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Abstract. Modern semiempirical methods such as PM6 and PM7 are often used to explore the electronic structure dependent properties of molecules. In this work we report the evaluation of PM6 and PM7 methods towards linear and nonlinear optical polarizability calculations for different molecules and solid nanoclusters. The results are compared with reported experimental results as well as theoretical results from other high level theories for the same systems. It is found that both methods produce accurate results for small molecules and the accuracy increases with the increase in asymmetry of the medium sized organic molecules and accuracy reduces for solid nanoclusters.

INTRODUCTION

Quantum mechanical calculations provide a conceptual way to solve the electronic structures of atoms as well as complex molecules. Many computational methods with different accuracies, like *ab initio* methods, DFT, semiempirical methods and molecular dynamics formulations are available to solve those equations. Among them semiempirical methods are simple and powerful to explore the electronic structures with acceptable accuracy level. Even though, approximations and parameterizations of semiempirical methods limits its accuracy on the other hand they increase its computational efficiency by several times than the *ab initio* methods. Hence they are constantly employed to model the linear and nonlinear optical properties of molecular as well as solid state systems [1]. Often two issues, they cannot be used for all the elements in the periodic table and their drastic approximations, are noted as the limitations of semiempirical methods. By the introduction of PM6 and PM7 methods, which could be used for all the elements in the periodic table and with the exact substitution of empirical parameters, the limitations can be overcome [2]. In the recent past many reports were tried to validate the prediction of molecular properties by these methods to other high

level theories and the experimental results. In this report, we investigate the variation in accuracy of semiempirical results with respect to different molecular structures and clusters.

COMPUTATIONAL METHODOLOGY

All the calculations were carried out using MOPAC2012 package in a Fedora 20 OS. For present study, three types of molecules such as, small molecular systems, medium sized organic systems and simple nanoclusters were chosen. In which, CO, CO_2 and benzene are often considered as benchmarking systems and used to validate the computational results. Three fluorenyl molecular derivatives are studied to identify the structure dependent variation in the accuracy of results. Further, three ZnO nanoclusters of different point groups has also been studied to explore the point group dependent variation in the results. Structures of the molecules are either obtained as cif files or drawn using ChemDraw software. Initially all the drawn molecular geometries were optimized using Universal Force Filed (UFF) algorithm embedded in Avgadro package and the cif files are directly converted into input files. Further the molecules were optimized using corresponding PM6 and PM7 methods with GNORM values about 0.01, 0.25. 0.1 for small

molecular systems, organic molecules and nanoclusters respectively. FORCE calculations were carried out to validate the geometry and if any negative frequencies are obtained in the calculation, geometrical parameters have been changed and the molecule was reoptimized. For all the system static polarizability and hyperpolarizability values were calculated at TDHF level.

RESULTS AND DISCUSSION

Small Molecular Systems

The polarizability values of benzene obtained from PM6 and PM7 methods are slightly higher than that of the experimental values. In the case of second order hyperpolarizability calculations, the calculated semiempirical values were slightly lesser than that of the experimental values. In both the cases, the accuracy of PM6 and PM7 are of equal to the high level *ab initio* methods. The obtained results are given in the Table 1.

TABLE 1. Polarizability and Second Hyper-polarizability values of Benzene molecule [3]

| Method	α (a.u.)	γ (a.u.)
MP2 CPHF	63.14	15868
MP2 TDHF	65.35	53290
MP2 FF	63.93	22967
B3LYP	66.53	21989
PM6	68.56	14614
PM7	68.83	15756
Exp	66.80	177550

The results of CO and CO_2 molecules are compared with the results of standard methods. i.e., for CO, CC3 results and for CO_2, MP2 results have been taken as benchmark references. In this case also semiempirical methods provide accurate results with that of the *ab initio* methods.

Organic Molecular Systems

Three fluorenyl derivatives, 7-Nitro-9H-fluoren-2-ylamine (7N9HF2Y), 1-(7-Nitro-9H-fluoren-2-yl)-pyrrolidine (1-7N9HF-2YA) and [2-(7-Nitro-9H-fluoren-2-yl)-vinyl]-1-1'-dipyrrolidine (2-7N9HF-2YP) molecules have been considered for analysis.

TABLE 2. Polarizability and First Hyper- polarizability values of CO molecule [4]

Method	α (a.u.)	β (a.u.)
HF	12.53	8.58
CCSD	13.35	16.93
CC3	13.35	16.13
B3LYP	13.52	18.37
PM6	10.21	20.25
PM7	10.11	19.47
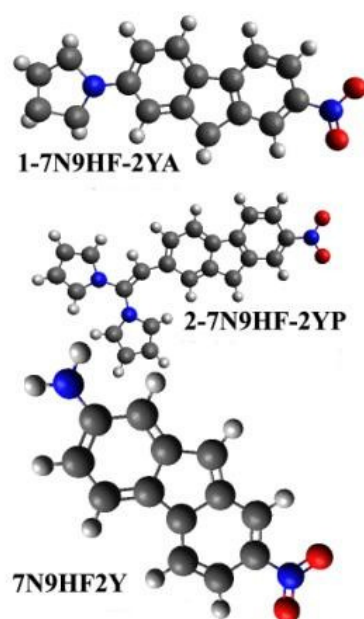
FIGURE 1. Molecular structure of fluorenyl derivatives

TABLE 3. Polarizability and First Hyper- polarizability values of CO_2 molecule [5]

Method	α (a.u.)	β (a.u.)
MP2	15.81	0.0045
CIS	18.11	--
TD-DFT	14.48	--
ZINDO-CI	12.12	--
PM6	18.54	0.0021
PM7	19.36	0.0045

In the present study, second order nonlinear susceptibility values of the fluorenyl derivatives were calculated and it is observed that the accuracy of the results increases with increase in asymmetry in molecular structures. The obtained results are shown in Table 4.

**TABLE 4. First Hyper- polarizability values of Fluorenyl derivatives [6]**

β (X 10⁻³⁴ esu)	HF	PM6	PM7
7N9HF2Y	30.20	26.30	31.31
1-7N9HF-2YA	42.67	32.37	45.66
2-7N9HF-2YP	83.13	71.26	81.39

ZnO nanocluster Systems

TABLE 5. Polarizability and hyperpolarizability calculations of ZnO nanoclusters of different point groups [7]

Method	ZnO (D_{2h}, 0.00)			ZnO (C_s, 0.82)			ZnO (C_{2V}, 1.50)		
	α (a.u.)	β (a.u.)	γ (a.u.)	α (a.u.)	β (a.u.)	γ (a.u.)	α (a.u.)	β (a.u.)	γ (a.u.)
B3LYP	62.67	0.1	2420	167.27	637	5660	85.6	608	4750
PM6	36.78	0.09	519.2	44.76	1091	4273	49.16	1161	7323
PM7	42.21	0.91	808.6	40.22	937	4332	41.35	823	9633

In order to study the effect of point groups and molecular energies, three solid clusters of point groups D_{2h}, C_s, C_{2V} with energies 0.00, 0.82 and 1.5 of ZnO have been considered for the calculations, respectively. The calculated results are compared with the B3LYP level reports. It is clear from the results that the point group of the systems greatly influences the accuracy of the results, i.e., more asymmetric the molecule, more accurate the results. The obtained results are given in Table 5.
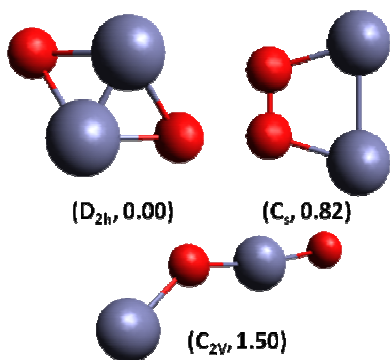
FIGURE 2. Molecular structures of ZnO nanoclusters

CONCLUSION

Accuracy of polarizability calculations was evaluated by two different semiemipirical methods, PM6 and PM7. For small molecular systems, the accuracy of results are comparable to that of the ab initio results. Whereas, in the case of fluorenyl derivatives and ZnO nanoclusters the accuracy of the results varies with the molecular symmetry.

ACKNOWLEDGMENTS

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