-bonded and charged molecules for our study. The quadrupole polarizabilities have been calculated with our NIACPKS approach. Different functionals have been employed to observe the consequences of exchange–correlation effect on these properties. For comparison, the ab initio calculations are performed using full CI and CCSD method. The article is organized as follows. Brief theory is presented in Sect. 2; computational details are mentioned in Sect. 3. Results are discussed in Sect. 4, and derived conclusions are presented in Sect. 5.

2 Theory

In presence of the static electric field, Hamiltonian depends upon the electric field perturbation. Following the terminology used by Buckingham [34] McLean and Yoshimine

[35], the energy of such system can be expressed in terms of perturbation as,

$$E(F) = E^0 - \mu_i^0 F_i - \frac{1}{3} \Theta_{ij}^0 F_{ij} - \frac{1}{15} \Omega_{ijk}^0 F_{ijk} - \frac{1}{105} \Phi_{ijkl}^0 F_{ijkl} \\ + \cdots - \frac{1}{2} \alpha_{ij} F_i F_j - \frac{1}{3} A_{ijk} F_i F_j F_k - \frac{1}{6} C_{ijkl} F_i F_j F_k F_l \\ - \frac{1}{6} \beta_{ijk} F_i F_j F_k - \frac{1}{6} B_{ijk,l} F_i F_j F_k F_l + \cdots \quad (1)$$

Here, Einstein summation is used, with i and j spanning x , y and z directions. F_i represents an electric field component and F_{ij} an electric field gradient, which denotes the non-homogeneous nature of the electric field. E^0 , μ^0 , Θ^0 , Ω^0 , are the energy and permanent multiple moments of the free molecule, α_{ij} its dipole polarizability and β_{ijk} the corresponding (first) hyperpolarizability. $A_{k,ij}$ is the dipole–quadrupole polarizability and $B_{ij,kl}$ the dipole–dipole–quadrupole hyperpolarizability. It is clear from the energy expression that the dipole moment and polarizability of molecule are the first and second derivatives of ground state energy with respect to electric field perturbation at zero field, respectively. Similarly, dipole–quadrupole polarizability is the second derivative of energy with respect to electric field perturbation, F and field gradient, F' at their zero values.

$$\mu_i = - \left(\frac{\partial E}{\partial F_i} \right)_{F=0} \quad (2)$$

$$\alpha_{ij} = - \left(\frac{\partial^2 E}{\partial F_i \partial F_j} \right)_{F=0} \quad (3)$$

$$A_{ijk} = \left(\frac{\partial^2 E}{\partial F_i \partial F_{jk}} \right)_{F=0, F'=0} \quad (4)$$

According to Hellmann-Feynman theorem, for the exact wave function and variational method, the first derivative of energy with respect to electric field is equal to the expectation value of the derivative of the Hamiltonian. For electric properties, derivative of energy is equal to expectation value of dipole moment operator. When the respective method used for the calculation is variational, then according to Wigner's $(2n + 1)$ rule, response up to 3rd order can be calculated from the 1st order response of wave function or density. The response properties can be calculated using various methods, such as perturbative method and field dependent methods. The perturbative methods involve coupling of the excited states for example sum-over states (SOS), whereas field-dependent approaches involve the finite-field and coupled schemes which include coupled-perturbed Hartree–Fock (CPHF) method. In CPHF, Hamiltonian has field dependence and coupled equations have an implicit dependence on the first-order response thus they need to be solved iteratively. When this approach is implemented in DFT, it is known as coupled-perturbed Kohn–Sham method (CPKS). This is the

conventional approach used for calculation of first-order response of the electric field perturbation. The derivative of KS equation with respect to field gives the CPKS equation.

$$K^{(\lambda)}c + Kc^{(\lambda)} = S^{(\lambda)}c\varepsilon + Sc^{(\lambda)}\varepsilon + Sc\varepsilon^{(\lambda)} \quad (5)$$

In case of electric perturbation, the derivative of KS-operator matrix, $K^{(\lambda)}$, consists of the two-electron and the response term. The $K^{(\lambda)}$ has an explicit dependence on perturbed coefficients $c^{(\lambda)}$, and as a result, the CPKS equation needs to be solved iteratively for self consistency. The two-electron term in $K^{(\lambda)}$ constitutes complicated functional derivative of Coulomb as well as the exchange–correlation term with respect to the electric field perturbation, which is algebraically complicated and time consuming step in the completely analytic CPKS method.

Recently, we have developed a new approach, where the KS matrix derivative is calculated by finite difference approximation. Plugging this numerically obtained derivative of the KS-operator matrix, $K^{(\lambda)}$, the coefficient matrix, c , and the eigenvalues, ε , of the unperturbed DFT calculation in the analytic CPKS equation yields a single-step solution. The perturbed coefficients, $c^{(\lambda)}$, in terms of the atomic orbital basis are obtained analytically by solving Eq. 5. The derivative density matrix can then be calculated by putting $c^{(\lambda)}$ and the coefficient matrix c from the unperturbed DFT calculation in the following equation

$$P_{\mu\nu}^{(\lambda)} = 2 \sum_i^{occ} c_{\mu i}^{\dagger(\lambda)} c_{\nu i} + c_{\mu i}^{\dagger} c_{\nu i}^{(\lambda)} \quad (6)$$

The components of dipole polarizability and dipole–quadrupole polarizability can be obtained by taking a trace of the perturbed density matrix and dipole and quadrupole integrals, respectively.

$$\alpha_{ij} = Tr(P_i^{(\lambda)} \mu_j) \quad (7)$$

$$A_{i,jk} = Tr(P_i^{(\lambda)} \theta_{jk}) \quad (8)$$

This way the calculation of functional derivative of Coulomb and exchange–correlation term is avoided and self consistency is overcome with our approach. This makes NIA-CPKS useful for response property calculation of large molecule in large basis. NIA-CPKS approach has been implemented in deMon2 k [16]. For the detailed discussion of the implementation of dipole polarizability and dipole–quadrupole polarizability, we suggest to refer our previous papers [12, 13, 17, 18, 33].

3 Computational details

We present here the dipole–dipole polarizabilities and dipole–quadrupole polarizabilities of HF, BH, H₂CO, CO

and NO⁺ molecules for different internuclear separation. For HF and BH, polarizabilities are studied from 0.25R_e to 2.5R_e. In case of formaldehyde, bond is stretched up to 1.75R_e, and for triple-bonded systems CO and NO⁺, values are reported up to 1.5R_e. Here, for diatomic molecule, R_e is the inter-nuclear distance at equilibrium geometry, and for H₂CO, we defined R_e as equilibrium bond length of double bond between carbon and oxygen. For H₂CO, R_e was taken to be 2.27334 a.u. [36]. The inter-nuclear distance of single bonded HF and BH have been taken as 1.7328 a.u. [37]. and 2.3289 a.u. [38], respectively, whereas R_e for triple-bonded CO and NO⁺ was used as 2.132242 a.u. [39]. and 2.00919 a.u. [40], respectively. All calculations have been done using centre of mass coordinate representation. Polarizabilities of BH calculated within DFT have been compared with finite-field (FF) full CI results and for other molecules comparisons have been made with results calculated through (FF) coupled perturbed singles and doubles (CCSD). Here, by finite-field full CI, we mean polarizabilities calculated with full CI using finite difference of dipole moments at +0.001 a.u. and −0.001 a.u. field values. Similar definition holds for (FF) CCSD. All DFT calculations have been carried out using NIA-CPKS implemented within deMon2 k software. The benchmark full CI and CCSD calculations were performed using GAMESS [41]. Three different functionals and three different basis sets were used for the calculation. The functional chosen were local functional, VWN [42] and non-local PBE [43] and BLYP [44, 45]. We report here the polarizabilities of HF calculated with aug-cc-pVDZ, Sadlej and DZP basis set. Polarizabilities of BH molecule are calculated with cc-pVDZ basis. We have used Sadlej basis set for calculating polarizabilities of H₂CO molecule. Polarizabilities of CO and NO⁺ are reported with cc-pVDZ and aug-cc-pVDZ basis, respectively. Chosen basis sets are seen to be working well for the respective molecules. We have employed GEN-A2* [46] auxiliary basis for calculation along with all three functional. In our earlier work, it has been observed that PBE functional with GEN-A2* basis works well for polarizability calculation [17]. Atomic units are used to define dipole–dipole polarizability and dipole–quadrupole polarizability throughout the paper. Diatomic molecules were kept along z axis. For the formaldehyde molecule, double bond was aligned along z axis and the molecule was kept in xz plane. Diatomic molecules are of C_{∞v} symmetry and H₂CO belongs to C_{2v} point group symmetry. According to Buckingham [34] for molecules of C_{∞v} symmetry, there are two independent components of dipole–quadrupole polarizability viz A_{xzx} and A_{zzz}. Molecules of C_{2v} symmetry have four independent components. Thus, we report here A_{x,xz}, A_{y,yz}, A_{z,xx}, A_{z,yy} components for formaldehyde. The reported components of dipole–quadrupole polarizabilities are traceless quantities.

4 Results and discussion

HF and BH molecule are studied thoroughly to understand the effects of exchange and correlation functional in determining dipole–dipole polarizability and dipole–quadrupole polarizability at different inter-nuclear separation. For these two small systems, we have compared the results with extensive ab initio calculations in different basis sets. Formaldehyde molecule has double bond between carbon and oxygen atom. It is an interesting molecule for spectroscopic studies, and hence, the study of electric properties of this molecule is of interest. CO and NO^+ are the simplest triple-bonded molecules. CO is significant molecule in astrophysical studies of interstellar molecular clouds [47]. The effect of electron correlation plays key role in determining exact polarizabilities of CO. NO^+ is iso-electronic with CO, yet the electric polarizabilities of the two molecules are markedly different.

The DFT calculations are done with our recently developed NIA-CPKS approach. As stated in the introduction, this approach has been already validated for calculation of dipole–dipole polarizabilities and dipole–quadrupole polarizabilities [12, 18]. The considered set of molecules has been studied enormously with different methods for equilibrium and distorted geometries. However, very few of these studies are on the behaviour of DFT for calculation of polarizability at different geometries. In fact, this study represents the first case of dipole–quadrupole polarizability of molecules at different inter-nuclear distances. As pointed out earlier, the static correlation becomes dominant in such cases.

Table 1 reports the dipole–quadrupole polarizability of HF molecule with aug-cc-pVDZ basis set. For both HF and BH, we report the polarizabilities from $0.25R_e$ to $2.5R_e$. The benchmarking of the DFT results of HF is done with CCSD results. It is seen from the Table 1 that from $0.25R_e$ to $1.75R_e$, dipole–quadrupole polarizability components of

HF, calculated from DFT, are in reasonable agreement with the CCSD values. The difference between CCSD and DFT polarizability increases progressively with increasing inter-nuclear distance from $2R_e$ to $2.5R_e$. The CCSD absolute values of A_{xx} and A_{zz} components are generally lower than the DFT absolute value up to $1.5R_e$ and $1.25R_e$, respectively. Beyond this, the absolute values of both these components at CCSD level are larger than those at DFT level. However, we find interestingly for A_{zz} component that at $2.5R_e$, absolute value at CCSD level is again lower than DFT level. Similarly, at $0.25R_e$, the trend of CCSD and DFT for these two components is different. However, for $0.5R_e$, values of CCSD and DFT are of opposite sign, showing the sensitivity of results to the nature of electron correlation. Within DFT, all the functionals behave more or less the same way. We have also reported the trend of A_{zz} component of dipole–quadrupole polarizability in Sadlej and DZP basis set. The qualitative results of A_{zz} component are given in Fig. 1a, b. The CCSD results with Sadlej basis confirm the same type of nature observed for aug-cc-pVDZ basis set. For the DZP basis minima is observed for at $2.25R_e$, which was not very clear in Sadlej and aug-cc-pVDZ basis sets. In case of DFT results, such nature is absent for A_{zz} component.

Dipole–dipole polarizabilities of HF and BH molecule were studied earlier with DZ, DZP and Sadlej basis set only up to $2R_e$ [12, 33]. However, we have presented in this paper the results beyond $2R_e$. The qualitative results of α_{xx} and α_{zz} component are plotted as a function of internuclear distance up to $2.5R_e$, in Fig. 2a, b, respectively. These results were obtained using aug-cc-pVDZ basis set. The Fig. 2a for α_{xx} component shows that the DFT results are higher than the CCSD values from $0.25R_e$ to $1.75R_e$. Around $2R_e$, these tend to get closer to CCSD results. Among the DFT functionals, BLYP functional is behaving better for α_{xx} component at stretched internuclear distance of HF molecule. It is known from earlier ab initio results

Table 1 Dipole–quadrupole polarizability (A_{xx} and A_{zz} component in a.u.) of HF molecule calculated with aug-cc-pVDZ basis set

R	A_{xx}				A_{zz}			
	CCSD	PBE	BLYP	VWN	CCSD	PBE	BLYP	VWN
$0.25R_e$	0.1390	0.1285	0.1023	0.1461	0.5479	0.6004	0.6020	0.6135
$0.5R_e$	−0.0855	−0.2386	−0.3169	−0.2333	0.0814	−0.0531	−0.1146	−0.0177
$0.75R_e$	−0.3903	−0.5777	−0.6200	−0.5786	−1.4773	−1.7959	−1.8405	−1.7490
R_e	−1.1851	−1.4501	−1.5664	−1.4625	−5.1534	−5.7271	−5.8589	−5.6264
$1.25R_e$	−2.5850	−2.8773	−2.9139	−2.9308	−12.8003	−12.9077	−13.1898	−12.7676
$1.5R_e$	−4.7225	−4.9743	−5.0327	−5.0003	−27.0958	−24.8101	−25.3343	−24.5520
$1.75R_e$	−7.7849	−7.4373	−7.4566	−7.4424	−50.5080	−41.6793	−43.0311	−41.1576
$2R_e$	−11.7439	−10.2256	−10.2138	−10.2449	−80.8617	−63.8439	−65.2206	−63.6135
$2.25R_e$	−16.1125	−13.1443	−12.9308	−13.2416	−104.5977	−91.6369	−92.7657	−91.7436
$2.5R_e$	−20.0254	−15.9318	−15.1593	−16.1200	−107.2612	−122.8090	−122.1649	−123.6400

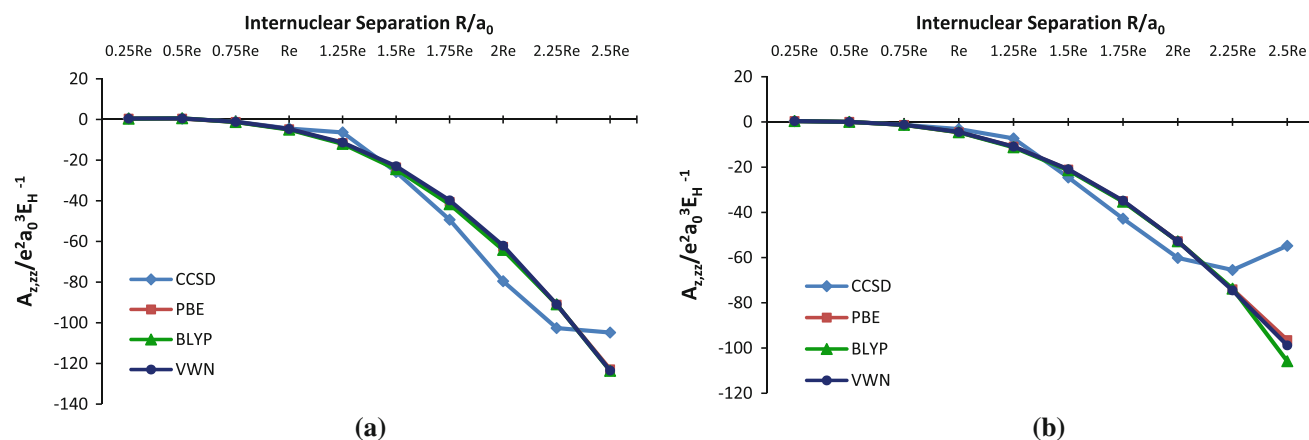


Fig. 1 Dipole–quadrupole polarizabilities A_{zzz} component (in a.u.) of HF molecule calculated with Sadlej and DZP basis. **a** Sadlej basis, **b** DZP basis

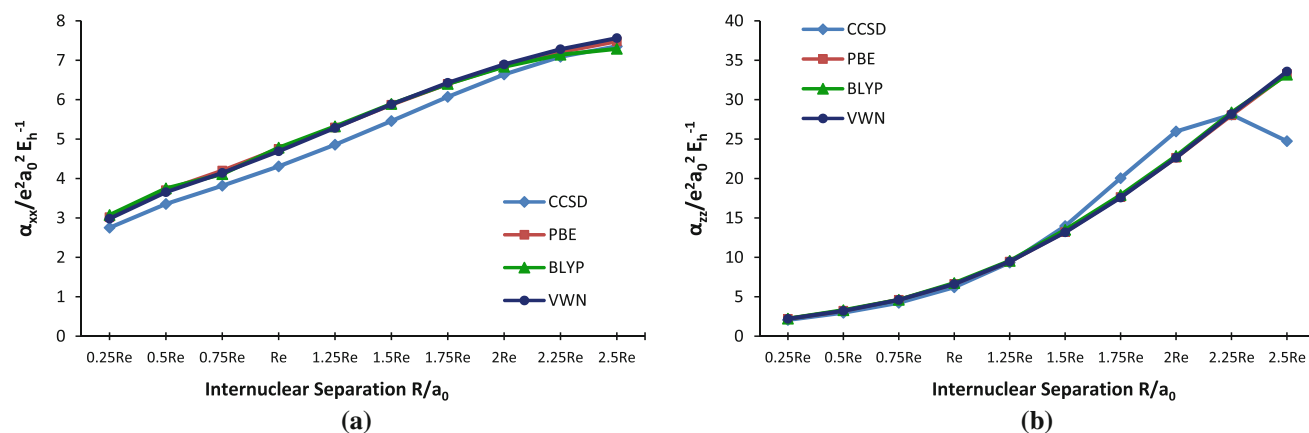


Fig. 2 Dipole–dipole polarizability (α_{xx} and α_{zz} components in a.u.) of HF molecule calculated with aug-cc-pVDZ basis set. **a** α_{xx} component, **b** α_{zz} component

that between $2R_e$ and $2.5R_e$ α_{zz} component of dipole–dipole polarizability shows a maximum. The same is observed in Fig. 2b for CCSD results for α_{zz} with maxima at $2.25R_e$. However, such maximum is missing for DFT results of α_{zz} component. In Table 2, we report α_{zz} component of HF molecule calculated with Sadlej and DZP basis. For these basis sets, relaxed extended (ECCSD) results were available in literature [48] and thus the benchmarking of DFT results is done with the ab initio results. DFT results are in agreement with the ECCSD results up to $1.25R_e$, whereas from $1.5R_e$ to $2.5R_e$, the discrepancy between DFT and ECCSD has been increased. DFT results are almost double the ECCSD at $2.5R_e$. The ECCSD results also show maxima between $2R_e$ and $2.5R_e$ for Sadlej and DZP basis sets; however, for DFT results, such maxima is absent even for Sadlej and DZP basis sets. This is due to the missing multireference effects in DFT, which are important at stretched geometry of the molecule. All three functionals are behaving relatively in same manner.

We have selected BH molecule for examining the trend of DFT polarizabilities with fully correlated method, that is, full CI. The calculations were performed with cc-pVDZ basis set. The plots of A_{xxz} and A_{zzz} component of dipole–quadrupole as a function of internuclear distance are given in Fig. 3a, b, respectively. It is observed from Fig. 3a, b that full CI result of A_{xxz} component shows minima at $0.75R_e$ and A_{zzz} component shows maxima at $2R_e$. The minimum observed for A_{xxz} component of compressed internuclear distance is generated correctly by DFT. For all stretched bond length, A_{xxz} component using DFT is in closer agreement with CCSD results. From Fig. 3b, it is seen that A_{zzz} components calculated with full CI and DFT are overlapping perfectly up to $1.25R_e$. However, from $1.5R_e$ to $2.5R_e$, DFT and full CI results are extremely different from each other. Full CI results show maxima at $2R_e$. However, DFT values are monotonically increasing from $0.5R_e$ to $2R_e$. Figure 4a, b gives α_{xx} and α_{zz} component of dipole–dipole polarizability, respectively, as a

Table 2 Dipole–dipole polarizability (α_{zz} component in a.u.) of HF molecule calculated with Sadlej and DZP basis set

R	(Sadlej) α_{zz}				(DZP) α_{zz}			
	ECCSD (relaxed)	PBE	BLYP	VWN	ECCSD (relaxed)	PBE	BLYP	VWN
0.25 R_e		2.5278	2.5733	2.5167		1.2719	1.2660	1.2719
0.5 R_e		3.5763	3.5851	3.5502		1.6121	1.6013	1.6006
0.75 R_e	4.555	4.9020	5.0421	4.9207		2.6260	2.5902	2.5858
R_e	6.415	6.8278	7.0402	6.8223	4.32	4.5779	4.5469	4.5049
1.25 R_e	9.917	9.6270	9.8269	9.6474		7.3926	7.5045	7.3992
1.5 R_e	14.117	13.4703	13.7561	13.3765	12.83	10.9102	10.9988	10.8783
1.75 R_e		17.9996	18.3744	17.8898		14.7890	14.8353	14.7507
2 R_e	19.869	22.9549	23.4120	22.9218	20.04	18.9031	18.8927	18.9635
2.25 R_e		28.5109	28.7059	28.6137		23.1197	23.0268	23.3154
2.5 R_e	17.532	33.9022	34.1594	34.2550	14.07	26.8402	29.2665	27.5165

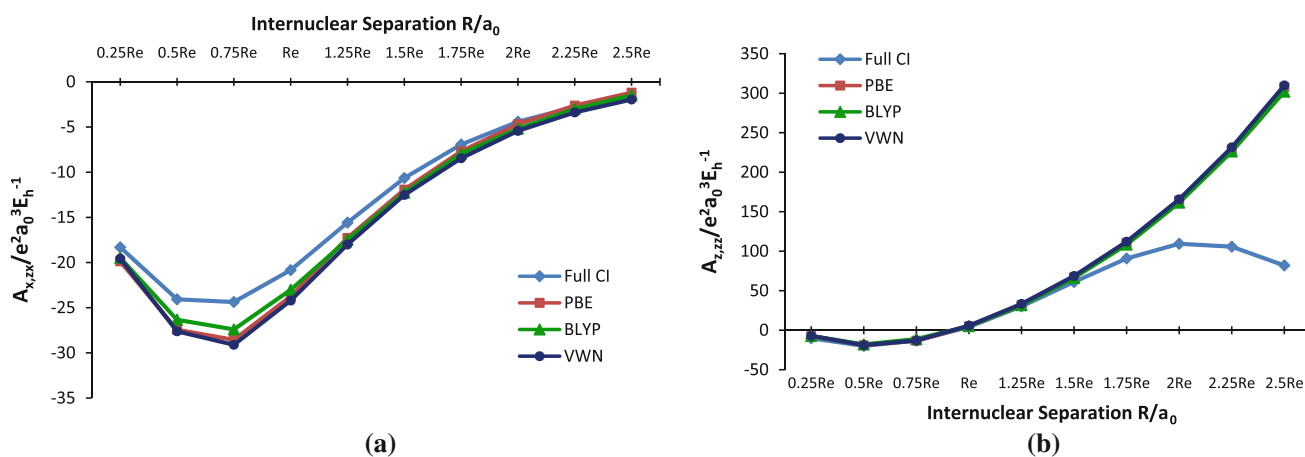
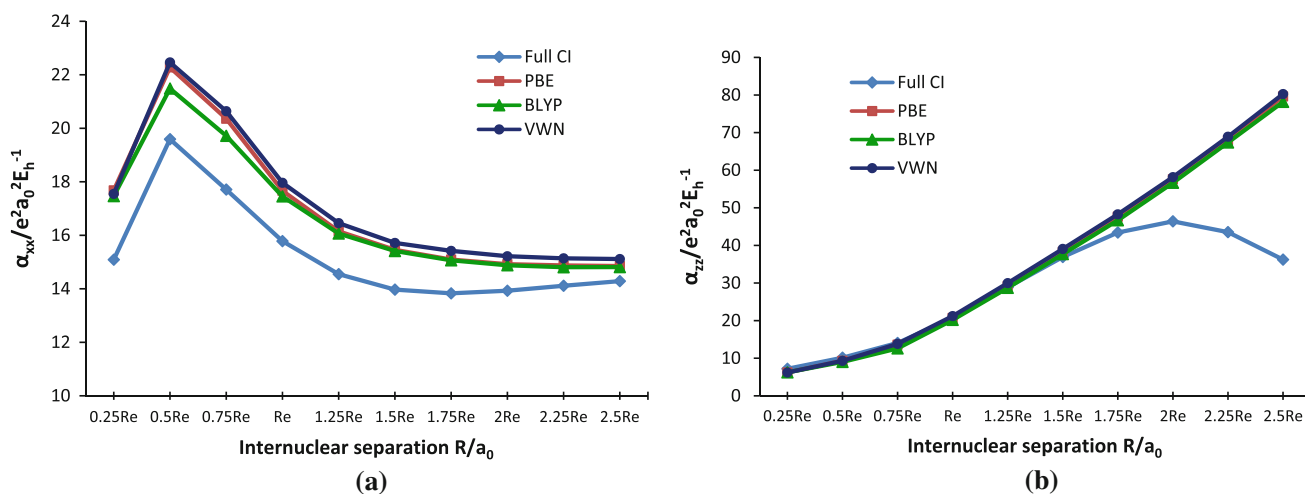
**Fig. 3** Dipole-quadrupole polarizability (A_{xzx} and A_{zzz} component in a.u.) of BH molecule calculated with cc-pVDZ basis. **a** A_{xzx} , **b** A_{zzz} **Fig. 4** Dipole–dipole polarizability (α_{xx} and α_{zz} component in a.u.) of BH molecule calculated with cc-pVDZ basis. **a** α_{xx} component, **b** α_{zz} component

Table 3 Dipole–quadrupole polarizability (A_{xzx} and A_{yzy} component in a.u.) of H_2CO molecule calculated with Sadlej basis set

R	A_{xzx}				A_{yzy}			
	CCSD	PBE	BLYP	VWN	CCSD	PBE	BLYP	VWN
$0.5R_e$	−105.3668	−123.3545	−122.5987	−126.9520	−24.0572	−27.6558	−27.2636	−28.3365
$0.75R_e$	−54.6198	−66.9920	−69.7492	−68.3393	−13.9728	−16.1727	−16.1685	−16.3437
R_e	−30.7291	−33.8981	−35.6182	−35.0209	−8.9462	−9.4478	−9.3923	−9.7489
$1.25R_e$	−23.8936	−24.0637	−24.3109	−24.5842	−9.1030	−9.0831	−9.5465	−9.2090
$1.5R_e$	−24.2319	−22.2892	−23.2432	−22.9006	−12.0100	−10.3122	−10.3107	−10.5230

Table 4 Dipole–quadrupole polarizability (A_{zxx} and A_{zyy} component in a.u.) of H_2CO molecule calculated with Sadlej basis

R	A_{zxx}				A_{zyy}			
	CCSD	PBE	BLYP	VWN	CCSD	PBE	BLYP	VWN
$0.5R_e$	2.5475	2.7049	2.6317	2.8099	18.9927	23.8598	24.1470	24.3599
$0.75R_e$	−1.3386	−2.3637	−3.3004	−2.5537	16.5441	20.4492	21.1140	20.7444
R_e	1.6791	1.9273	1.7018	1.9270	13.1453	14.8440	15.6685	15.1748
$1.25R_e$	5.1013	5.4509	5.3992	5.4098	13.8293	12.8652	12.8671	13.2185
$1.5R_e$	10.1629	9.2171	8.1626	8.9939	17.4727	14.5610	14.2680	14.9262
$1.75R_e$	17.4084	13.4194	13.2170	13.2467	22.2680	18.4675	18.5961	18.5851

function of internuclear separation. The dipole–dipole polarizability shows maxima at $0.5R_e$ for α_{xx} and at $2R_e$ for α_{zz} . Among the three functionals, BLYP results for A_{xzx} and α_{xx} are closer to full CI polarizabilities and VWN is most away, and this is observed clearly for $0.5R_e$ to R_e .

Tables 3 and 4 report four different components of dipole–quadrupole polarizabilities of formaldehyde molecule, viz. A_{xzx} , A_{yzy} , A_{zxx} , A_{zyy} . All four components were calculated up to $1.75R_e$. For equilibrium bond distance, R_e , DFT results are in good agreement with CCSD. For compressed and stretched C–O bond length, the agreement between DFT and CCSD results is poor. Exceptionally, for A_{xzx} component, DFT results are closer to the CCSD values from $1.25R_e$ onwards. Dipole–dipole polarizabilities of H_2CO are reported in Table 5. The DFT results of dipole–dipole polarizabilities are also in good agreement with CCSD at R_e . At stretched bond length, DFT results are seen to be in closer agreement with CCSD for α_{xx} and α_{yy} components. However, α_{zz} component of polarizability DFT values are in poor agreement with CCSD at $0.25R_e$, $0.5R_e$ and $1.5R_e$. Choice of functionals does not have any significant effect on polarizabilities. All functionals provide similar trends. For dipole–dipole polarizabilities, PBE functional is giving better results than the other two functionals. The same is true for dipole–quadrupole polarizabilities. We had observed same in our earlier work.

Dipole–quadrupole polarizabilities and dipole–dipole polarizabilities of CO are reported in Tables 6 and 7, respectively. We chose cc-pVDZ basis set for CO molecule. Our DFT results are compared with CCSD.

Dipole–quadrupole polarizabilities do not show any kind of maxima or minima for CCSD as well as DFT. A_{xzx} component is getting close to CCSD results at $1.5R_e$. The A_{zzz} component from DFT studies is matching well with CCSD results for $0.75R_e$ to $1.25R_e$. However, at $0.25R_e$ and $1.5R_e$, DFT results are nearly 1.5 a.u. higher than CCSD. Dipole–dipole polarizabilities are also calculated with the same basis. The α_{xx} calculated from CCSD is lower than of DFT, except for $0.5R_e$. For $1.5R_e$, DFT results are close to CCSD results for CO molecule. The α_{zz} component calculated with DFT is very close to CCSD value for $0.5R_e$ to R_e , whereas the difference between DFT and CCSD results increases gradually from $1.25R_e$ onwards. The difference between CCSD and DFT polarizability is the highest at $1.5R_e$, which is roughly around 2.2 a.u. For NO^+ molecule, we have chosen aug-cc-pVDZ basis set, which is known to be a good basis set for the charged systems. The dipole–quadrupole polarizabilities and dipole–dipole polarizabilities of NO^+ are reported in Tables 8 and 9, respectively. Analogous to earlier observations dipole–quadrupole polarizabilities from DFT are in good agreement with CCSD at equilibrium distance. The agreement between DFT and CCSD results is poor for A_{xzx} component at compressed and stretched bond lengths. However, A_{zzz} component is matching well up to R_e , and beyond R_e at stretched bond lengths, the difference between DFT and CCSD results is progressively increasing. Similarly, it is noted from Table 9 that dipole–dipole polarizability results of DFT are matching well with CCSD at R_e . PBE results are in better agreement with CCSD. For α_{xx} component,

Table 5 Dipole–dipole polarizability (α_{xx} , α_{yy} , and α_{zz} components in a.u.) of H₂CO calculated with Sadlej basis set

<i>R</i>	CCSD	PBE	BLYP	VWN
α_{xx}				
0.5R _e	39.0835	45.1711	45.5139	46.3509
0.75R _e	21.4087	24.4389	25.0645	24.8203
R _e	17.6397	18.6775	19.0055	18.9713
1.25R _e	18.1913	19.1347	19.3387	19.2501
1.5R _e	19.5864	20.4541	20.6378	20.6467
1.75R _e	20.7258	21.5436	21.8873	21.7621
α_{yy}				
0.5R _e	12.9961	14.7552	14.7501	15.0376
0.75R _e	10.9896	11.9052	12.0091	11.9825
R _e	12.6302	13.1869	13.0977	13.1946
1.25R _e	15.2292	15.6796	15.8382	15.6594
1.5R _e	17.6122	17.8411	18.0592	17.7919
1.75R _e	18.7842	19.3913	20.0983	19.3205
α_{zz}				
0.5R _e	14.3390	16.1506	16.1796	16.3944
0.75R _e	18.0182	19.5760	19.7552	19.7753
R _e	22.2218	23.2344	23.6541	23.4099
1.25R _e	29.3833	29.5416	30.1213	29.7370
1.5R _e	40.3062	38.0035	37.8495	37.9803
1.75R _e	51.1393	46.5293	47.6017	47.7805

DFT results are higher than CCSD for compressed internuclear distances, whereas at 1.25R_e and 1.5R_e, CCSD and DFT results are showing much closer agreement. The DFT results of α_{zz} component are higher than CCSD for 0.5R_e

and 0.75R_e. R_e onwards CCSD results are higher than DFT. The difference between DFT and CCSD result increases from R_e to 1.5R_e; highest difference is observed at 1.5R_e. In general higher level, ab initio methods and DFT results of dipole–quadrupole and dipole–dipole polarizabilities are in good agreement with each other equilibrium bond distance, R_e, for all molecules. However, for stretched internuclear distances, DFT failed to produce correct trend of dipole–quadrupole and dipole–dipole polarizabilities.

5 Conclusions

In this paper, we have presented a comprehensive study of the dipole–quadrupole polarizability and dipole–dipole polarizability as a function of internuclear distance of the molecule. The polarizabilities calculated with DFT for all selected molecules are compared with ab initio results. In general, for all molecules, DFT results are in good agreement with higher level ab initio results near equilibrium distance. In case of HF molecule, DFT results failed to produce the trend shown by CCSD results for dipole–quadrupole polarizabilities at stretched geometry. Dipole–dipole polarizabilities have shown the characteristic maxima along stretched bond length from CCSD calculations. Such trend is absent in DFT calculations. The same is noticed from the comparison between ECCSD and DFT for dipole–dipole polarizability. Variation of the basis does not change the trend remarkably. It merely leads to shift of polarizability values. For BH molecule, our comparison

Table 6 Dipole–quadrupole polarizability (A_{xx} and A_{zz} component in a.u.) of CO molecule with cc-pVDZ basis set

<i>R</i>	A_{xx}				A_{zz}			
	CCSD	PBE	BLYP	VWN	CCSD	PBE	BLYP	VWN
0.5R _e	−11.0405	−10.4939	−10.3742	−10.6007	−8.2220	−7.0801	−7.0195	−7.07277
0.75R _e	−12.0212	−12.1767	−11.9978	−12.2982	−9.1283	−9.4075	−9.2772	−9.50384
R _e	−13.3118	−13.6301	−13.4555	−13.8046	−10.4617	−10.6818	−10.5129	−10.85385
1.25R _e	−14.7177	−14.9277	−14.8022	−15.1228	−14.0259	−13.5037	−13.3065	−13.73289
1.5R _e	−16.0352	−16.0960	−16.0392	−16.2166	−19.7852	−18.6237	−18.4403	−18.8481

Table 7 Dipole–dipole polarizability (α_{xx} and α_{zz} component in a.u.) of CO molecule with cc-pVDZ basis set

<i>R</i>	α_{xx}				α_{zz}			
	CCSD	PBE	BLYP	VWN	CCSD	PBE	BLYP	VWN
0.5R _e	7.2040	6.9793	6.9296	7.0406	6.2551	6.0944	6.0739	6.1183
0.75R _e	7.8068	8.0090	7.9379	8.0837	8.5195	8.6137	8.5890	8.6199
R _e	8.1849	8.4058	8.3384	8.4759	12.8212	12.5540	12.4860	12.5440
1.25R _e	8.3037	8.3956	8.3358	8.4534	19.1591	18.0385	17.8870	18.0425
1.5R _e	8.1660	8.1345	8.0870	8.1617	26.5255	24.2463	23.9985	24.1973

Table 8 Dipole–quadrupole polarizability (A_{xx} and A_{zz} component in a.u.) of NO^+ molecule calculated with aug-cc-pVDZ basis set

R	A_{xx}				A_{zz}			
	CCSD	PBE	BLYP	VWN	CCSD	PBE	BLYP	VWN
$0.5R_e$	−2.0460	−2.2025	−2.2710	−2.2386	−1.6587	−1.5884	−1.6100	−1.6137
$0.75R_e$	−2.5754	−2.6514	−2.5200	−2.6942	−2.0282	−2.0689	−2.0938	−2.1063
R_e	−2.9880	−2.9464	−2.9551	−2.9464	−2.7018	−2.4991	−2.4492	−2.4991
$1.25R_e$	−3.4824	−3.2025	−3.3465	−3.2653	−4.7649	−3.6084	−3.7038	−3.6577
$1.5R_e$	−4.2482	−3.4906	−3.6329	−3.6227	−8.4365	−5.5060	−5.5161	−5.5545

Table 9 Dipole–dipole polarizability (α_{xx} and α_{zz} component in a.u.) of NO^+ with aug-cc-pVDZ basis set

R	α_{xx}				α_{zz}			
	CCSD	PBE	BLYP	VWN	CCSD	PBE	BLYP	VWN
$0.5R_e$	3.6746	3.8647	3.9193	3.9104	3.6528	3.7685	3.8301	3.8084
$0.75R_e$	4.7381	4.8782	4.9021	4.9397	5.7138	5.7306	5.7638	5.7468
R_e	5.8408	5.8988	5.9239	5.8988	9.0726	9.0687	9.1008	9.0687
$1.25R_e$	6.7481	6.7742	6.8255	6.8245	13.407	13.5208	13.633	13.5564
$1.5R_e$	7.374	7.3709	7.3439	7.4319	18.769	18.336	18.2351	18.3893

between fully correlated full CI polarizabilities and DFT highlights the significance of electron correlation for determining electric properties. Similarly, for double-bonded and triple-bonded systems, the correlation effects play important role and this is clear from our observations for H_2CO , CO and NO^+ molecule.

We have also studied the effect of different functionals. Among the three functionals, that is, VWN, PBE and BLYP, PBE shows closer agreement with CCSD and full CI results. This is in general true for all molecules. However, at stretched internuclear distance, no functional is showing satisfactory results. This is because the ground state equilibrium geometry is dominated by dynamic electron correlation, whereas the static correlation is important in case of non-equilibrium geometries. The results indicate that while the existing DFT functionals describe dynamic correlation appropriately, these are unable to consider static correlation effects. Thus, DFT is unable to account the multireference effects that are significant for strongly correlated systems. Recently, efforts have been done to include the missing correlation by combining DFT with ab initio methods such as multireference (MR) and CI [49–53]. Such method has been proved to be working excellent for describing energy and density of systems where static correlation effects are important [53–55]. To the best of our knowledge, such combined implementation of multireference and DFT methods has not been done for calculation of electric response properties. In near future, we aim to study the behaviour of such combined method for electric property

calculation. We expect such implementation would lead to correct description of electric charge distribution of low lying excited states and open-shell systems as well as breaking of chemical bond.

Acknowledgments Authors acknowledge facilities at the Centre of Excellence in Scientific Computing at Council of Science and Industrial Research-National Chemical Laboratory (CSIR-NCL), India. S.V.S. acknowledges financial support from the (CSIR), India. S.V.S. is also grateful to Dr. Nayana Vaval for her constant support and productive discussions. S.P. acknowledges partial financial support from the SSB grant of CSIR, India and the J.C. Bose fellowship grant of DST, India.

References

- Gutsev GL, O'Neal RH Jr, Belay KG, Weatherford CA (2010) Chem Phys 368:113
- Jha PC, Seal P, Sen S, Ågren H, Chakrabarti S (2008) Comput Mater Sci 44:728
- Champagne B, Perpète EA, Jacquemin D (2000) J Phys Chem A 104:4755
- Pereiro M, Baldomir D (2007) Phys Rev A 75:033202
- Calaminici P, Jug K, Koester AM (1998) J Chem Phys 109:7756
- Pradhan K, Reveles JU, Sen P, Khanna SN (2010) J Chem Phys 132:124302
- Berlanga-Ramírez EO, Aguilera-Granja F, Montejano-Carrizales JM, Díaz-Ortiz A, Michaelian K (2004) Phys Rev B 70:014410
- Hohm U, Maroulis G (2006) J Chem Phys 124:124312
- Karamamanis P, Maroulis G (2006) J Chem Phys 124:071101
- Maroulis G, Hohm U (2007) Phys Rev A 76:032504
- Quinet O, Liégeois V, Champagne B (2005) J Chem Theory Comput 1:444
- Sophy KB, Pal S (2003) J Chem Phys 118:10861

13. Sophy KB, Shedge SV, Pal S (2008) *J Phys Chem A* 112:11266
14. Flores-Moreno R, Köster AM (2008) *J Chem Phys* 128:134015
15. Flores-Moreno R (2006) Ph.D. Thesis, Cinvestav, Mexico City, Mexico
16. Köster AM, Calaminici P, Casida ME, Flores-Moreno R, Geudtner G, Goursot A, Heine T, Janetzko FM, del Campo J, Patchkovskii S, Reveles JU, Salahub DR, Vela A deMon2 k, developers, Cinvestav (2006) Mexico City, Mexico. See <http://www.demon-software.com>
17. Shedge SV, Carmona-Espíndola J, Pal S, Köster AM (2010) *J Phys Chem A* 114:2357
18. Shedge SV, Pal S, Köster AM (2011) *Chem Phys Lett* 510:185
19. Hohenberg P, Kohn W (1964) *Phys Rev* 136:B864
20. Kohn W, Sham LJ (1965) *Phys Rev* 140:A1133
21. Parr RG, Yang W (1989) *Density functional theory of atoms and molecules*. Oxford University Press, New York
22. Savin A (1996) In: Seminario JM (ed) *Recent developments and applications of modern density functional theory*. Elsevier, Amsterdam, p 327
23. Baerends EJ (2001) *Phys Rev Lett* 87:133004
24. Becke AD (2003) *J Chem Phys* 119:2972
25. Bally T, Sastry GN (1997) *J Phys Chem A* 101:7923
26. Zhang Y, Yang W (1998) *J Chem Phys* 109:2604
27. Perdew JP, Leary M (1997) *Phys Rev B* 56:16021
28. Gunnarsson O, Lundqvist BI (1976) *Phys Rev B* 13:4274
29. Perdew JP, Savin A, Burke K (1995) *Phys Rev A* 51:4531
30. Perdew JP (1985) In: Dreizler RM (ed) *Density functional methods in physics*. Plenum, New York, pp 265
31. Dutoi AD, Head-Gordon M (2006) *Chem Phys Lett* 422:230
32. Ruzsinszky A, Perdew JP, Csonka GI, Vydrov OA, Scuseria GE (2006) *J Chem Phys* 125:194112
33. Sophy KB, Pal S (2004) *J Mol Struct Theochem* 676:89
34. Buckingham AD (1967) In: Hirschfelder JO (ed) *Advances in chemical physics*. Interscience, New York, p 107
35. McLean AD, Yoshimine M (1967) *J Chem Phys* 47:1927
36. Fowler PW (1982) *Mol Phys* 47:355
37. Bishop DM, Pipin J, Kirtman B (1995) *J Chem Phys* 102:6778
38. Huber KP, Herzberg G (1979) *Constants of diatomic molecules*, vol 4. Princeton, Van Nostrand
39. Kobayashi R, Koch H, Jorgensen P (1993) *Chem Phys Lett* 211:94
40. Mérawa M, Bégue D, Pouchan C (2003) *J Mol Struct Theochem* 633:157
41. Gamess, Schmidt MW, Baldrige KK, Boatz JA, Elbert ST, Gordon MS, Jensen JJ, Koseki S, Matsunaga N, Nguyen KA, Su S, Windus TL, Dupuis M, Montgomery JA (1993) *J Comput Chem* 14:1347
42. Vosko SH, Wilk L, Nusair M (1980) *Can J Phys* 58:1200
43. Perdew JP, Burke K, Ernzerhof M (1996) *Phys Rev Lett* 77:3865
44. Becke AD (1988) *Phys Rev A* 38:3098
45. Lee C, Yang W, Parr RG (1988) *Phys Rev B* 37:785
46. Calaminici P, Janetzko F, Köster AM, Mejia-Olvera R, Zuniga-Gutierrez B (2007) *J Chem Phys* 126:044108
47. van der Bout P, Steed JM, Bernstein LS, Klemperer W (1979) *Astrophys J* 234:503
48. Vaval N, Pal S (2004) *Chem Phys Lett* 398:194
49. Gusarov S, Malmqvist PA, Lindh R, Roos BO (2004) *Theor Chem Acc* 112:84
50. Gräfenstein J, Cremer D (2000) *Chem Phys Lett* 316:569
51. Kusakabe K (2001) *J Phys Soc Jpn* 70:2038
52. Yamanaka S, Nakata K, Takada T, Kusakabe K, Ugalde JM, Ymaguchi K (2006) *Chem Lett* 35:242
53. Wu Q, Cheng C, Voorhis TV (2007) *J Chem Phys* 127:164119
54. Nakata K, Ukai T, Yamanaka S, Takada T, Ymaguchi K (2006) *Int J Quant Chem* 106:3325
55. Yamanaka S, Nakata K, Ukai T, Takada T, Ymaguchi K (2006) *Int J Quant Chem* 106:3312