

The molecular electric dipole, quadrupole and octupole moments of a selected set of 21 spin-compensated molecules are determined employing the extended version of the Piris natural orbital functional 6 (PNOF6) [1], using the triple- $\zeta$  Gaussian basis set with polarization functions developed by Sadlej, at the experimental geometries. The performance of the PNOF6 is established by carrying out a statistical analysis of the mean absolute errors with respect to the experiment. The calculated PNOF6 electric moments agree satisfactorily with the corresponding experimental data, and are in excellent agreement with the values obtained by accurate *ab initio* methods, namely, the coupled-cluster single and doubles (CCSD) and multi-reference single and double excitation configuration interaction (MRSD-CI) methods.

The interpretation and understanding of intermolecular forces, particularly those related to long-range electrostatic interactions, require knowledge of the electrostatic moments, i.e., the electric moments are essential in order to provide simple ways to figure out the electric field behaviour of complex molecules without knowing the original field [2]. Moreover, electrical properties give information about molecular symmetry. Theoretical calculations are essential to provide molecular electric moments independently of experimental conditions, at the same time that the predictive quality of the method is tested.

The natural orbital functional (NOF) theory [3] is an alternative to conventional *ab initio* approaches and density functional theory (DFT). In this context, the last functional proposed by Piris, PNOF6, has proved a more balanced treatment of both dynamic and non-dynamic correlations [1,4-6]. To our knowledge, this is the first NOF study of higher multipole moments such as quadrupole and octupole moments.

### Exact energy functional

$$E[\Gamma, \mathbf{D}] = \sum_{ik} H_{ik} \Gamma_{ki} + \sum_{ijkl} \langle ij|kl \rangle D_{kl,ij}$$

$\Gamma_{ki}$ : 1-RDM       $D_{kl,ij}$ : 2-RDM

### Natural Orbital Functional

$$E[N, \Gamma, \mathbf{D}] \Rightarrow E[N, \Gamma] = \sum_{ik} H_{ik} \Gamma_{ki} + V_{ee}[N, \Gamma]$$

$$\Gamma_{ki} = n_i \delta_{ki}, \quad \Gamma(\mathbf{x}'_1 | \mathbf{x}_1) = \sum_i n_i \phi_i(\mathbf{x}'_1) \phi_i^*(\mathbf{x}_1)$$

$$E[N, \{n_i, \phi_i\}] = \sum_i n_i H_{ii} + V_{ee}[N, \{n_i, \phi_i\}]$$

### Cumulant expansion of the 2-RDM

$$D_{pq,rt}^{\sigma\sigma,\sigma\sigma} = \frac{n_p^\sigma n_q^\sigma}{2} (\delta_{pr} \delta_{qt} - \delta_{pt} \delta_{qr}) + \lambda_{pq,rt}^{\sigma\sigma,\sigma\sigma} \quad (\sigma = \alpha, \beta)$$

$$D_{pq,rt}^{\alpha\beta,\alpha\beta} = \frac{n_p^\alpha n_q^\beta}{2} \delta_{pr} \delta_{qt} + \lambda_{pq,rt}^{\alpha\beta,\alpha\beta}$$

$$\lambda_{pq,rt}^{\sigma\sigma,\sigma\sigma} = -\frac{\Delta_{pq}^{\sigma\sigma}}{2} (\delta_{pr} \delta_{qt} - \delta_{pt} \delta_{qr}), \quad \Delta_{pq}^{\sigma\sigma'} = \Delta_{qp}^{\sigma'\sigma}$$

$$\lambda_{pq,rt}^{\alpha\beta,\alpha\beta} = -\frac{\Delta_{pq}^{\alpha\beta}}{2} \delta_{pr} \delta_{qt} + \frac{\Pi_{pr}}{2} \delta_{pq} \delta_{rt}, \quad \Pi_{pr} = \Pi_{rp}^*$$

Total Spin Conserving Rule:  $2 \sum_{pq} \lambda_{pq,qp}^{\alpha\beta,\alpha\beta} = N^\beta - \sum_p n_p^\alpha n_p^\beta$

Sum Rules:  $\sum_q \Delta_{qp}^{\sigma\sigma} = n_p^\sigma h_p^\sigma, \quad \sum_q \Delta_{qp}^{\sigma\sigma'} = \Pi_{pp}$

$$\text{PNOF6}(N_c) \quad E = \sum_{g=1}^F E_g + \sum_{f \neq g} \sum_{p \in \Omega_f} \sum_{q \in \Omega_g} E_{pq}^{int}$$

$$E_g = \sum_{p \in \Omega_g} n_p (2\mathcal{H}_{pp} + \mathcal{J}_{pp}) + \sum_{p,q \in \Omega_g, p \neq q} E_{pq}^{int}$$

$$E_{pq}^{int} = (n_q n_p - \Delta_{qp}) (2\mathcal{J}_{pq} - \mathcal{K}_{pq}) + \Pi_{qp} \mathcal{L}_{pq}$$

$$\sum_{p \in \Omega_g} n_p = 1, \quad g = \overline{1, F} \quad \Omega_{g1} \cap \Omega_{g2} = \emptyset$$

### Dipole Moment

$$\mu_\alpha = -\int \rho(\mathbf{r}) r_\alpha dV + \sum_{i=1}^{NUC} Z_i R_{i\alpha}$$

### Quadrupole Moment

$$\Theta_{\alpha\beta} = -\frac{1}{2} \int \rho(\mathbf{r}) (3r_\alpha r_\beta - \delta_{\alpha\beta} r^2) dV$$

$$+ \frac{1}{2} \sum_{i=1}^{NUC} Z_i (3R_{i\alpha} R_{i\beta} - \delta_{\alpha\beta} R_i^2)$$

### Octupole Moment

$$\Omega_{\alpha\beta\gamma} = -\frac{5}{2} \int \rho(\mathbf{r}) r_\alpha r_\beta r_\gamma dV$$

$$+ \frac{1}{2} \int \rho(\mathbf{r}) r^2 (r_\alpha \delta_{\beta\gamma} + r_\beta \delta_{\alpha\gamma} + r_\gamma \delta_{\alpha\beta}) dV$$

$$+ \frac{5}{2} \sum_{i=1}^{NUC} Z_i R_{i\alpha} R_{i\beta} R_{i\gamma}$$

$$- \frac{1}{2} \sum_{i=1}^{NUC} Z_i R_i^2 (R_{i\alpha} \delta_{\beta\gamma} + R_{i\beta} \delta_{\alpha\gamma} + R_{i\gamma} \delta_{\alpha\beta})$$

### $\Delta$ and $\Pi$ matrices in PNOF6

$\Delta_{qp}$	$\Pi_{qp}$	Orbitals
$e^{-2S} h_q h_p$	$-e^{-S} (h_q h_p)^{1/2}$	$q \leq F, p \leq F$
$\frac{\gamma_q \gamma_p}{S_\gamma}$	$-\Pi_{qp}^\gamma$	$q \leq F, p > F$
$e^{-2S} n_q n_p$	$e^{-S} (n_q n_p)^{1/2}$	$q > F, p \leq F$
		$q > F, p > F$

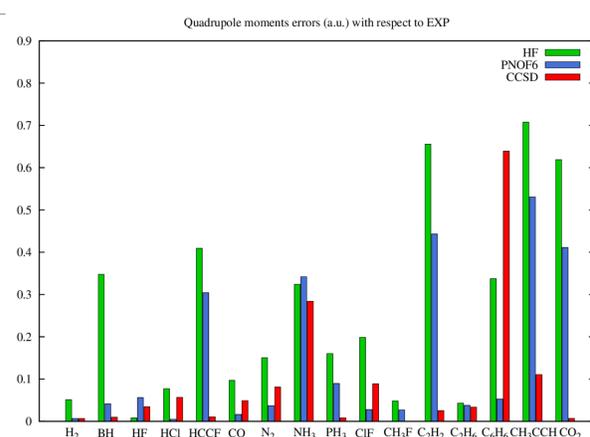
$$\Pi_{qp}^\gamma = (n_q h_p + \frac{\gamma_q \gamma_p}{S_\gamma})^{1/2} (h_q n_p + \frac{\gamma_q \gamma_p}{S_\gamma})^{1/2} \quad \gamma_p = n_p h_p + \alpha_p^2 - \alpha_p S_\alpha$$

$$S = \sum_{q=F+1}^{F+FN_c} n_q, \quad S_\alpha = \sum_{q=F+1}^{F+FN_c} \alpha_q, \quad S_\gamma = \sum_{q=F+1}^{F+FN_c} \gamma_q$$

$$\alpha_p = \begin{cases} e^{-S} h_p, & p \leq F \\ e^{-S} n_p, & p > F \end{cases}$$

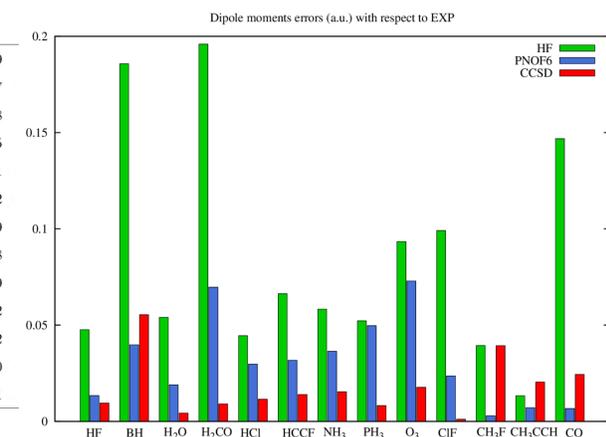
### zz-component of Quadrupole moment at EXP. geometries by using the Sadlej-pVTZ basis set

Molecule	HF	PNOF6 ( $N_c$ )	CCSD	EXP.
H <sub>2</sub>	0.4381	0.3935 17	0.3935	0.39 ± 0.01
HF	1.7422	1.6939 7	1.7156	1.75 ± 0.02
BH*	2.6772	2.3706 38	2.3388	2.3293 <sup>†</sup>
HCl	2.8572	2.7753 8	2.7233	2.78 ± 0.09
HCCF	3.3530	3.2482 9	2.9335	2.94 ± 0.10
CO	1.5366	1.4562 9	1.4889	1.44 ± 0.30
N <sub>2</sub>	0.9397	1.0530 9	1.1712	1.09 ± 0.07
NH <sub>3</sub>	2.1258	2.1080 12	2.1661	2.45 ± 0.30
PH <sub>3</sub>	1.7217	1.6507 13	1.5695	1.56 ± 0.70
ClF	0.9413	1.1122 6	1.0514	1.14 ± 0.05
CH <sub>3</sub> F	0.3482	0.3269 10	0.3002	0.30 ± 0.02
C <sub>2</sub> H <sub>2</sub>	5.3655	5.1531 12	4.6850	4.71 ± 0.14
C <sub>2</sub> H <sub>6</sub>	0.6329	0.6275 13	0.6234	0.59 ± 0.07
C <sub>6</sub> H <sub>6</sub>	6.6418	6.3571 12	5.6653	6.30 ± 0.27
CH <sub>3</sub> CCH	4.2913	4.1146 12	3.6939	3.58 ± 0.01
CO <sub>2</sub>	3.8087	3.6012 8	3.1966	3.19 ± 0.13
MAE	0.2646	0.1517	0.0902	



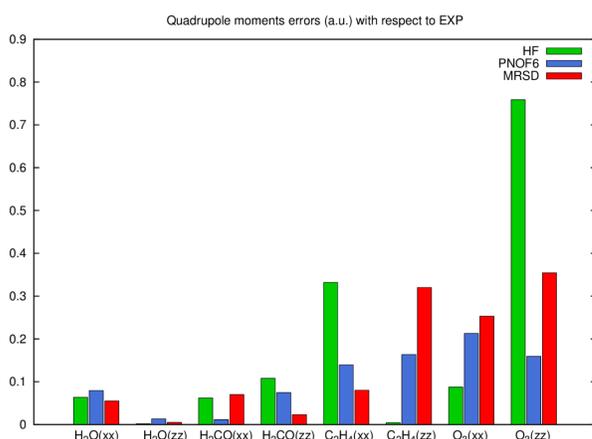
### z-component of Dipole moment at EXP. geometries by using the Sadlej-pVTZ basis set

Molecule	HF	PNOF6 ( $N_c$ )	CCSD	EXP.
HF	0.7565	0.7223 7	0.6994	0.7089
BH*	0.6854	0.5395 38	0.5551	0.4997
H <sub>2</sub> O	0.7808	0.7458 9	0.7225	0.7268
H <sub>2</sub> CO	1.1134	0.9872 10	0.9084	0.9175
HCl	0.4746	0.4598 8	0.4416	0.4301
HCCF	0.3535	0.3189 9	0.2733	0.2872
NH <sub>3</sub>	0.6372	0.6153 12	0.5943	0.5789
PH <sub>3</sub>	0.2780	0.2755 13	0.2340	0.2258
O <sub>3</sub>	0.3033	0.1370 7	0.2276	0.2099
ClF	0.4453	0.3226 6	0.3451	0.3462
CH <sub>3</sub> F	0.7706	0.7283 10	0.6919	0.7312
CH <sub>3</sub> CCH	0.3203	0.3141 12	0.2866	0.3070
CO	-0.0987	0.0414 9	0.0725	0.0481
MAE	0.0843	0.0309	0.0177	



### zz- and xx- components of Quadrupole moment

Molecule	HF	PNOF6 ( $N_c$ )	MRSD-CI	EXP.
H <sub>2</sub> O (xx)	1.7966	1.7808 9	1.8050	1.86 ± 0.02
H <sub>2</sub> O (zz)	0.0981	0.0869 9	0.0950	0.10 ± 0.02
H <sub>2</sub> CO (xx)	0.1019	0.0516 10	0.1100	0.04 ± 0.12
H <sub>2</sub> CO (zz)	0.0921	0.1255 10	0.2230	0.20 ± 0.15
C <sub>2</sub> H <sub>4</sub> (xx)	2.7819	2.5892 13	2.3700	2.45 ± 0.12
C <sub>2</sub> H <sub>4</sub> (zz)	1.4942	1.3266 13	1.1700	1.49 ± 0.11
O <sub>3</sub> (xx)	1.1175	1.2426 7	1.2830	1.03 ± 0.12
O <sub>3</sub> (zz)	-0.2387	0.3606 7	0.1680	0.52 ± 0.08
MAE	0.1772	0.1066	0.1448	

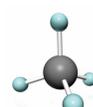


### Quadrupole moment of H<sub>2</sub> molecule varying N<sub>c</sub> coupling parameter

PNOF6(1)	PNOF6(3)	PNOF6(5)	PNOF6(17)	CCSD	EXP.
0.3697	0.4030	0.3965	0.3935	0.3935	0.39 ± 0.01

### xyz octupole moment for methane

PNOF6(1) / sadlej-pVTZ:	$\Omega(\text{xyz}) = 2,0600$ a.u.
PNOF6(14) / sadlej-pVTZ:	$\Omega(\text{xyz}) = 2,1142$ a.u.
CCSD / sadlej-pVTZ:	$\Omega(\text{xyz}) = 2,0595$ a.u.
EXP(JCP,62,3807(1975)):	$\Omega(\text{xyz}) = 2,95 \pm 0,17$ a.u.



### Conclusions

PNOF6( $N_c$ ) is able to predict electric properties as accurate as high-level electronic structure methods such as CCSD or MRSD-CI, therefore the functional computes quite accurately the charge distribution of molecular systems.

For dipole moment, the MAE value for the selected set of molecules is **0,309 a.u.**, while the MAE obtained for quadrupole moment is **0,1291 a.u.**, which competes with the corresponding to CCSD (**0,0902 a.u.**) and MRSD-CI (**0,1448 a.u.**) methods. Remark the results obtained for Carbon Monoxide, Benzene, and Ozone.

### References

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